ELEMENTS OF
PHYSICAL
METALLURGY
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AND MATERIALS

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PREFACE

This is a textbook for courses in fundamentals of physical metallurgy. Since it treats basic principles, it is suitable for engineering and science students as well as for those whose major interest is metallurgy. It is desirable that the students have a general background in chemistry, physics, and mathematics, but no previous knowledge of metallurgy is assumed. An introductory section orients the student in this new field and briefly surveys the background that gives significance to the principles discussed in the body of the text; for example, a number of topics in process metallurgy are briefly discussed for the benefit of students who are not specializing in metallurgy.

The introductory section is followed by four chapters on the structure of metals and alloys. Chapter 3 opens with an elementary consideration of atomic structure, starting with the concepts of quantization of energy and continuing through the Bohr and wave theories of atomic structure. Nuclear structure and nuclear reactions of interest in metallurgy are also considered. The solid (crystalline) structures produced by an assembly of atoms are taken up in Chapter 4, along with a brief discussion of liquid and gaseous metals. The method of designating crystal planes and directions by Miller indices is shown, and the use of Miller indices is illustrated by applications to x-ray diffraction. The principles of electron diffraction and neutron diffraction are also presented. Imperfections in crystal structures are introduced in this chapter, principal attention being given to vacancies and dislocations. Important applications of these structural features are discussed in later sections of the book.

The phases that are commonly encountered in metallurgical systems (solid, liquid, and vapor phases) are described in Chapter 5. In addition, the mode of transformation from one phase to another is considered in some detail for such important transformations as that involved in the solidification of a liquid. This treatment of phases prepares the student for the study of phase diagrams in Chapter 6. In treating phase diagrams, actual alloy systems, such as the iron-carbon, the copper-nickel, and the aluminum-silicon two-component diagrams, are used as illustrative examples wherever possible. Gas-metal systems and isothermal sections of three-component diagrams are also studied. Both schematic drawings and actual photomicrographs illustrate typical microstructures. The relation of structure to the properties of alloys is illustrated by a study of such commercial alloys as steels, brasses, and bronzes. Nonequilibrium aspects of phase relations in metal systems are also discussed, for example the technique of zone melting. The section on structure concludes with a treatment of macrostructure.
Chapters 7 through 10 further develop the concept that metallic structures and properties are related, but the emphasis is on properties of metals and alloys. This section begins with a chapter on physical properties: electrical and magnetic properties and the corresponding special alloys, thermal properties, and optical properties. Chapter 8 considers elasticity, starting with the concepts of stress and strain. Problems of elastic deformation of metal crystals are treated, using the generalized Hooke’s law, and the significance of preferred orientation is illustrated. A section on stresses in design emphasizes stress raisers and residual stresses. Chapter 9, “Plasticity of Metals,” presents a quantitative theory of plastic deformation, including the ideas of flow stress, flow curve, and fracture stress. A section on tests of plastic properties summarizes the test procedures for tensile, hardness, impact, endurance, damping, rupture, and creep tests of alloys. High- and low-temperature properties are also considered. Chapter 10, “Corrosion,” concludes the section on properties of metals and alloys. This chapter emphasizes the mechanisms of corrosion and considers the types of corrosion control that are suggested by knowledge of these mechanisms.

The final section of the book, Chapters 11 through 14, treats the important topic of reactions in metals. Diffusion, which underlies almost all reactions in metals, is considered first and is illustrated by examples of oxide formation, carburizing, metal bonding, and homogenization. Chapter 12 is devoted to quantitative aspects of recovery, recrystallization, and grain growth. Isothermal reaction curves are used in the presentation. The subject of age hardening, including both precipitation hardening and order hardening, is considered in the next chapter. The transition lattice theory of hardening is described and illustrated by sketches. Diffusion-kinetics reaction hardening, which is the basis of nitriding and of internal-oxidation hardening, is explained. Chapter 14 effectively covers the general problem of the heat treatment of steel. Typical subjects are quantitative considerations of austenitization, TTT and continuous cooling diagrams, hardenability expressed as ideal diameter and by Jominy curve, interrupted quenching, nature of martensite and of tempering, and applications to carbon steels, AISI steels, and tool steels.

An unusual feature is the Appendix on the literature of metallurgy. The usefulness of the technical literature is discussed, and then such types as textbooks, handbooks, monographs, abstracts, journals, patents, and manufacturers’ literature are considered in some detail, and the outstanding examples of each are given.

The major aim of the book, then, is to give the student an understanding of the basic principles of physical metallurgy. The study of practical applications, however, is an integral part of this main purpose. In part, the uniting of practice and principles is accomplished by treating current practical achievements in physical metallurgy as examples of fundamental...
principles. In addition, quantitative problems are given at the end of most chapters. These exercises have been chosen for their value in illustrating the use of metallurgical principles in answering practical questions concerning the behavior of metals and alloys.

Numerous tables concisely presenting representative data on commercial alloys give the student an over-all picture of the uses of these alloys. However, for detailed information on properties and processes the student is referred to standard reference works such as the Metals Handbook. The index is arranged for easy location of information on a given alloy—information that may be distributed among several chapters to illustrate several fundamental principles. The index is also designed to serve as a glossary in the manner described in the footnote on page 2.

The subject matter of this book is the achievement of many scientists of the past and present. The author can claim responsibility only for the present manner of treating this subject matter. Even here much of the credit must go to others, especially to Morris Cohen, who influenced literally every page. Although it is impractical to acknowledge individually the assistance of all the persons who generously supplied information, illustrations, and suggestions, their help contributed materially to the present book. Entire chapters were read critically by the following persons, and their suggestions are gratefully acknowledged: W. A. Anderson, B. Averbach, P. A. Beck, B. F. Brown, H. C. Brown, W. J. Buehler, E. J. Crane, B. D. Cullity, W. C. Dunlap, S. A. Duran, M. G. Fontana, R. E. Grace, F. E. Harris, M. F. Hawkes, R. H. Hopp, C. H. Lorig, J. R. Low, J. D. Lubahn, K. F. McKean, L. Martin, A. C. Menius, J. B. Newkirk, and W. E. Ruder.

Many prominent faculty members of metallurgy departments throughout the country provided suggestions for the present work, based on classroom use of the first edition. These courtesies are sincerely appreciated, and the resulting improvements are gratefully acknowledged.

The illustrations made available by individuals and companies are credited in the text. Especial gratitude is expressed for illustrations prepared specifically for this use. Mr. Shotaro Morozumi contributed to several of the illustrative models. The equilibrium diagrams are, with a few exceptions, adapted from those given in the Metals Handbook. Many rough sketches were skillfully converted into finished, effective illustrations by the Addison-Wesley Art Department. The original magnification values are given for photomicrographs, but in instances where these have been reduced the reduction is noted in the figure legend.

The cordial and expert assistance of the staff of the Addison-Wesley Publishing Company helped make the work especially pleasant.

A. G. GUY

November, 1958
Lafayette, Indiana
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CHAPTER 1
INTRODUCTION

"Available materials set a limit to the techniques of any age."
J. B. DERRICK

THE FIELD OF METALLURGY

Metals play an important role in the modern world. Consider, for example, the hundreds of ways in which metallic objects influence one's daily life—sleeping, eating, riding, working, playing. Industry is even more dependent on the daily use of metals, and continued industrial progress demands constant improvement in their properties. The effective application of alloys is an important responsibility of engineers in every field of modern technology. However, even a brief acquaintance with metals reveals that they are surprisingly complex and that many different aspects of their behavior must be considered in a given application. The most important features of metals and alloys will be presented in the following chapters, but it is helpful first to look at the broad field of metallurgy and also to consider its relation to other fields of knowledge. This over-all view will aid in maintaining a proper perspective during the intervals when attention must be focused on small, specialized portions of the entire subject.

What is metallurgy? Metallurgy might be described as the art and science of procuring and adapting metals to satisfy human wants. A moment's reflection reveals what a tremendous task this is. Although there is an abundance of metal atoms on the earth's surface, most of them are not in usable condition; they are combined with nonmetal atoms, such as oxygen, in substances similar to stone or clay. The first step in making metals available for human use is freeing the metal atoms from this combined state. This is the province of extractive metallurgy. Typical of the huge, complex equipment required for this purpose is the iron blast furnace; one such furnace can produce two million pounds of metal in a single day. Moreover, even after further melting, refining, and alloying, the metal is only partially prepared for its final use.

A useful metal object—fountain pen clip, lamp base, or airplane wing—must have a specific form. In this phase of metallurgy (known as
mechanical metallurgy), many widely different forming processes* are used, but the hot rolling process perhaps best exhibits the essential metal qualities. Gigantic rollers press and knead several tons of roughly formed metal into the shape of a beam or a railroad rail. After rolling, as the hot, solid metal cools to room temperature, it gradually loses much of its capacity for deformation. At the same time it gains the strength that is needed for most engineering purposes.

A less spectacular aspect of metal production and forming is the control of these processes with the aid of various tests and by the application of basic principles. For example, the methods of thermodynamics and physical chemistry may be employed to determine optimum operating conditions, while chemical analyses and physical tests are relied upon to control these optimum values. A control technique characteristic of metallurgy is the examination of the internal structure of solid metals. This powerful method has many applications, including the accurate interpretation of critical incidents in the previous history of metals. Specific alloy diagrams and more general alloying principles are also extremely useful and are widely applied to such problems as the improving of metallic properties by suitable alloying.

Relation of metallurgy to other subjects. The section above speaks of the cooperation of art and science in the complex processes of adapting metals to human wants. Another significant aspect of metallurgy is its relation to other fields of science and engineering. All human knowledge is related, and metallurgy is an outstanding example of a subject connected by generous transition zones to many other areas of knowledge. These relationships are of two kinds: the art and science of metallurgy depend on the techniques and principles of other subjects and, on the other hand, metallurgy is responsible for supplying construction materials for use in other fields.

An example of the first of these relationships is the fact that metallurgy

* The subject “forming processes” is considered in some detail in Chapter 2. It is also referred to in connection with other topics in later chapters, for example in Chapter 9. Many other subjects are similarly mentioned in several places in the text. For the convenience of readers who wish more information when such a subject is first mentioned, or who wish to refresh their memories when the subject is referred to in a later section, the index is arranged to serve as a glossary. For this purpose the following system is employed. Italic type is used for the number of the page on which the definition of the term is given. For example, the index entry for “forming processes” reads

Forming processes 1 f., 27 ff., 352 ff., 437.

The italicized number, 27, indicates that the definition is given on that page; the boldface entry, 27 ff., indicates that the principal treatment of this subject is given on page 27 and the following pages.
relies heavily on chemistry. Most of the chemical elements are metals, and the metallurgist shares much of the chemist's interest in the properties and reactions of these metallic elements. In fact, physical metallurgy might be considered a subdivision of the larger field of physical chemistry. Physics also makes many contributions to metallurgy. Since all metallic behavior is intimately associated with the nature of individual atoms and their interactions, atomic theory is of basic importance in the study of metals. Nuclear reactions have already become a part of metallurgy as well as of physics, and of course the study of the physical properties of metals involves both these fields. Engineering subjects also contribute to metallurgical practice. Typical examples are the influence of chemical engineering in ore processing and the role of mechanical engineering in mechanical testing and fabrication. In spite of this many-sided nature, metallurgy achieves a remarkable unity as a result of its singleness of purpose—the study of metals.

To ensure effective use of metals in thousands of applications, the second type of cooperation between metallurgy and other fields of knowledge is essential. Modern architecture is one illustration of the interdependence of design and the materials of construction. Similar mutual influence is evident in the building of an internal combustion engine or of a television set. It would be difficult to overestimate the importance of this interaction on metallurgy. The nature of current applications largely determines the metals that are produced, the properties that are studied, and the forming processes that are developed. The automobile industry has greatly affected many phases of metallurgy, and recently new demands have been made by jet propulsion and atomic energy. Properties almost unknown a few years ago are now subjects of extensive study.

Such structural materials as plastics, wood, ceramics, and rubber are also available for industrial applications and under certain conditions one of these may be chosen in preference to a metal. The use of plastics in toys is an example. There are no general rules for the proper choice of a structural material, and only by comparing many properties of alternative materials can a logical decision be made. In some instances it is possible to obtain superior properties by combining metallic and nonmetallic components. Typical of such combinations are the use of a metallic surface on a wooden propeller to resist erosion, and the use of ceramic coatings to protect metals from corrosion.

The Study of Metallurgy

In view of the wide scope of metallurgy and its complex relations with other subjects, evidently it would not be easy to learn "all about metallurgy." Fortunately, it is practical to consider particular sections
INTRODUCTION

[CHAP. 1]

of this extremely broad field. For example, it is possible to work with many problems of alloy properties and behavior (physical metallurgy) while giving a minimum of consideration to details of the production and forming of the alloy being studied. This procedure does not show a lack of interest in the previous history of the alloy; rather, it illustrates the advantages of a convenient and effective division of labor in a complex field. When the many difficult tasks of alloy preparation are assumed by other branches of metallurgy, physical metallurgy is free to concentrate on the study of alloy properties in relation to industrial applications. This useful specialization is the basis for restricting the present book largely to a consideration of physical metallurgy.

Even physical metallurgy has a broad scope. Usually each field of application has characteristic service conditions and may require specific sets of metallic properties. Also, a given type of application may involve a special "art"—a practical skill that is acquired only with increasing experience. As a further complication, there is continuous change with time in each field of application, and constant effort is required to keep abreast of the current state of the art.

It is apparent that a course in physical metallurgy cannot produce a specialist in all uses of metals. However, such a course can provide a foundation for later specialization. This approach is possible because a comparatively small number of essential ideas forms the basis of all the various applications of metals. These ideas include: the concepts of atomic structure and crystal structure; the visualization of alloy behavior by means of equilibrium diagrams; an understanding of the nature of physical, mechanical, and chemical properties; and an appreciation of the special reactions that can occur within solid metals and alloys. With this basic information as a starting point, it is not difficult to establish and maintain a reasonable competence in applying metals to specific industrial problems.

This emphasis on a fundamental understanding of the nature of metals should not be taken to mean that practical information on tensile strength, ductility, etc., is unimportant. Handbook-type data of this kind are essential, and the Appendix will serve as a guide to this and other sources of vital design values. However, a good background in the principles of metallic behavior is necessary for accurate interpretation and reasonable use of such data. As a first step in forming this background, the following chapter briefly surveys metallurgy as a whole.
CHAPTER 2

A SURVEY OF METALLURGY

"History, as it lies at the root of all science, is also the
first distinct product of man's spiritual nature; his earliest
expression of what can be called Thought."

CARLYLE

HOW IT BEGAN

Earth's beginning. The story of metals can begin with a picture of a
huge ball of vapor consisting of iron, silicon, aluminum, and the other
elements in the gaseous state. This was the nascent earth, circling the sun
in the company of the other planets. Slowly, liquefaction and then solidi-
fication began to occur. Over the course of a few billion years the earth
assumed its present form—an immense core of a complex iron-nickel alloy,
a thick intermediate layer of heavy rocks, and a relatively thin outer shell
of lighter rocks. Since only a few miles of this outer shell are available for
commercial mining operations, the chemical analysis of this region is of
especial interest. Most of the percentages of abundance of elements listed
in Table 2-1 are discouragingly low. Imagine trying to separate 999,980
parts of worthless earth or gangue in order to obtain 20 parts of lead.
Fortunately, a number of geologic processes have worked to concentrate
the various metallic minerals such as PbS (galena) into ore bodies that
can be mined profitably. In lead mines there is about five percent lead,
in contrast to the average in the earth's crust of 0.002 percent.

As the earth cooled and the steam condensed to produce oceans and
lakes, somehow the miracle of life happened. Man's precursor of a billion
years ago was probably a microscopic one-celled organism. Some 999
million years later the first manlike creature had developed. In time, as
he began to use stones as implements, it was inevitable that accidentally
he should find usable pieces of metallic gold, copper, and silver, the three
principal metals that occur in the uncombined or native condition. Also,
meteorites gave him a small supply of iron-nickel alloy, "metal from
heaven," as it was known in nearly every early language. Unlike man's
early brittle stone implements, these metals were malleable* and could

* Many terms are used to describe the capacity of a solid metal for permanent
deformation. The most general of these is plasticity—the ability of the metal to
be shaped by any process. This characteristic of metals is considered in Chapter
9. The ability of a metal to be formed by hammering is called malleability, and
its capacity to be drawn out (as in the drawing of wire) is called ductility. Since
the usual tension test draws out the metal, this test is considered to determine
the ductility of the metal (and also certain strength properties, Chapter 9).
6
A SURVEY OF METALLURGY
[CHAP. 2]

Table 2-1
RELATIVE ABUNDANCE OF ELEMENTS IN THE EARTH’S CRUST*

<table>
<thead>
<tr>
<th>Element</th>
<th>Average content in earth’s crust</th>
<th>Element</th>
<th>Average content in earth’s crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>46.6%</td>
<td>Tungsten</td>
<td>0.003%</td>
</tr>
<tr>
<td>Silicon</td>
<td>27.7</td>
<td>Zinc</td>
<td>0.004</td>
</tr>
<tr>
<td>Aluminum</td>
<td>8.1</td>
<td>Lead</td>
<td>0.002</td>
</tr>
<tr>
<td>Iron</td>
<td>5.0</td>
<td>Cobalt</td>
<td>0.001</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.6</td>
<td>Beryllium</td>
<td>0.001</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2.1</td>
<td>Molybdenum</td>
<td>0.0001</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.63</td>
<td>Tin</td>
<td>0.0001</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.19</td>
<td>Antimony</td>
<td>0.0001</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.037</td>
<td>Cadmium</td>
<td>0.0001</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.026</td>
<td>Mercury</td>
<td>0.0001</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.020</td>
<td>Bismuth</td>
<td>0.00001</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.017</td>
<td>Silver</td>
<td>0.00001</td>
</tr>
<tr>
<td>Copper</td>
<td>0.010</td>
<td>Platinum</td>
<td>0.000001</td>
</tr>
<tr>
<td>Uranium</td>
<td>0.008</td>
<td>Gold</td>
<td>0.000001</td>
</tr>
</tbody>
</table>


be hammered into useful objects. Their pleasing luster and colors sometimes led to their use as jewelry.

Occasionally, pieces of metallic ore must have been mixed in the campfires of ancient man, and the action of reducing gases would have produced the free metal. Undoubtedly, lumps of metal were found in the ashes of campfires many times before man realized that he was producing metal from the ore, but once the discovery was made, the age of metals had begun. No longer was the artisan restricted to the meager supply of native metals, for large quantities of iron, copper, silver, lead, and tin were smelted in ancient times. Other metals widely distributed in the earth’s crust, such as aluminum, were not produced by early man because of the difficulty of reducing their ores by pyrometallurgical processes. (Pyro is derived from the Greek word meaning fire.)

Ancient philosophy and metals. Long before man began to reduce metals from their ores, he was speculating about their nature. Perhaps he first thought of them as being alive, especially the meteorites. Even by the time of the Greek philosophers the ideas were still crude. Empedocles believed that the four elements, earth, air, fire, and water, were
combined in various proportions to produce all the substances on the earth. Copper, for example, probably was considered to be made of earth with some water and fire added. The four-element theory owes its importance to the fact that it was adopted by Aristotle. Supported by the authority of his name, it continued to be the generally accepted view of the structure of matter until a scant 500 years ago.

Democritus, another Greek philosopher, advanced an atomic theory of a sort. He believed the universe to be composed of atoms and empty space, with the atoms differing in size, weight, form, and hardness. Obviously this idea is quite different from the present atomic theory, but it shows that the concept of an indivisible particle is an old one.

In spite of the fact that there was almost no experimental work of the type so prevalent in the modern world, men of the pre-Christian era had learned much about metallurgy. They cast metals into intricate shapes. They made some implements by forging, in order to produce a more serviceable product. They increased the hardness of iron by the cementation process, now known to be the addition of carbon to the iron. They further hardened this cemented iron by heating to a red heat and then quickly cooling (quenching) in water. To make the hardened cemented iron less brittle, they reheated it to an intermediate temperature, an operation now called tempering. But if these ancient metallurgists had the "know-how," they were poor in the "know-why." Far from understanding why the cemented iron becomes hard after heating and quenching, they did not even realize that carbon is an indispensable addition if iron is to be made hard by this procedure. Not until the beginning of experimental science in the seventeenth century did metallurgy make rapid advances in theory as well as in practice.

Alchemy. One of the accomplishments of the early metallurgists was the manufacture of copper-base alloys that resembled gold, for use in jewelry. Perhaps some of the craftsmen believed that they had actually made gold. In any event, for over a thousand years alchemists mixed and brewed and distilled in a vain search for such desirable substances as the philosophers' stone for changing base metals to gold, and the elixir of life for preserving one's youth.

Albertus Magnus (A.D. 1250) was the most important of the alchemists. He was skeptical of some aspects of alchemy, since he had been able to reduce alchemical "gold" to powder by heating it. Nevertheless, the poor state of technical knowledge at this time is clear from the following comment on his work by Biringuccio, in about 1550.

"What shall I say of what Albertus Magnus writes in his work De Mineralibus, where he says that he has seen gold generated in the head of a dead man? He
says that when this was dug up by chance and found to be extraordinarily heavy, it was seen to be full of very fine sand. Because of its weight those who saw it thought that it was metal and by experimenting finally found it to be of the purest gold. It seems to me that his words have no other significance than that the ready disposition of the thing and the great influence of the heavens had generated this precious metal. Since I heard it thus I wanted to pass it on to you. To tell the truth it is not easy to believe this, and certainly to me it seems incredible, yet considering who tells of it and thinking how great are the forces of superior causes and of Nature, we can receive it, having faith and respect for the learning of those who relate it, since by ourselves we lack full understanding of the causes of things.**

The art of metallurgy. About 1550 two books were published describing the contemporary mining and metallurgical practices: De Re Metallica by Agricola and Pirotechnia by Biringuccio. The advanced state of metallurgical art is shown by the topics covered in these books, which included methods for preparing brass, welding cracked bells, making wire, and separating lead, silver, and gold from copper. On the other hand, the poverty in the science of metals is indicated by the fact that zinc was not recognised as the alloying element in brass, that the fundamentals of alloying were not understood, and that even the basic attributes of a metal were not appreciated.

Although metals such as copper had been melted very early in man's history, iron was reduced from its ore in a pasty condition that prevented complete separation of the slag from the iron. Such a material is called wrought iron. It had the disadvantage that it could not be cast but had to be forged to the desired shape. Finally, about a.p. 1360, primitive forerunners of the present blast furnace began to produce slag-free molten iron that could be cast—a material known as pig iron or cast iron. It must have been a disappointment to metallurgists of this period to find that castings made from this molten iron were brittle compared with wrought iron. The brittleness was caused by the action of about four percent carbon in the cast iron, and only within the past 100 years have economical means for removing this carbon been developed. Nevertheless, the combination of cast iron, wrought iron, and hardenable cemented wrought iron (blister steel) supplied craftsmen of this period with a variety of ferrous construction materials in addition to the nonferrous metals such as lead, tin, and copper.


† The term ferrous, which by derivation refers to iron alloys, is occasionally extended to include nickel and cobalt as well. All other metals are nonferrous; nickel and cobalt are usually included in this group.
Modern Times

Chemistry. The scientific era dates from about 1600. Almost immediately metallurgy benefited from such advances in chemistry as the identification of many of the elements. An important development occurred in 1740 when Huntsman invented the crucible process for making steel. This procedure involved melting blister steel or wrought iron together with charcoal and fluxes in a heated crucible. Although little more than a remelting operation, this process did eliminate the slag particles and so produced a high-quality steel. Crucible steel, however, was expensive and could be used only for such costly articles as tools, razors, and knives. A low-cost steel of good quality to meet the growing needs of the industrial revolution became available only in the 1860's, with the discovery of the Bessemer and open-hearth processes.

The science of metals is generally considered to have begun in the eighteenth century with the French chemist Réaumur. He was especially interested in the treatment of iron and steel and studied the problem of changing pure iron into steel by cementation (adding carbon). Although his analysis of the mechanism of the hardening of steel was marred by the fact that he thought in terms of "sulfur and salts" in the iron rather than of carbon, still his basic ideas were surprisingly accurate. Réaumur also studied the grain size of steel and found that larger grain sizes are produced by high heating temperatures. As in current practice, he considered a coarse-grained steel inferior for use in tools.

In this period also, scientists began to recognize the fundamentals underlying the hardening of steel. The significance of the quenching temperature and the rate of cooling was learned first. Later, in 1781, the Swedish chemist Bergman explained the importance of carbon in distinguishing iron from steel, and he also suggested the role of allotropy. This important phenomenon can be described briefly. At high temperatures iron exists in a crystal form that can dissolve appreciable carbon, while at lower temperatures the iron changes to a different (allotropic) form that has almost no solubility for carbon. When steel is quenched from a high temperature the iron changes its crystal structure and entraps the carbon atoms. Somehow this causes the steel to harden.

Physical metallurgy. Problems such as the nature of steel hardening are in the province of the science of the structure and properties of metals, physical metallurgy. This branch of metallurgy had its hesitant beginning in 1808 when Alois de Widmanstätten polished the surface of a meteorite

* It is now known that a similar process was used in India about A.D. 1000 to make Wootz steel.
and upon etching it discovered the beautiful geometric pattern that now bears his name (Fig. 2-1). (Widmanstätten patterns are discussed in Chapter 6.) Since this meteorite was a nickel-iron alloy, it was soon deduced that metals and alloys are actually crystalline, even though they lack the geometrical surfaces of many nonmetallic crystals. In time many methods for investigating the structure of metals were developed: metallography, x-ray diffraction, the electron microscope, and neutron bombardment. Knowledge of the properties of metals also grew in this period; data on the strength of iron and other materials were published about 1825 in response to interest in the design of iron bridges.

Metallography. Although the use of the microscope to study the structure of alloys is recorded as early as 1841, it was not until about 1890 that this technique received general recognition, largely as a result of the work of Sorby in England. The following modern procedure is used to obtain a
A photomicrograph of a metal. A specimen about one inch in its largest dimension is cut from the metal to be examined. A mirror polish is produced on one face of the specimen by grinding on an abrasive wheel, polishing on successively finer emery papers, and lapping on revolving cloth-covered wheels with fine abrasives. In order to reveal the structural details (grain boundaries, a second phase, or inclusions), this polished surface is etched with a chemical solution, such as three percent nitric acid in ethyl alcohol. The etchant attacks various parts of the specimen at different rates and reveals the structure. Most metal structures are too fine to be seen with the unaided eye and can be observed only under a microscope like the one shown in Fig. 2-2. A metallograph permits visual observation of a specimen as well as the making of a photomicrograph. The photomicrograph of Fig. 2-3 shows thin plates of iron carbide in a background of essentially pure iron. This photomicrograph is at about 500 diameters; the usual range of magnification is 50 to 2000 diameters (×50 to ×2000).

Fig. 2-3. A metallograph and a photomicrograph of steel made by its use. (Courtesy Bausch & Lomb Optical Company.)
Equilibrium diagrams. The behavior of an alloy is closely dependent on its structure. However, the grain structures of even some pure metals are not simple, and the problem of knowing the stable structure of most alloys becomes very complex indeed. As an aid to understanding alloy behavior, a convenient method of representing structure in relation to temperature and concentration is needed. About 1900 a solution was found in the equilibrium diagram for two-metal and three-metal alloy systems. Chapter 6 considers this type of diagram in detail. Because the structure and properties of alloys are so radically affected by temperature changes, the invention of a simple, accurate thermometer for use over a wide range of temperatures is of especial significance. The thermocouple devised by Le Chatelier in 1888 consists of a pair of dissimilar wires joined at the place whose temperature is of interest. The voltage measured across the other ends of the wires is an indication of the temperature. Using experimental data obtained by a thermocouple and employing the principles (discovered by Willard Gibbs) that govern the equilibrium of various solid and liquid phases, Roozeboom produced an equilibrium diagram for the iron-carbon system. This event represented a great advance in the understanding of steel heat-treating and of alloy-behavior.

Atomic structure. Early in the present century, ideas on the structure of matter and on the structure of the atoms of which matter is composed were taking their current form. The metallographers must have been disappointed to learn that the best light microscope, magnifying 1000 diameters, was still one-thousandfold too poor to reveal the individual atoms. However, a new kind of light of very short wavelength, the x-ray, was discovered about this time, and it was used to reveal the atomic crystal structure, but nevertheless to obtain valuable information on the location of the atoms in metals. This knowledge of the regular arrangement of the atoms in metals served only to whet the appetite of the metal scientists for an understanding of the fundamental causes behind this regularity. They wanted to know why iron changes its crystalline arrangement above a certain temperature. They tried to learn more about the processes of melting and solidification. The search led to inquiries concerning the structure of atoms, to Bohr's theory of an atom fashioned like the solar system, and to the wave mechanical picture of electron shells of hazy probability surrounding an amazingly complex nucleus. Scarcely any of the final answers have yet been found, but the direction of research is definitely charted.

Extractive Metallurgy

The nature of a metallic ore was described at the beginning of the chapter. The first step in obtaining metals that can be used in engineering
Reduction of ore to metal. The type of reduction method that can be used to obtain a given metal is largely dependent on the stability of the metallic compound to be reduced. A rough measure of stability is the heat of formation \( \Delta H \), defined as the number of calories absorbed when a gram molecular weight of compound is formed. For example, when iron oxide, \( \text{Fe}_2\text{O}_3 \), forms from iron and oxygen at 1340°F by the reaction

\[
2\text{Fe} + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3, \tag{2-1}
\]

\( \Delta H = -192.6 \) kilocalories, where the minus sign indicates that in this instance the heat is evolved rather than absorbed. Strictly speaking, a related thermodynamic quantity, the free energy \( \Delta F \), should be used to measure stability under these conditions. Briefly, the total energy (enthalpy) \( H \) of a system can be considered to be composed of two portions: (1) the "bound" or unavailable energy, \( TS \), where \( S \) is the entropy and \( T \) is the absolute temperature in °K, and (2) energy available to do useful work, the free energy \( F \). That is,

\[
F + TS = H. \tag{2-2}
\]

When this equation is used to define free energy it is written as

\[
F = H - TS. \tag{2-3}
\]

In chemical reactions at constant temperature the significant quantities are the differences \( \Delta F, \Delta H, \) and \( \Delta S \) between the values for the reacting substances (\( \text{Fe} \) and \( \text{O}_2 \) in Eq. 2-1) and for the products of reaction (\( \text{Fe}_2\text{O}_3 \)). Therefore, Eq. (2-3) is ordinarily used in the form

\[
\Delta F = \Delta H - T \Delta S. \tag{2-4}
\]

* The following treatment is based on a series of articles by L. M. Pidgeon in Metal Progress for August, October, and November, 1956.

† All the \( \Delta H \) and \( \Delta F \) values considered in this section are standard values. Essentially, this means that the oxygen in Eq. (2-1) is at atmospheric pressure.
A SURVEY OF METALLURGY

## Table 2-2

**FREE ENERGY OF FORMATION OF THE OXIDES OF SEVERAL METALS**

(kilocalories per oxygen atom)

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta F$ @ 440°F</th>
<th>$\Delta F$ @ 1340°F</th>
<th>$\Delta F$ @ 2240°F</th>
<th>$\Delta F$ @ 3140°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>+0.96</td>
<td>+11.3</td>
<td>-14.4</td>
<td>Na -7.9</td>
</tr>
<tr>
<td>Hg</td>
<td>-8.8</td>
<td>Cu -23.3</td>
<td>Cu -15.2</td>
<td>Cu -10.7</td>
</tr>
<tr>
<td>Cu</td>
<td>-31.5</td>
<td>Pb -28.7</td>
<td>Pb -18.7</td>
<td>Ni -13.0</td>
</tr>
<tr>
<td>Cd</td>
<td>-37.1</td>
<td>Ni -35.0</td>
<td>Ni -24.2</td>
<td>Zn -15.0</td>
</tr>
<tr>
<td>Pb</td>
<td>-40.4</td>
<td>Cd -37.7</td>
<td>Co -29.5</td>
<td>Co -19.9</td>
</tr>
<tr>
<td>Ni</td>
<td>-46.1</td>
<td>Co -38.8</td>
<td>Fe -35.1</td>
<td>Cr -49.1</td>
</tr>
<tr>
<td>Fe</td>
<td>-47.9</td>
<td>Fe -44.8</td>
<td>Na -38.6</td>
<td>Mn -55.1</td>
</tr>
<tr>
<td>Fe</td>
<td>-50.4</td>
<td>C -47.9</td>
<td>Zn -38.9</td>
<td>U -59.6</td>
</tr>
<tr>
<td>Zn</td>
<td>-54.8</td>
<td>Zn -61.4</td>
<td>C -58.3</td>
<td>V -80.5</td>
</tr>
<tr>
<td>Cu</td>
<td>-71.3</td>
<td>Na -65.5</td>
<td>Cr -59.5</td>
<td>Si -61.9</td>
</tr>
<tr>
<td>Cr</td>
<td>-81.6</td>
<td>Cr -69.7</td>
<td>Mn -65.6</td>
<td>C -68.5</td>
</tr>
<tr>
<td>Na</td>
<td>-83.0</td>
<td>Mn -74.5</td>
<td>V -69.5</td>
<td>Ti -70.1</td>
</tr>
<tr>
<td>Mn</td>
<td>-83.1</td>
<td>V -79.0</td>
<td>Si -73.1</td>
<td>Mg -76.1</td>
</tr>
<tr>
<td>V</td>
<td>-89.0</td>
<td>Si -83.4</td>
<td>Ti -80.5</td>
<td>Al -82.0</td>
</tr>
<tr>
<td>Si**</td>
<td>-94.0</td>
<td>Ti -91.1</td>
<td>Li -92.0</td>
<td>Ba -86.0</td>
</tr>
<tr>
<td>Ti†</td>
<td>-102.1</td>
<td>Al -108.2</td>
<td>Al -95.1</td>
<td>Ca -95.5</td>
</tr>
<tr>
<td>U</td>
<td>-119.1</td>
<td>U -106.0</td>
<td>U -98.6</td>
<td>Be -96.6</td>
</tr>
<tr>
<td>Al</td>
<td>-120.7</td>
<td>Li -110.2</td>
<td>Ba -99.0</td>
<td>Mg -101.3</td>
</tr>
<tr>
<td>Ba</td>
<td>-121.5</td>
<td>Ba -110.5</td>
<td>Mg -101.3</td>
<td>Mg -101.3</td>
</tr>
<tr>
<td>Li</td>
<td>-127.7</td>
<td>Mg -117.7</td>
<td>Be -108.3</td>
<td>Mg -113.3</td>
</tr>
<tr>
<td>Mg</td>
<td>-130.8</td>
<td>Be -119.6</td>
<td>Ca -113.3</td>
<td>Ca -113.3</td>
</tr>
<tr>
<td>Be</td>
<td>-131.3</td>
<td>Ca -126.0</td>
<td>Ca -126.0</td>
<td>Ca -128.2</td>
</tr>
</tbody>
</table>

*Fe$_2$O$_3$ **Quartz †Rutile ‡The dioxide, UO$_2$ ††CO


If $\Delta F$ is negative the reaction in question can occur, while if $\Delta F$ is positive the reaction is impossible. For example, the value of $\Delta F$ for the formation of Fe$_2$O$_3$, Eq. (2-1), is $-134.5$ kilocalories, and it is common experience that such oxidation of iron does occur. However, the $\Delta F$ value for the reverse reaction has the opposite sign and is $+134.5$ kilocalories. Therefore Fe$_2$O$_3$ will not spontaneously decompose into iron and oxygen.

Table 2-2 lists free-energy values for the oxides of several metals. The values tabulated are the free energy per oxygen atom in the compound, for which the notation $\Delta F'$ will be used. For example, the value at 1340°F
for iron oxide \((\text{Fe}_2\text{O}_3)\) is \(\Delta F' = \frac{\Delta F}{3} = -134.5/3 = -44.8\) kilocalories. The metal oxide at the top of each column is the least stable of those listed; those farther down have increasingly greater stability. For example, at 440°F silver oxide should tend to decompose spontaneously to form metallic silver (see Problem 1 at end of chapter), while calcium oxide would be extremely difficult to reduce. In the case of calcium oxide a free-energy decrease of 138.1 kilocalories accompanies its formation, and therefore it is necessary to increase the free energy by this amount to release metallic calcium from the oxide. Several methods for supplying the energy needed to reduce metals from their oxides will now be considered.

**Thermal decomposition.** It can be seen in Table 2-2 that the free-energy values for the formation of a given metal oxide become smaller (negative) numbers as the temperature increases. Eventually, at a sufficiently high temperature, the free energy would become positive. The oxide could then spontaneously decompose to yield the free metal—a process known as thermal decomposition. Actually this method is practicable only for the few metals whose oxides have positive free energies for formation at relatively low temperatures. The "noble" metals silver, gold, platinum, etc., exist as native metals in the earth's crust by virtue of this characteristic. A popular experiment in general chemistry is the reduction of \(\text{HgO}\) to metallic mercury by merely heating the oxide in a test tube. The free-energy values in Table 2-2 explain why it is necessary to raise the temperature well above 440°F (to about 900°F) to produce this reaction. Thermal decomposition of compounds other than oxides is currently employed in commercial practice. Important examples are the deposition of titanium from gaseous \(\text{Tl}_2\) by decomposition on a hot surface and the production of nickel by thermal decomposition of nickel carbonyl, \(\text{Ni} \text{(CO)}_4\).

**Reduction of oxides by carbon or carbon monoxide.** Many important metals are reduced from their oxides by being heated in contact with carbon, usually in the form of coke. The coke performs two functions in these processes. First, its burning helps supply the heat needed to keep the reacting substances at a high temperature—a condition that favors high reaction rates and permits undesirable products to be eliminated as a molten slag. Second, the oxidation of carbon releases energy needed for reduction of the metal oxide. This oxidation occurs in two steps:

\[
\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}, \quad (2-5)
\]

\(\Delta F\) values for which are listed in Table 2-2, and,

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2, \quad (2-6)
\]
The $\Delta F$ values for the latter reaction are readily calculated, since the formation of CO$_2$ by the reaction

$$C + O_2 \rightarrow CO_2$$  \hfill (2-7)

involves a free-energy change of $-94.5$ kilocalories, which is practically independent of temperature. The method for this calculation is outlined in Problem 2.

The production of iron from Fe$_3$O$_4$ is an example of reduction by carbon and carbon monoxide. The reaction involved is the reverse of Eq. (2-1), namely,

$$Fe_3O_4 \rightarrow 2Fe + \frac{3}{2}O_2.$$  \hfill (2-8)

The free-energy change (per oxygen atom) accompanying this reaction at a given temperature is the negative of the value listed in Table 2-2 and therefore represents an increase in energy. However, the reaction can be made to occur if the corresponding amount of energy is supplied by the reaction of either Eq. (2-5) or Eq. (2-6). For example, the combination of the reactions of Eqs. (2-8) and (2-6) can be written

$$Fe_3O_4 + 3CO \rightarrow 2Fe + 3CO_2.$$  \hfill (2-9)

The free-energy change per oxygen atom for the over-all reaction is the algebraic sum of the $\Delta F'$ values for the two separate reactions, which are tabulated below. The values listed for the decomposition of Fe$_3$O$_4$ were taken from Table 2-2 with a change in sign. To obtain values for oxidation of CO to CO$_2$, values for the C to CO reaction were taken from Table 2-2 and were used with the value for the C to CO$_2$ reaction, Eq. (2-7).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta F'$, kilocalories per oxygen atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>440°F</td>
</tr>
<tr>
<td>Fe$_3$O$_4 \rightarrow 2Fe + \frac{3}{2}O_2$</td>
<td>+54.8</td>
</tr>
<tr>
<td>C + $\frac{3}{2}O_2 \rightarrow CO$</td>
<td>-37.1</td>
</tr>
<tr>
<td>CO + $\frac{3}{2}O_2 \rightarrow CO_2$</td>
<td>-57.4</td>
</tr>
</tbody>
</table>

Thus at 440°F the reaction of Eq. (2-9) has a $\Delta F'$ value of $+54.8 - 57.4 = -2.6$ kilocalories per oxygen, and therefore the reaction can occur.

Combination of Eqs. (2-8) and (2-6) leads to the over-all equation describing the reduction of Fe$_3$O$_4$ by carbon, namely,

$$Fe_3O_4 + 3C \rightarrow 2Fe + 3CO.$$  \hfill (2-10)
At 440°F the $\Delta F$ for this reaction is $+54.8 - 37.1 = 17.7$ kilocalories per oxygen atom, and therefore the reaction will not occur at this temperature. However, these data show that at 1340°F, and especially at 2240°F, reduction by carbon is thermodynamically more favorable than reduction by carbon monoxide.

Although carbon and carbon monoxide are the most widely used reducing agents for metals, other substances can be employed in a similar manner. For example, hydrogen can take up oxygen by the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$. The free-energy change for this reaction is roughly the same as for the oxidation of CO to CO₂. Reduction with hydrogen may be used when it is important to avoid contamination of the metal with carbon.

**Reduction by electrolysis.** The energy necessary to reduce a metal from the combined state can often be supplied electrically. The principal requirements for the successful application of this method are:

1. The metal or a suitable metallic complex must be present in the ionized condition. An aqueous solution is preferable; an example of this type of electrolysis is described later for the refining of copper (Fig. 2-10). Among alternative electrolytes are fused (molten) salts such as that used in the production of aluminum (Fig. 2-11).

2. The electrolyte must be stable under the conditions of electrolysis. Although an aqueous solution is satisfactory for most metals, water would be decomposed by the electrical potentials needed for the electrolysis of compounds of aluminum or more reactive metals.

3. The reduced metal must be deposited in a convenient form. For example, copper is deposited as an excellent, dense slab from aqueous solution, and aluminum is obtained as a molten pool that can be cast into ingots. On the other hand, the reactive metal titanium has such a high melting point that it must be deposited in the solid state in fused electrolytes, and no satisfactory, coherent deposit has yet been obtained under these conditions.

The advantage of the electrolytic method for the reduction of reactive metals can be shown easily for aluminum. From the data of Table 2-2 it can be seen that Al₂O₃ cannot be reduced by carbon at the temperatures listed. For example, at 1800°F the reaction

$$\text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + \frac{3}{2}\text{O}_2$$

\[(2-11)\]

* A factor not considered in this treatment is the occurrence of FeO as a stage in the reduction of Fe₂O₃. This factor changes the numerical free-energy values somewhat but does not alter the general features described here.

† It is possible to reduce Al₂O₃ by carbon at the very high temperatures obtainable in an electric arc furnace, but an objectionable carbide is then formed.
has a $\Delta F'$ value of $+101.6$ kilocalories per oxygen atom, while the reduction of carbon would furnish only $\Delta F' = -47.9$ kilocalories. However, it can be shown that the necessary amount of energy can easily be supplied electrically. During the electrolysis of a gram molecular weight of $\text{Al}_2\text{O}_3$, an electrical charge of 69 is transported between the anode and the cathode by the applied voltage, $E$; here $\mathfrak{F}$ is the Faraday constant, 96,500 coulombs (23,070 calories/volt).* By definition, the electrical energy supplied is the product of the charge transported and the applied voltage; $69E$ or, in general,

$$\Delta F = -n\mathfrak{F}E,$$

(2-12)

where $n$ is the number of equivalents and the minus sign indicates that free energy is liberated in the process. Since $\Delta F$ in Eq. (2-12) is for three oxygen atoms in the case of aluminum,

$$3 \mathfrak{F}E = \Delta F' = \frac{3}{6} \mathfrak{F}E = \frac{3}{2} \mathfrak{F}E.$$ 

Therefore, at 1800°F, which is the temperature at which the electrolysis of aluminum is carried out, it is necessary that $3E$ be at least $101.6/2 = 50.8$ kilocalories. Solving for the minimum voltage, $E = 50,800/23,070 = 2.20$ volts. Thus, theoretically, a low voltage is sufficient to supply the energy needed to decompose compounds having great chemical stability. Although the actual voltages used in commercial operations are somewhat higher, the value for aluminum extraction is only about 5 volts.

Displacement by another metal. A familiar experiment in chemistry is the displacement of copper from a solution of $\text{CuSO}_4$ when a piece of more reactive metal, such as iron, is placed in the solution. This reaction is used commercially in certain phases of the extractive metallurgy of copper to plate copper out of solution onto pieces of scrap iron. The same type of reaction can also occur between a solid metal oxide and a metal that lies below it in Table 2-2. In the Goldschmidt (thermit) process, $\text{Fe}_2\text{O}_3$ is reduced by powdered aluminum metal according to the reaction

$$\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe},$$

(2-13)

* It should be recalled that one Faraday is required to electrolyze one gram atomic weight of a univalent ion, such as $\text{Ag}^+$. Since aluminum is trivalent ($\text{Al}^{3+}$), and since there are two aluminum atoms per molecule, six Faradays are required in this case.

† The theoretical value is lowered still further when the reaction of the liberated oxygen with the carbon of the anode is taken into account.
with a $\Delta F^\circ$ value of about $-60$ kilocalories per oxygen atom. Another example of a displacement reaction is the Kroll process for producing metallic (sponge) titanium by reduction of gaseous TiCl$_4$ with liquid magnesium. The main reaction is

$$2\text{Mg(liquid) + TiCl}_4\text{(gas) \rightarrow 2MgCl}_2\text{(liquid) + Ti(solid)},$$

(2-14)

and at the reaction temperature of 1375°F the $\Delta F^\circ$ value is about $-25$ kilocalories per chlorine atom, which is similar to the value for the oxides in Table 2-2.

Iron and steel. An important example of the extraction of a metal from its ore is the production of iron and steel. Many different processes are currently in use, but it is convenient to consider first the sequence shown in the flowsheet of Fig. 2-4. If the ore is sufficiently rich it can be used directly from the mine, but much of the ore in the United States is now a lower-grade material that must be freed of a portion of its gangue by an ore-dressing operation before it can be smelted profitably.

Blast furnace. This furnace (Fig. 2-5) illustrates a commercial utilization of carbon monoxide and carbon as reducing agents for iron oxide. Special skip cars are used to charge ore, coke, and limestone into the furnace at the top. The coke is for reduction of the ore and for heating. The limestone combines with the gangue of the ore and with the ash of the coke so they can be removed as a low-melting slag. Air heated to about 1500°F is blown in at the bottom of the furnace through tuyeres and burns the coke to produce a temperature of about 3000°F. Hot gases rich in carbon monoxide pass upward through the furnace and heat the descending materials. In the upper part of the furnace the iron oxides are reduced only by carbon monoxide, but at temperatures above about 1200°F reduction by carbon begins to be important. Molten iron accumulates at the bottom of the furnace and is removed at intervals of several hours.

Open-hearth furnace. The crude pig iron produced by the blast furnace is converted into steel in an open-hearth furnace, Fig. 2-6. This furnace is a reverberatory type, in which a long flame originating at a burner at one end of the furnace plays over the surface of the metal bath. The necessary flame temperature can be attained economically only if the air for combustion is preheated to about 1800°F by being passed through heat exchangers, called checker chambers. The starting materials in this process are usually scrap steel, molten pig iron, and limestone. Early in the melting operation the limestone helps form a slag over the surface of the metal bath, which allows purification of the bath to proceed at a com-
A SURVEY OF METALLURGY

Iron Ore
100 tons: 50% Fe, 6% SiO₂, 2% Al₂O₃

Coke
50 tons

Air
25 tons

Limestone
25 tons

Blast furnace

Plant fuel
54 tons: 94% Fe, 4% C, 1% Si

5 tons: 32% SiO₂, 15% Al₂O₃, 45% CaO

To waste

Basic open hearth

Steel scrap
50 tons

Limestone
6 tons

Iron ore
3 tons

Steel

Slag

Steel ingots
100 tons

Casting

6 tons: 50% CaO, 15% SiO₂, 15% FeO

To waste

FIG. 2-4. Flowsheet for the production of steel using the blast-furnace and basic open-hearth processes. (From Schuhmann, Metallurgical Engineering, Vol. 1, Addison-Wesley, 1952.)

trollable rate. Oxidation of the carbon, manganese, and silicon of the pig iron is effected largely by iron oxide dissolved in the metal bath from the slag, although early in the process iron ore is also added to the bath for this purpose.

When a suitable chemical analysis has been achieved and when any non-metallic materials such as oxides have floated to join the slag, the "heat" is ready for deoxidation, that is, the removal of a certain proportion of the oxygen content of the molten metal by the addition of such deoxidizers as ferromanganese. Depending on the degree of deoxidation, three types
FIG. 2-5. Cross section of the general construction of a modern blast furnace.

FIG. 2-6. The operation of an open-hearth furnace. (Courtesy Bethlehem Steel Company.)
of steel can be produced—rimmed, semikilled, and killed, increasing in degree of deoxidation in that order. The deoxidized steel is teemed into ingot molds from a ladle, as shown in Fig. 2-7, and solidification is allowed to proceed. Since the volume of the steel decreases during solidification, there is a tendency for a hole or pipe to form inside the ingot. This condition is indicated by the large black areas at the top of the killed ingot in Fig. 2-8. Pipe formation can be reduced or eliminated by allowing gas pockets or "blow holes" to form, as shown in the semikilled and rimmed ingot structures. These blow holes result largely from the carbon monoxide produced by the reaction of iron oxide and carbon in the steel. Blow holes, if unoxidized, are closed by welding during the rolling operation.

Other steelmaking processes. There are a number of alternatives to the
open-hearth furnace for making steel from the pig iron produced by the blast furnace. In the Bessemer process, Fig. 2-9(a), a stream of air is forced through about fifteen tons of molten pig iron to convert it to steel. No external source of heat is needed, since the oxidation of the silicon, manganese, and carbon of the cast iron liberates enough heat to more than compensate for the cooling effects. A pig iron of the typical analysis given in the table below is changed into a typical Bessemer steel by a fifteen minute "blow," followed by deoxidation with both ferromanganese and ferrosilicon, and then rebattuburization with coke.

Bessemer steel is not of the highest quality because of (1) high sulfur and phosphorus content, (2) high nitrogen and oxygen content, (3) large numbers of nonmetallic inclusions such as slag particles, and (4) variation in properties from one heat to the next. However, this steel is widely used for applications requiring easy machining, good welding properties, or superior rigidity.

Electric-arc furnaces, Fig. 2-9(b), range in capacity up to 100 tons. Their operation is roughly similar to that of an open-hearth furnace, but the use of electrical heating permits better control of the composition and temperature of the metal bath than in the open-hearth furnace. The present high operating costs restrict the use of the electric-arc furnace to the manufacture of high-quality steels and of high-alloy steels that cannot be produced in the open-hearth furnace.

The oxygen steelmaking furnace shown in Fig. 2-9(c) is an important example of the use of oxygen in the manufacture of iron and steel. Scrap steel, molten pig iron, and slag-forming materials are charged into the furnace, and then a stream of oxygen is played on the surface of the bath. Some impurities are oxidized directly, while others are eliminated by the reactive slag that is quickly formed. Within about 30 minutes the heat is ready for pouring, having been converted into steel of quality similar to that produced in the open-hearth furnace.

### MATERIALS INVOLVED IN THE BESSEMER PROCESS

<table>
<thead>
<tr>
<th>Composition (balance of composition is essentially iron)</th>
<th>Material</th>
<th>&quot;Bessemer&quot; pig iron</th>
<th>Metal after &quot;blow&quot;</th>
<th>&quot;Bessemer&quot; steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>4.3%</td>
<td>0.05%</td>
<td>0.3%</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>0.6</td>
<td>0.05</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>1.5</td>
<td>0.005</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.09</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.04</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>0.02</td>
<td>0.50</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2-9. Important methods, in addition to the open-hearth furnace, for converting pig iron into steel: (a) Bessemer converter, (b) electric arc furnace, (c) oxygen furnace. [Illustrations (a) and (b) courtesy Bethlehem Steel Company.]
Copper. Unlike pig iron, which was first melted about the year 1350, and steel, first produced at low cost in 1860, copper and its alloys, brass and bronze, have been melted and manufactured at moderate cost for thousands of years. A typical modern method of copper production is considered here. While many iron ores contain fifty percent iron and can be charged directly into the blast furnace, ores of copper average less than one-tenth as rich and must be treated by ore-dressing methods in order to yield a product that can be smelted profitably. Ore-dressing operations are conveniently divided into comminution—crushing and grinding the ore to free the mineral particles from the gangue, and concentration—effecting the partial separation of the liberated mineral particles from the gangue. After the copper ore is finely ground it is concentrated by flotation, an operation in which air bubbles are attached to the mineral particles to float them to the top of a tank of water.

The concentrate produced by the ore-dressing procedures consists mostly of copper sulfide, but it also carries appreciable amounts of gangue and minerals containing iron, arsenic, precious metals, etc. The processes for producing relatively pure copper from this concentrate are roasting, smelting, fire refining, and electrolytic refining. Roasting is accomplished by bringing hot oxidizing gases into contact with the concentrate to change part of the copper sulfide to copper oxide. The roasted concentrate is smelted in a reverberatory furnace, similar in principle to an open-hearth furnace, to produce matte, a mixture of copper sulfide and iron sulfide. In this process the gangue is eliminated as a slag. The molten matte is next converted into copper and an iron-rich slag by blowing air through the matte in a device similar in principle to the Bessemer converter. Since the blister copper thus formed contains two percent of impurities, the molten copper is fire refined in a casting furnace. In this process most of the impurities and a portion of the copper are first oxidized, and then the oxidized copper is reduced to metallic copper by poling. The poling process consists of thrusting green wooden poles into the bath and allowing the evolved gases to reduce the copper oxide. When the oxygen content of the bath has been reduced to 0.05 percent, the metal is ready to be cast as tough-pitch copper, which still contains about 0.6 percent of impurities. Although some tough-pitch copper is used in manufacture, most of the copper produced in the United States is further refined by the electrolytic process. Figure 2-10 illustrates the principle of this method, by which anodes of fire-refined copper are changed into cathodes containing 99.95 percent copper. The precious metals are recovered in this step. As the final process in the production of copper, the cathodes are melted and cast into convenient shapes, such as wire bars for drawing into wire. OFHC, oxygen-free high conductivity, copper is made from cathodes by means of a special refining operation to eliminate the oxygen.
Aluminum. Since ancient man had found the easily accessible metals, a modern metal might be defined as one that is difficult to produce from its ore. Aluminum certainly belongs in this category since, despite the interest of a French king and the efforts of his scientists, the commercial production of this metal was achieved only in 1886—largely due to the efforts of an American college boy, Charles Martin Hall, working in his woodshed laboratory.

Although aluminum is the most abundant metallic element in the earth's crust, it occurs only in the combined state. Bauxite, a hydrated aluminum oxide, is the principal compound used in aluminum manufacture. The ore after mining may be subjected to ore-dressing treatments, but the essential refining step applied to the ore is the Bayer process for producing a very pure aluminum oxide. The crushed ore is treated with a hot sodium hydroxide solution, which dissolves the aluminum oxide and leaves the impurities as a residue. When the solution cools, aluminum hydroxide is precipitated and is converted to aluminum oxide by heating.

The principle discovered by Hall is that metallic aluminum is produced when aluminum oxide is electrolyzed in a bath of molten cryolite, an aluminum mineral. Figure 2-11 shows the cell in which electrolysis is accomplished; the aluminum is deposited at the cathode and oxygen is liberated at the anode. The molten aluminum is tapped from the furnace at intervals and cast into pigs. After remelting to remove nonmetallic impurities, this aluminum is 99.0 to 99.9 percent pure and is ready for alloying to produce the many commercial alloys. Aluminum of 99.99 percent purity can be obtained by a second electrolytic treatment.
FIG. 2-11. An electrolytic cell used in aluminum production. (Courtesy Aluminum Company of America.)

CASTING

METAL-FORMING METHODS

Seldom is the product of an ore-reducing operation in a form suitable for final use. Steel ingots, cast-iron pigs, copper wire bars, and aluminum ingots must all be further processed in order to produce an automobile axle, a plowshare, a transformer winding, or a saucepan. Some metal-forming methods are briefly outlined in this section.

Casting. By definition, casting is the pouring of molten metal into a mold, where solidification occurs. Almost every finished metal product has been cast at some stage of its manufacture. For example, all rolled and forged steels are initially in the form of cast ingots, and even after extensive hot-working, evidences of the cast structure may still remain in the form of voids, chemical segregation, or surface defects. However, of more interest for the present purpose is the wide use of casting processes for producing finished complex metal parts.

Sand casting. The most universally employed casting procedure involves pouring molten metal into a cavity in a mass of packed sand. Figure 2-12(a) shows a typical mold in cross section. It illustrates the use of chills to produce a local hard surface, a core to form a shaft opening, and a sprue for running the molten metal into the cavity. A wood or...
metal pattern approximately the shape of the final casting is used to produce the cavity in the sand mold. So that the pattern may be removed from either the cope (upper) or the drag (lower) section of the mold without disturbing the sand that has been packed around it, a taper or draft of a few degrees must be allowed on the vertical faces of the pattern. Patterns with and without adequate draft are shown in Fig. 2-13. It is evident that patterns having re-entrant angles would create special difficulties.

Since casting alloys decrease in volume as they solidify and cool to room temperature, it is necessary to make the pattern larger than the final casting by an amount known as the shrinkage allowance. Shrinkage is on the order of \( \frac{1}{4} \) inch per foot but varies considerably, depending on such factors as the kind of alloy being cast, the design of the casting, the pouring temperature, and the size of the casting. In making castings such as those of a U-shape it is necessary to “fake” or distort the pattern in order to obtain the desired form in the final casting. This is called distortion allowance. An additional machine finish allowance of \( \frac{1}{8} \) inch or more must be allowed on surfaces that are to be machined. Finally, even with the use of the best available information on shrinkage allowance, it is unlikely that final dimensions of the casting can be controlled exactly. Therefore size tolerances equal to half the shrinkage allowance are suggested for use with castings of new design.

Shell molding. This is a modification of sand casting in which a relatively thin shell forms the mold cavity into which the molten metal is poured. Typically, each of the two halves of a shell molding is made by placing a mixture of fine sand and a resin binder in contact with a heated metal pattern. Melting of the resin occurs in a thin layer of the sand-resin mixture at the surface of the pattern, and this thin shell remains attached to the pattern when the excess mixture is allowed to fall off. The shell is then baked at a high temperature, removed from the pattern, and finally assembled with the matching half to form the completed shell molding. Castings produced by this process have better surface finish and closer dimensional tolerances than do sand castings.

Permanent mold casting. A casting process in which steel molds and cores are employed is given the name permanent mold casting. When sand cores are employed with steel molds, the process is called semi-permanent mold casting. The principal advantage of these casting methods over sand casting is economy, but other advantages are improved mechanical
FIG. 2-14. Gooseneck die-casting machine in position for air pressure to force molten metal into the die cavity.

FIG. 2-15. Cross section of a centrifugal casting machine.

Die casting. This form of casting is essentially permanent mold casting in which pressure forces the molten metal into the mold cavity. However, the mold used is much more expensive (it is called a "die"), and a complex machine is employed to produce castings at a very high rate. Figure 2-14 shows one of the types of machines used in die casting. Die castings have excellent surface finish and dimensional accuracy, but volume production is necessary for a low cost per casting.

Centrifugal casting. Castings that have rotational symmetry, such as long cylinders, are conveniently made by pouring the casting alloy into a metal, graphite, or sand mold rotating about its axis of symmetry. A machine for producing such centrifugal castings is shown in Fig. 2-15. Nonmetallic inclusions and slag particles, being less dense than the liquid metal, are forced to the inner surface of the casting and are removed in a later machining operation. The mechanical properties of these castings properties, closer tolerances, and better surface conditions. The minimum number of castings for which it is economical to use permanent molds is on the order of one thousand.
are superior to those of sand castings, but gravity segregation* is encountered in some alloys.

\textit{Investment casting.} The "lost wax" process used for many years by jewelers and dentists has recently been adapted to the production of small industrial castings. In this method, a wax pattern of the part to be made is embedded (invested) in a fluid ceramic material that subsequently becomes solid. This mold is heated, causing the wax to melt and flow out, leaving a cavity of the desired shape. Molten metal is poured into the mold cavity, and after the metal has solidified the mold material is broken away, leaving the final casting. Investment castings, which are often called \textit{precision castings}, have excellent surfaces and dimensional accuracy, and for this reason they are used for parts made of nonmachinable and nonforgable alloys. Also, extremely complex sections can be produced by this method, since there are no problems of draft, parting lines, and so on, as in sand casting.

\textit{Plaster casting.} If the sand-casting process is changed so that plaster of Paris is substituted for sand as the molding material, the method is called plaster casting. The principal advantages are improved surface conditions and dimensional control.

\textit{Slush casting.} Hollow castings, such as statues, can be made by pouring a low-melting point alloy into a bronze or a plaster mold and quickly pouring out the excess molten metal after a thin solid shell has formed. The resulting slush casting can be finished by electroplating or lacquering.

\textit{Continuous casting.} A process that is growing in importance is that of casting alloys of copper and metals of lower melting points in suitably long lengths, usually for hot-rolling. One of a variety of devices used is a vertical water-cooled mold open at both ends, where the molten metal is poured in at one end and the final billet, a foot or more square, is withdrawn from the other. As the continuous casting process is developed further it promises to give lower costs and improved metal properties. The continuous casting of steel is in the developmental stage at present.

\textit{Choice of casting method.} Because of the many factors involved, it is difficult to say just which fabricating method is the best for making a given metal article. Table 2-3 gives a rough comparison of five of the principal casting processes with respect to a number of factors that influence the designer in his choice of a production method. Since hundreds of alloys, ranging from weak, low-melting, lead-base materials to strong, high-

\* The term \textit{segregation} refers to the inhomogeneous distribution of alloying elements that exists in some materials. If one of the component metals is heavy (lead in brass, for example), the force of gravity—or centrifugal force—acting on the heavy particles in the liquid alloy will tend to concentrate these heavy particles in the bottom portion of the casting. Other causes of segregation are considered in Chapter 6.
## Table 2-3
### Comparison of Casting Methods (Approximate)

<table>
<thead>
<tr>
<th></th>
<th>Sand casting</th>
<th>Permanent mold cast</th>
<th>Die casting</th>
<th>Centrifugal casting</th>
<th>Investment casting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Relative cost in quantity</strong></td>
<td>medium</td>
<td>low</td>
<td>lowest</td>
<td>high</td>
<td>highest</td>
</tr>
<tr>
<td><strong>Relative cost for small number</strong></td>
<td>lowest</td>
<td>high</td>
<td>highest</td>
<td>medium</td>
<td>low</td>
</tr>
<tr>
<td><strong>Permissible weight of casting</strong></td>
<td>unlimited</td>
<td>100 lbs</td>
<td>30 lbs</td>
<td>several tons</td>
<td>5 lbs</td>
</tr>
<tr>
<td><strong>Thinnest section castable, inches</strong></td>
<td>1/4</td>
<td>1/4</td>
<td>3/16</td>
<td>1/8</td>
<td>0.005</td>
</tr>
<tr>
<td><strong>Typical dimensional tolerance, inches</strong></td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td><strong>Relative surface finish</strong></td>
<td>poor</td>
<td>good</td>
<td>best</td>
<td>fair</td>
<td>very good</td>
</tr>
<tr>
<td><strong>Relative mechanical properties</strong></td>
<td>fair</td>
<td>good</td>
<td>very good</td>
<td>best</td>
<td>fair</td>
</tr>
<tr>
<td><strong>Relative ease of casting complex design</strong></td>
<td>fair</td>
<td>fair</td>
<td>good</td>
<td>poor</td>
<td>best</td>
</tr>
<tr>
<td><strong>Relative ease of changing design in production</strong></td>
<td>best</td>
<td>poor</td>
<td>poorest</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td><strong>Range of alloys that can be cast</strong></td>
<td>unlimited</td>
<td>copper base and lower melting preferable</td>
<td>aluminum base and lower melting preferable</td>
<td>unlimited</td>
<td>unlimited</td>
</tr>
</tbody>
</table>
melting supersteels, are cast commercially, it is impossible to give general rules that accurately cover the whole field. However, the qualitative information of Table 2-3 can often be used in deciding on a suitable casting method in a particular instance.

**Working.** In many instances hot- or cold-worked* metals are employed in preference to cast metals because the working methods are more economical, as in the case of structural shapes like I-beams. However, a higher-cost wrought part is frequently chosen in preference to one that is cast because of the superior properties imparted to metals by the working operation. Some of the important characteristics that favor wrought metals are homogeneity, absence of voids, reproducibility of properties, higher ductility, greater impact strength, and more desirable grain structure. Several metal-working methods are considered briefly in this section.

**Forging.** The oldest metal-working process is hand forging, in which a metal heated to a temperature at which it is easily deformed is shaped by beating with a hand hammer. A logical development was the mechanical hammer and later the forging press. When dies are substituted for the flat anvils of a mechanical hammer, it is possible to forge complex parts such as crankshafts rapidly and economically by drop forging. Figure 2-16 shows an over-all view of a steam forging hammer, and Fig. 2-17 is a close-up view of the drop forging of an aluminum aircraft propeller blade.

Other types of forging processes include press forging, in which the force for deforming the hot metal is applied slowly by hydraulic pressure instead of by a series of impact blows. This method is especially useful in working large shafts or other parts of great thickness, since the effect of pressing extends far below the surface layers. Swaging can be considered to be the specialized forging of cylindrical bars not more than an inch or two in diameter. A rotary machine is used to open and close rapidly a pair of dies forming a cylindrical volume of the desired diameter. These dies reduce the diameter of a rod as it is slowly fed through them. Alloys which are difficult to work by other methods without cracking can frequently be swaged successfully. Forging machines, such as the one shown in Fig. 2-18, are used for a large number of hot- and cold-forging operations. Especially common are operations involving upsetting the end of a rod, as in heading a bolt, or piercing a cavity in a bar, as shown in Fig. 2-18. The oil-well tool-joint forging shown in Fig. 2-18 is made from the initial bar in three steps. The preliminary penetration of the end of the

* Generally cold-working is done at room temperature and hot-working is carried out at a high temperature, about 2000°F in the case of steel. However, a more rigorous distinction between these terms is made in Chapter 12.
bar is done in the top position in the forging machine. The bar is then placed in the central grip dies, and the piercing tool makes a much deeper cavity and forces the metal against the sides of the grip dies. Next the incompletely forged is placed in the lower grip dies, where the tool completes the piercing operation and punches a slug out of the end of the finished forging.

Rolling. Since its introduction in England by Cort in 1754, the rolling mill has become the most important metal-forming device. Not only is rolling the most economical method of forming steel into long lengths of uniform cross section, but it can be used also to make a wide variety of products. Its applications range from lead alloys to stainless steels, from
ingots two feet thick to paper-thin strips, from white-hot blooms to cold-rolled sheets, from the classic outline of a square billet to the abstractionist contours of a splice bar. Figure 2-19 indicates the stages in producing a number of commercial steel shapes by rolling and Fig. 2-20 shows the rolling of a structural beam.

**Extruding.** The extrusion of a metal or alloy is accomplished by forcing the heated material through a die, as shown by the sketch in Fig. 2-21. Some metals, such as magnesium, can have their cast forms converted to the wrought condition more successfully by extrusion than by rolling or forging. However, the principal uses of this process are the direct production of shapes of uniform cross section, as in rolling, and the manufacture of special products such as lead-covered cable. Collapsible tubes like those used for toothpaste are made by impact extrusion, Fig. 2-22. In this process a disk of cold lead or aluminum alloy is struck a sharp blow in a suitable die. This causes the metal to squirt up along the surface of a cylindrical plunger to form the tube in one-twentieth of a second.

**Tube drawing.** Metal pipe or tubing can be made by a number of processes. Ordinary water pipe is made by welding strip steel that has been
formed into a cylindrical shape. Tubing of nonferrous metals, such as copper tubing, is usually produced by extrusion. However, the manufacture of high quality steel seamless tubes requires two specialized processes, piercing and drawing. The initial central hole in a solid cylindrical billet is ordinarily produced by the Mannesmann process sketched in Fig. 2-23(a). The rolls, rotating on nonparallel axes, force the billet over the stationary mandrel, thus producing the desired cavity. Reduction of the wall thickness of the pierced billet can be carried out by the tube-drawing process sketched in Fig. 2-23(b). Wire drawing is done in a machine similar in principle to that used for tube drawing. Deep drawing of automobile bodies, cartridge cases, and the like is performed on sheet stock, using a punch and die. The first drawing operation in forming an aluminum container is illustrated in Fig. 2-24.

Stamping, spinning, etc. A widely used process for making large quantities of relatively small parts is stamping. Suitable flat blanks are first punched from sheet or strip stock, and in a subsequent operation the blanks are bent or formed to the desired shape. Spinning is a method for making small quantities of articles having rotational symmetry. A str-
Fig. 2-19. Cross sections of steel shapes produced by rolling processes.

Fig. 2-20. Rolling a structural beam. (Courtesy Bethlehem Steel Company.)
FIG. 2-21. An extrusion process.

FIG. 2-22. The process of impact extrusion of an aluminum shell. (Courtesy Aluminum Company of America.)

FIG. 2-23. (a) The piercing and (b) tube-drawing operations used in the manufacture of seamless tubing.

Cylindrical blank is mounted in a lathe and, as it rapidly rotates about its axis, is slowly formed into shape by pressure applied by steel tools. Large quantities of such pieces are more economically produced by deep drawing. Coining, the impressing of a design into a metal surface, and embossing, the raising of a design in relief above a metal surface, are done with a punch and die in a manner similar to stamping.
Miscellaneous forming methods. Besides the methods already considered for producing cast and wrought metal parts, there are a number of additional processes for forming metals. Machining, especially on automatic machines, could be put in this category, and perhaps some of the assembly procedures such as welding, bolting, riveting, soldering, brazing, and crimping. At least two additional processes deserve special mention—powder metallurgy and electroforming.

**Powder metallurgy.** This method of forming metal parts consists of pressing finely powdered metal in a die to form the desired shape (Fig. 2-25) and then heating (sintering) the resulting compact to cause the individual particles to weld together. The metal powders cost several times as much as ingot metal, and the process involves expensive equipment and procedures. Therefore powder metallurgy techniques are used primarily for such special purposes as the following:
Fig. 2-25. A 500-ton self-contained oil-hydraulic forming and containing press for powder metallurgy. The method of forming a powdered-metal compact is shown in the insert. (Designed and built by Hydropress, Inc., New York, N.Y.)

1. To achieve properties that cannot be realized by other processes, for example in porous bearings and cemented carbides.
2. To eliminate machining and other finishing operations by holding very close tolerances and maintaining excellent surface conditions, for example in small machine parts such as bushings and gears.
3. To produce high melting point (refractory) metals such as tungsten, molybdenum, and tantalum. An example of this type of product is heavy metal, a tungsten alloy containing 6 percent nickel and 4 percent copper. It has a density of 17 and is used for radium containers, balancing weights, and other applications where high density is needed.

A number of factors influence the design of powder metallurgy products. Since pressures on the order of twenty tons per square inch are used in the pressing operation, it is evident that commercially practical cross-sectional areas are fairly small. Also, the powder does not behave like a fluid under the compacting force, and excessive thicknesses must not be specified if low-density, low-strength areas are to be avoided. For the same reason,
undercut areas and holes perpendicular to the compression direction cannot be molded conveniently. However, the cross section in the direction of pressing may be quite complex; thus gears and cams are important powder metallurgy products.

The mechanical properties of pressed and sintered powders approach those of castings but are significantly poorer than those of wrought alloys. Consequently this process is not suitable for highly stressed parts or for those subject to impact loads. Properties approximating those of the wrought alloy can be achieved by additional pressing of the sintered compact, but this step adds to the manufacturing cost and is not common. Tolerances of 0.003 inch per inch are maintained on the diameter of self-lubricating porous bearings, an important powder metallurgy product.

**Electroforming.** This process involves forming a heavy electroplated layer on a mold (or matrix) and then removing the mold, leaving the plated shell as the final product. Electroforming is used principally for parts that cannot be made easily by the more common manufacturing methods. Outstanding advantages of the process are its ability to hold internal dimensions to within 0.001 inch and to produce internal finishes of extreme smoothness.

Related to electroforming are two other procedures involving thick electrodeposits. **Resizing** of a worn or mismachined part can be accomplished by depositing a heavy nickel or iron plate and then machining the surface. **Metal coating** of nonconductors such as wood or plastics has recently been developed considerably; e.g., nickel-coated wood aircraft propellers have improved strength, efficiency, and weathering properties.

**Comparison of mechanical properties.** The engineer usually cannot simply seek the forming process to suit his design. Rather, he must adjust the design separately for each particular forming process. Many factors influence this adjustment, not the least important of which are the mechanical properties characteristic of a given alloy fabricated by a given method. Unfortunately, so many alloys are in use, and their properties are affected by such a large number of variables, that it is impossible to give any simple rules for alloy-process selection. However, Table 2-4, which gives average mechanical properties of typical alloys used with the various forming processes, may serve as a rough, preliminary guide.

Although the final choice of the best alloy and the ideal process for any application may involve a considerable amount of practical testing, that choice can be made more quickly and more surely if a substantial body of information on the properties and behavior of various alloys is available. With the present broad survey of metallurgy as a background, the balance of this book is devoted to putting such a body of information at the disposal of the engineer.
COMPARISON OF MECHANICAL PROPERTIES

Table 2-4
AVERAGE PROPERTIES* OF TYPICAL ALLOYS USED IN METAL-FORMING PROCESSES

<table>
<thead>
<tr>
<th>Process</th>
<th>Alloy</th>
<th>Tensile strength, lb/in²</th>
<th>Yield strength, lb/in²</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand casting</td>
<td>Cast iron 3.3% C 0.7% Mn 1.8% Si balance Fe</td>
<td>32,000</td>
<td>—</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Aluminum 5% Si balance Al</td>
<td>19,000</td>
<td>9,000</td>
<td>6.0</td>
</tr>
<tr>
<td>Permanent mold casting</td>
<td>Aluminum 5% Si balance Al</td>
<td>24,000</td>
<td>9,000</td>
<td>9.0</td>
</tr>
<tr>
<td>Die casting</td>
<td>Aluminum 5% Si balance Al</td>
<td>30,000</td>
<td>14,000</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>Zinc 4% Al 0.04% Mg 1% Cu balance Zn</td>
<td>47,000</td>
<td>—</td>
<td>7.0</td>
</tr>
<tr>
<td>Centrifugal casting</td>
<td>Aluminum 9% Al balance Cu Bronze 3% Fe</td>
<td>88,000</td>
<td>32,000</td>
<td>40.0</td>
</tr>
<tr>
<td>Forging</td>
<td>Aluminum 9% Al balance Cu Bronze 3% Fe</td>
<td>85,000</td>
<td>34,000</td>
<td>42.0</td>
</tr>
<tr>
<td></td>
<td>Magnesium 3% Al 0.3% Mn 1% Zn balance Mg</td>
<td>38,000</td>
<td>25,000</td>
<td>15.0</td>
</tr>
<tr>
<td>Rolling</td>
<td>Magnesium 3% Al 0.3% Mn 1% Zn balance Mg</td>
<td>37,000</td>
<td>22,000</td>
<td>21.0</td>
</tr>
<tr>
<td>Extruding</td>
<td>Magnesium 3% Al 0.3% Mn 1% Zn balance Mg</td>
<td>39,000</td>
<td>26,000</td>
<td>15.0</td>
</tr>
<tr>
<td>Cold drawing</td>
<td>Steel 0.4% C balance Fe 0.8% Mn</td>
<td>115,000</td>
<td>74,000</td>
<td>12.0</td>
</tr>
<tr>
<td>Powder metallurgy</td>
<td>iron</td>
<td>35,000</td>
<td>25,000</td>
<td>7.0</td>
</tr>
<tr>
<td>Electroforming</td>
<td>nickel</td>
<td>110,000</td>
<td>—</td>
<td>16.0</td>
</tr>
</tbody>
</table>

* Mechanical properties are discussed in detail in Chapter 9. For the present it is sufficient to note that the tensile strength is the greatest load that can be supported by one square inch of metal before the metal breaks; yield strength is the greatest load that the metal can support per square inch and yet behave (roughly) in an elastic manner; ductile metals stretch on being loaded to their tensile strength; the amount of such permanent stretching is reported as the percent elongation of the original length of the test section (usually two inches in length).
References


Problems

1. (a) Write the chemical equation for the formation of silver oxide, Ag₂O, from silver and oxygen. (b) At 440°F (500°C) ΔH for this reaction is -6.85 kilocalories. Using the value of ΔF from Table 2-2, calculate the ΔS value at 440°F. (c) Even though the reaction in (a) is exothermic, explain in terms of free energy why it cannot occur spontaneously. (d) Explain why the reverse of reaction (a) would then tend to occur spontaneously.

2. (a) Show that Eq. (2-7) is the sum of Eqs. (2-5) and (2-6). (b) Use this fact to establish a method for obtaining values of ΔF at various temperatures for the reaction of Eq. (2-6). (c) Verify the values for 440, 1340, and 2240°F given on page 16.

3. At 1340°F the free energies of formation of three metal oxides per formula weight are

\[
\begin{align*}
\text{FeO} & \quad \Delta F = -28.7 \text{ kilocalories} \\
\text{SiO}_2 & \quad \Delta F = -103.5 \\
\text{TiO}_2 & \quad \Delta F = -182.2
\end{align*}
\]

Which of these three metals can be reduced by the usual pyrometallurgical process involving carbon and carbon monoxide? Explain.

4. Consider an ore that contains 50% Fe₂O₃ and 50% Al₂O₃. Compare the purity of the desired product if (a) this ore is reduced with carbon and carbon monoxide in an effort to obtain iron, or (b) this ore is reduced electrolytically in an effort to obtain aluminum.

5. What is wrong with the definition, "Metallography is the study of the structure of metal atoms"?

6. If the final dimensions of a casting must be held to ±0.02 inch, is the choice of a casting method restricted by this fact? Explain.

7. Frequently the tensile strength of a given alloy is about the same in the cast as in the wrought condition. Are the mechanical properties in these two conditions therefore about the same?
CHAPTER 3

ATOMIC STRUCTURE

"All nature, then, as self-sustained, consists
Of twain of things, of atoms and of void
In which they're set—"

LUCRETIUS (60 B.C.)

INTRODUCTION

The properties of an alloy are dependent on its structure. Since this fact underlies the study and use of most properties of industrial interest, it is desirable to learn first about metallic structure. In later chapters an adequate knowledge of various properties can then be built on this foundation.

The study of metallic structure is conveniently begun with a consideration of metal atoms. These atoms are the fundamental units that compose an actual alloy member, such as a bridge girder. Therefore, the nature of these atoms must determine all the physical, mechanical, and chemical properties of the alloy. Given a few characteristics of the constituent atoms of the alloy, it should be possible to calculate the exact values of these properties. Atomic theory has approached this goal in the case of some structure-insensitive properties. By definition, these properties depend only on the major structural or compositional aspect of a material and are insensitive to small discontinuities in structure or variations in composition. Elastic behavior is an example of a structure-insensitive mechanical property; intrinsic magnetization and heat of sublimation are corresponding examples of physical and chemical properties.

Most properties of engineering interest (the various strength properties are the most notable in this respect) are markedly sensitive to relatively minor changes in structure and/or composition, such as the discontinuity in crystal structure represented by a grain boundary. Present atomistic theories of structure-sensitive properties are only qualitative and are usually not suitable for application to problems of engineering design. In spite of this limitation, a knowledge of atomic structure is useful in working with these properties. It provides a frame of reference for useful correlations among the large number of mechanical, physical, and chemical properties. Also, atomic theory often suggests how a specific result can be generalized, allows relative values to be assigned to several materials under consideration, or even approaches quantitative prediction. Finally, it is
certain that this basic understanding of the behavior of metals will con-
tinue to develop and will approach the goal of complete prediction of
properties.

PRINCIPLES OF ATOMIC THEORY

It is not surprising that the tiny particles that compose an atomic sys-
tem behave differently than the massive objects which are a part of our
daily experience. A familiar example of this difference is the contrast
between the violent Brownian motion in a liquid on the microscopic level
and the engineering concept of the same liquid at rest. Intimately asso-
ciated with this difference in behavior is Heisenberg's uncertainty prin-
ciple, an important restriction on the observation of the properties of any
object. This principle defines the minimum, inevitable disturbance of the
object that occurs in the process of observing it. A useful statement of the
principle is

$$\Delta x \times \Delta p = \hbar.$$  \hspace{1cm} (3-1)

That is, the product of $\Delta x$, the uncertainty inherent in measuring the
position of an object, and $\Delta p$, the uncertainty in momentum, cannot simul-
taneously be less than (about) Planck's constant, $\hbar$, which has the value
$6.62 \times 10^{-27}$ erg·sec. (These uncertainties are completely negligible in
ordinary observations, such as the description of a marble rolling down an
inclined plane.) They are of vital importance, however, in adequately treat-
ing phenomena on an atomic scale. A quantitative illustration is provided
by Problem 1, which considers how a single electron might be observed
with a minimum disturbance of its motion.

Since, unlike a marble, a moving electron cannot be said to be at a cer-
tain point at a given instant, there is an advantage in using a representa-
tion of the electron that embodies the inevitable uncertainty in its posi-
tion. A convenient representation of this kind is based on the de Broglie
equation,

$$\lambda = \frac{\hbar}{p},$$  \hspace{1cm} (3-2)

which associates a wavelength $\lambda$ with a particle having a momentum $p$.
Thus an electron with a velocity of $0.727 \times 10^8$ cm/sec would be charac-
terized by the wavelength* \hspace{1cm} 

$$\lambda = \frac{\hbar}{mv} = \frac{6.62 \times 10^{-27}}{(9.11 \times 10^{-30})(0.727 \times 10^8)} = 1.00 \times 10^{-8} \text{ cm.}$$

* For simplicity the approximation $p = mv$ is used throughout this chapter,
although it is quantitatively correct only when $v$ is much less than the speed of
light.
Comparison of Eqs. (3-1) and (3-2) shows that the de Broglie wavelength $\lambda$ is equal to the minimum uncertainty in the position of a particle having the momentum $p$ [see also Problem 1(d)]. Thus a representation of the electron in terms of $\lambda$ nicely meets the requirements of the uncertainty principle. This method is illustrated below by several examples.  

Another concept of fundamental importance in atomic theory is quantization of energy. It is found that a definite packet of energy, one quantum of energy, is involved in a unit atomic process. For example, if energy is liberated in a given reaction, the energy is radiated as quanta of a definite magnitude, $E$. The magnitude of $E$ is determined by the unit atomic process. The corresponding frequency, $\nu$, of this radiant energy is related to $E$ by the Einstein equation  

$$E = h\nu, \tag{3-3}$$

where $E$ is the energy in ergs contained in one quantum and $\nu$ is the frequency in cycles per second. This equation states that there is a one-to-one relationship between the frequency of the radiation (green light or x-rays, for example) and the magnitude of the energy packets, the quanta, that make up the radiation. The frequency of green light having a wavelength $\lambda = 0.5 \times 10^{-4}$ cm is

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{0.5 \times 10^{-4}} = 6 \times 10^{14} \text{ cycles per second},$$

where $c$ is the velocity of light. A quantum of this radiation therefore is equal to

$$E = h\nu = (6.62 \times 10^{-27})(6 \times 10^{14}) = 3.97 \times 10^{-12} \text{ erg} = 2.48 \text{ ev}.*$$

Since the wavelength of x-rays is about 5000 times shorter than that of green light, the energy of an x-ray quantum is about 5000 times greater than the energy of a quantum of green light.

Equation 3-3 applies not only to the release of energy but also to the absorption of energy. Thus, an atomic process involving the absorption of energy will occur only if adequately large quanta are supplied by a means such as high-frequency radiation. Quanta smaller than the critical magnitude are incapable of causing the process to occur. Problem 3 of this chapter considers a typical phenomenon produced because of this difference in the magnitude of quanta.

* The electron volt (ev) is a conveniently small unit compared with the erg, since $1 \text{ ev} = 1.60 \times 10^{-12} \text{ erg}$. By definition, one ev is the energy gained by an electron in falling through a potential difference of one volt.
Although the uncertainty principle shows that the positions of electrons in an atom are not sharply defined, both theory and experiment agree that there are precise energy levels for these electrons. This explains why modern theory describes the state of an atom primarily in terms of the energies of its electrons and is relatively unconcerned with the "physical picture" of the atom. To illustrate this approach it is convenient to choose the simple atomic system represented by the hydrogen atom, which consists of a nucleus with a single positive charge $e$, and an electron with an equal negative charge. The electrical potential energy $W$ of this system depends only on the distance $r$ separating the two charges:

$$W = -\frac{e^2}{r},$$

(3-4)

when we adopt the usual convention that the potential energy is zero when the charges are separated by an infinite distance (see Problem 4).

With this knowledge of the potential energy, it is shown below how the wave representation of the electron can be used to calculate the values of total energy, $E_n$, that are possible for this system. This demonstration will be more meaningful, however, if the same result is first obtained using the Bohr theory. Although the theory has serious limitations, it has the advantage of mathematical simplicity and therefore continues to find a number of applications such as the present one.

**Bohr theory.** Essentially, the Bohr theory determines the kinetic energy $K$ of the electron and then finds the total energy from the relation $E = K + W$. However, this procedure requires two arbitrary assumptions about the behavior of electrons: (1) electrons can have certain definite energy values, and (2) these values are determined by the condition that the angular momentum of an electron must be an integral multiple of $\hbar/2\pi$. That is,

$$mvr = n\left(\frac{\hbar}{2\pi}\right),$$

(3-5)

where $n$ can have the values 1, 2, 3, ...

In this theory the electron is pictured as moving with the velocity $v$ in an orbit of radius $r$. Since the kinetic energy of the electron is $\frac{1}{2}mv^2$, it can be shown, as in Problem 5, that

$$E = K + W = -\frac{e^2}{2r}.$$  

(3-6)

When the "quantizing condition" of Eq. (3-5) is applied, the energy values
of the atomic system are found to be

$$E_n = -\left(\frac{2\pi^2 me^4}{\hbar^2}\right)\frac{1}{n^2}. \quad (3-7)$$

That is, the electron in the simple atomic system being considered can have only certain energy values. Ordinarily the electron is in the lowest energy state, which is given by $n = 1$:

$$E_1 = -\frac{2\pi^2 me^4}{\hbar^2} = -13.6 \text{ ev.}$$

If energy is supplied to the system, for example in the form of heat, the electron cannot increase its energy by any arbitrary amount. Rather, it must occupy one of the states given by Eq. (3-7). Thus, it might change to the state for which $n = 2$, $E_2 = -3.4 \text{ ev}$, by absorbing the necessary 10.2 ev of energy from its surroundings. The atom would then be in an excited state since it would have more energy than the lowest energy state, $E_1$. Such excited states are unstable and tend to change to a state of lower energy with the release of a quantum of energy. In this case the change $E_2 \to E_1$ would release a 10.2 ev quantum of energy in the form of ultraviolet light of wavelength $1216 \text{ Å}$ (see Problem 6).

Wave mechanics. It is interesting to consider this simple atomic system again, in terms of de Broglie waves, to see how the same result can be obtained without the use of arbitrary assumptions. Since the general treatment of wave mechanics involves advanced mathematics, a greatly simplified approach is used here to allow emphasis of the essential concepts.

When wave motion is involved in a physical system, the characteristics of the system determine the principal waveforms that can exist. The influence of the length of an organ pipe on the musical tones that it produces is a familiar example of this principle. In this case there are two alternative, equivalent methods for describing these tones: (1) by explicitly describing the tones in question (particular sinusoidal waves), or (2) by stating the features of the organ pipe that determine what tones are produced. The second method has the advantage that it is a general description covering a variety of special cases.

Schroedinger recognized that de Broglie waves were similar to the first method and that it was desirable to recast this concept into the second, general form. An example of the type of description that Schroedinger developed is the equation

$$\frac{d^2\psi}{dz^2} + k^2\psi = 0. \quad (3-8)$$
Trial will show that a solution of this equation is the wave function \( \psi = A \sin \frac{2\pi x}{\lambda} \), which is simply a sine wave whose amplitude is \( A \). This wave function can be expressed in terms of the de Broglie wavelength \( \lambda \) as \( \psi = A \sin \left( \frac{2\pi x}{\lambda} \right) \), since the term \( \frac{2\pi x}{\lambda} \) correctly expresses the condition that \( \psi \) should describe one wavelength (from sin 0 to sin 2\( \pi \)) as \( x \) goes from zero to \( \lambda \). Furthermore, it follows from Eq. (3-2) that \( \lambda \) can be written in terms of the total energy \( E \) and the potential energy \( W \), as shown in Problem 7.

\[
\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E - W)}}.
\]  

(3-9)

The wave function then becomes

\[
\psi = A \sin \left( \frac{2\pi x}{\sqrt{8\pi^4 m(E - W)}} \right).
\]

Comparison of this expression for \( \psi \) with the original solution of Eq. (3-8) shows that

\[
k = \sqrt{\frac{8\pi^2 m(E - W)}{h}}
\]

and

\[
k^2 = \frac{8\pi^2 m}{h^2} (E - W).
\]

Substitution of this value for \( k^2 \) in Eq. (3-8) gives a form of the famous Schrödinger equation*

\[
\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - W) \psi = 0.
\]

(3-10)

Although in the present derivation it was convenient to consider \( k \) in Eq. (3-8) to be a constant, this is not a necessary restriction on Eq. (3-10).

In using the Schrödinger equation to determine the values of \( E_n \) for the hydrogen atom, the first step is to substitute for \( W \) the actual expression for the potential energy, \( -\frac{e^2}{r} \), Eq. (3-4). The equation can then be solved, and it is found that there are only certain values of the wave function, \( \psi_1, \psi_2, \ldots, \psi_n \), that satisfy the equation. Furthermore, the equation is satisfied only if for each of these wave functions there is a corresponding, definite value of the energy \( E_n \). Thus, values \( E_1, E_2, \ldots, E_n \) identical

* The corresponding equation for a three-dimensional problem is obtained by replacing \( d^2\psi/dx^2 \) by the sum \( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \). For convenience, this sum can be represented by the symbol \( \nabla^2 \psi \), so that the Schrödinger equation is often written as \( \nabla^2 \psi + \left( \frac{8\pi^2 m}{h^2} \right) (E - W) \psi = 0 \).
with those given by the Bohr theory, Eq. (3-7), are obtained as a natural consequence of the wave representation of the electron. Also, the wave functions can be used to picture the atom in terms of a calculated probability of finding the electron at a given distance from the nucleus. Figure 3-1(a) is a sketch of the diffuse electron density calculated for an unexcited hydrogen atom. The corresponding illustration for the more complex magnesium atom, Fig. 3-1(b), shows a high electron density near the center where the ten core electrons are concentrated and a lower density for the two outer, valence electrons.

This simplified treatment of wave mechanics has focused attention on the principal quantum number \( n \), which plays a dominant role in determining the energies of an atomic system. However, a more rigorous treatment reveals that four quantum numbers (principal, secondary, magnetic, and spin) are needed for the most general description of electronic "states" and energies. This mathematical analysis also demonstrates that only a limited number of electronic states are possible for a given value of each quantum number. Some of these essential features of modern atomic theory are illustrated in the following discussion.

Electronic structures of the elements. The characteristic properties of an element such as magnesium or iron are determined by the energies of the various electrons in its atom. These energies in turn are dependent on the quantum numbers that enter into the solution of the appropriate Schrödinger wave equation. Therefore the electron energies are conveniently designated by sets of quantum numbers. In general, electrons...
with different principal quantum numbers \( (1, 2, 3, \text{ etc.) } \) differ greatly in energy; those that are different only in their secondary quantum numbers \( (s, p, d, f, \text{ etc.) } \) usually differ only slightly in energy. This is illustrated by the relative values of the four different electron energy levels in a magnesium atom, Fig. 3-2(a).

Because of the differences in energy, the electrons in a given atom tend to occupy the lowest possible quantum states. For example, the single electron of the hydrogen atom is in the \( 1s \) state, since this state has the lowest energy. Also, the two electrons in the helium atom occupy this state, and the electron configuration of helium can be represented as \( (1s)^2 \), where the 2 designates the number of electrons in the \( 1s \) state. The Pauli exclusion principle requires that a given quantum state (specified by four quantum numbers) be occupied by only one electron. Consequently, no more than two electrons can be accommodated in this first energy level. Therefore in a lithium atom, which has three electrons, one of the electrons

* These two electrons do not have identical quantum numbers. In this case the spin quantum numbers are different (one is \( +\frac{1}{2} \) and the other is \( -\frac{1}{2} \)). If all the quantum numbers are taken into account, it can be shown that \( 1 \) the maximum number of electrons that can exist in the \( n \)th principal quantum state is \( 2n^2 \), \( 2 \) the maximum number of electrons that can exist in a secondary quantum state is \( 2(2l - 1) \), where \( l \)-values of \( 1, 2, 3, \) and \( 4 \) correspond to secondary quantum numbers \( s, p, d, \) and \( f \), respectively.

---

Fig. 3-2. Schematic illustration of the relative electron energies in two free atoms: (a) magnesium, (b) iron.
ELECTRONIC STRUCTURES OF THE ELEMENTS

When an electron is in the next higher energy state, 2s. The electron configuration of the lithium atom is thus \((1s)^2(2s)^1\). With further increases in the number of electrons, the electron configurations of the atoms change in the following regular manner:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic number</th>
<th>Electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>4</td>
<td>((1s)^2(2s)^2)</td>
</tr>
<tr>
<td>Boron</td>
<td>5</td>
<td>((1s)^2(2s)^2(2p)^1)</td>
</tr>
<tr>
<td>Carbon</td>
<td>6</td>
<td>((1s)^2(2s)^2(2p)^2)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>7</td>
<td>((1s)^2(2s)^2(2p)^3)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8</td>
<td>((1s)^2(2s)^2(2p)^4)</td>
</tr>
<tr>
<td>Fluorine</td>
<td>9</td>
<td>((1s)^2(2s)^2(2p)^5)</td>
</tr>
<tr>
<td>Neon</td>
<td>10</td>
<td>((1s)^2(2s)^2(2p)^6)</td>
</tr>
<tr>
<td>Sodium</td>
<td>11</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^1)</td>
</tr>
<tr>
<td>Magnesium</td>
<td>12</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2)</td>
</tr>
</tbody>
</table>

This regularity in the sequence of principal and secondary quantum numbers is interrupted by several series of transition elements. In these elements, after one or two electrons have entered an outer orbit (the 4s orbit in the instance shown here), the additional electrons enter an inner orbit (3d in this example). Thus, the first series of transition elements develops as follows:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic number</th>
<th>Electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>18</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2)</td>
</tr>
<tr>
<td>Potassium</td>
<td>19</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2)</td>
</tr>
<tr>
<td>Calcium</td>
<td>20</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Scandium</td>
<td>21</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Titanium</td>
<td>22</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Vanadium</td>
<td>23</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Chromium</td>
<td>24</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Manganese</td>
<td>25</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Iron</td>
<td>26</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Cobalt</td>
<td>27</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Nickel</td>
<td>28</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
<tr>
<td>Copper</td>
<td>29</td>
<td>((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2(4s)^2)</td>
</tr>
</tbody>
</table>

The reason for this behavior is that the energy of the 4s electrons is less than but close to that of the 3d electrons for this group of transition elements. The relation of these energies is shown in Fig. 3-2(b) for iron.
This circumstance not only causes the variable valences of these elements, but also the pronounced property changes on alloying, since the electron energy states are easily changed by the effect of atomic interactions in the alloys. The importance of the transition elements in connection with ferromagnetism is discussed in Chapter 7.

Periodic table. The approximate regularity of the development of electron configurations in the various elements leads to a similar approximate regularity in many of the properties of the elements. Figure 3-3 illustrates this behavior with respect to the distances between neighboring atoms in solid metals. It is seen that the alkali metals lithium, sodium, potassium, rubidium, and cesium have larger interatomic distances than their neighboring atoms. This is a direct result of the possession by these metals of a single $s$-type electron. The remaining electrons are in stable levels closer to the nucleus and screen the valence electron from the positive charge of the nucleus. Thus the attractive force is weak, and consequently the orbit of the valence electron is large. It is safe to predict that element 87, francium, also will be found to have a maximum value of interatomic distance.

![Diagram showing periodicity of interatomic distances in solid metals.](image-url)
ATOMIC STRUCTURE

Since useful predictions of this kind can be made on the basis of similarities in electronic structure, many tables highlighting these similarities have been devised. A convenient version is given in Fig. 3-4. Elements belonging to the same group can often adequately replace one another in alloys. Although sulfur is the element commonly used to increase the machinability of steel, both selenium and tellurium have been successfully employed for this purpose in stainless steels and in nonferrous alloys. Tungsten, which increases the resistance to softening of steels at high temperatures, can be replaced by molybdenum or, less satisfactorily, by chromium. The number of such relationships in the periodic table is extremely large, and for this reason the periodic table is constantly used in development and research problems.

Electron Energies in Solids

The discussion in the previous section was concerned with “free” atoms, that is, atoms sufficiently isolated from one another that their interactions can be ignored. Most metal vapors, which are typically monatomic, are composed of free atoms of this kind. Brief consideration of the properties of solid (or liquid) metals, on the other hand, suggests that the constituent atoms must be exerting profound influences on one another. In principle it should be possible, as in the case of the hydrogen atom, to apply wave mechanics to the assembly of atoms in a solid metal to determine the characteristic energy values; in practice, mathematical difficulties have prevented the use of this rigorous method. Consequently, it has been necessary to introduce various approximations in solving the problem. Three solutions that form a connected sequence of increasing rigor will now be considered.

Drude-Lorentz theory. Not all the electrons in the atoms that compose a solid metal take an equal part in the interactions that result in the characteristic properties of strength, hardness, and so on. Evidence from x-ray spectra indicates that the inner (core) electrons, which form closed shells in an atom, are essentially unaffected and that only the outer (valence) electrons play an active role in metallic binding. The Drude-Lorentz theory made an extreme distinction between these two types of electrons; it completely neglected all of the atom except the valence electrons, and it pictured the aggregate of valence electrons from all the atoms in a given piece of metal as forming an “electron gas” that was free to move throughout the volume of the metal. The total energy of the electrons was determined as the sum of the kinetic energy (taken to be that of an ideal gas, $\frac{3}{2}RT$) and the potential energy $-W$, relative to a free electron in the space outside the metal. This total energy led to a gross overestimation of the
electronic specific heat and to other conflicts with experimental data, so that the principal legacy of this theory is the concept of an "electron cloud" within a metal.

**Sommerfeld theory.** This theory retained the concept of a uniform potential within the metal, but it used the Schroedinger equation to calculate the total energies $E$ in a manner analogous to that described above for the hydrogen atom. If the potential energy is set equal to zero inside a metal bar of length $L$, Fig. 3-5(a), the solution of the Schroedinger equation is:

$$\psi_1 = A \sin \left( \frac{\pi x}{L} \right)$$

$$\psi_2 = A \sin \left( \frac{2\pi x}{L} \right)$$

**Fig. 3-5.** Important concepts in the Sommerfeld theory. (a) Decreased potential energy within a metal bar of length $L$. (b) The first two wave functions that can exist in a bar of length $L$. 
equation is especially convenient, since Eq. (3-10) then has the form of Eq. (3-8), with
\[ k^2 = \frac{8\pi^2 mE}{h^2}. \tag{3-11} \]

From the discussion of Eq. (3-8) it follows that the solutions of this equation are sine waves, \( \psi = A \sin kx \). By analogy with the standing waves in an organ pipe it can be shown that a condition for these wave functions to exist in the metal is that the amplitude be zero at the two ends. Two wave functions that satisfy this condition are shown in Fig. 3-5(b) and, in general,
\[ \psi_n = A \sin \frac{n\pi x}{L}, \tag{3-12} \]
so that \( k_n = \frac{n\pi}{L} \). When this expression for \( k \) is substituted in Eq. (3-11), the corresponding permissible values of total energy are found to be
\[ E_n = \frac{n^2 \hbar^2}{8mL^2}. \tag{3-13} \]
for the one-dimensional problem considered here. When the same problem is solved for a three-dimensional block of metal whose volume is \( V \), a similar expression is obtained:
\[ E_n = \left(n_x^2 + n_y^2 + n_z^2\right) \frac{\hbar^2}{8mV^{2/3}} = n^2 \frac{\hbar^2}{8mV^{2/3}}, \tag{3-14} \]
where \( n^2 = n_x^2 + n_y^2 + n_z^2 \), and \( n_x, n_y, n_z \) can independently take on the values 1, 2, ..., \( n \).

The \( E_n \) of Eq. (3-14) are the permissible energy values that the valence electrons in a metal may have, but it is essential to know what energies the electrons actually possess. Consideration of Eq. (3-14) shows that each of the energy values \( E_1, E_2, E_3, \text{ etc.} \) is larger than the preceding one by the same amount, namely \( E_1 \). However, since there is an energy \textit{state} for each different set of the three numbers \( (n_x, n_y, n_z) \), the number of states that have a given energy increases rapidly with the value of \( n \) because of the increase in the number of different sets \( (n_x, n_y, n_z) \) whose sum of squares equals a given \( n^2 \) value. Therefore, if a plot is made for a large range of energy values such that the individual \( E_n \) values are so close together that they can be shown as a continuum (Fig. 3-6), the number of states per interval of energy, \( N(E) \), increases parabolically with increasing \( E \) in the manner shown by the heavy line in the figure.

The valence electrons tend to occupy the lowest available energy states. However, because of the mutual interactions among all the electrons that form the "electron cloud," it is necessary to consider that all the electrons...
are in a single system and that the Pauli exclusion principle applies. This means that a given state (specified by the three quantum numbers $n_x$, $n_y$, and $n_z$) can be occupied by only two electrons and that these must differ in the fourth quantum number, (+) or (−) spin. Since there are about $10^{23}$ valence electrons in a piece of metal, an enormous number of states of continuously increasing energy are occupied. The behavior of a typical metal, silver, is shown by the shaded area in Fig. 3–6. The energy value that divides the occupied from the unoccupied states is known as the Fermi level.

The energies of the electrons in the Fermi level are very high compared with the energies given by the Drude-Lorentz theory. For example, the 5.5 ev value in silver at 0°K corresponds to a thermal energy of 64,000°K. Electrons having such high energies are only slightly affected by the small additional thermal energy supplied when the metal is heated to room temperature. The electrons close to the Fermi level have unoccupied states available to them, and only these electrons can be affected by ordinary thermal energy. The dashed line in Fig. 3–6 shows the nature of the change in electron energies that occurs on heating to room temperature. Since only a small fraction of the electrons are influenced by a change in temperature, the Sommerfeld theory correctly predicts the small electronic specific heat of metals, a value only about 1/200 that given by the Drude-Lorentz theory. Electrical conduction is explained in a similar manner. In the absence of an applied voltage the electrons are moving randomly, and the effect of those traveling in a positive direction is balanced by the effect of an equal number moving in a negative direction, so that there is no net current in the metal. An applied voltage does not produce a net effect for the vast majority of the electrons because the energy states into which they might be promoted by additional electrical energy are already occupied. Again, only those electrons near the Fermi level experience a net change in energy and contribute to the motion in a preferred direction that constitutes a current. While the Sommerfeld theory accounts satisfactorily for electrical conductivity in most metals, it fails to explain why other substances that also contain free electrons have virtually no conductivity and are considered to be excellent insulators. A solution to this problem is given by the zone theory.
Fig. 3-7. The variation in potential energy of an electron moving along a one-dimensional array of positive ions.

Zone theory. The two previous theories have neglected the effect of the ion cores and have assumed that a uniform potential exists within the metal. Evidently this is a poor approximation to the actual environment of an electron moving through the uniform array of positively charged atomic cores that compose a metal crystal. The potential field experienced by the electron must vary periodically with the repeated atomic pattern in the crystal. Figure 3-7 is a schematic illustration of the potential energy for a one-dimensional array of positive ions. In the spaces between ions the potential energy is zero, as in the Sommerfeld theory, but in the vicinity of an ion the potential energy has a large negative value. It is possible to determine the energies of the electronic states by using an appropriate expression for the periodic potential energy in solving the Schrödinger equation. The essential results of this analysis will be discussed in connection with the following, simpler treatment of this problem.

Since electrons have associated wave properties, it is possible for them to be diffracted by the periodic "grating" formed by the atoms of the crystal. The important technique of electron diffraction, which is based on this fact, is discussed in a later chapter. Electrons of low energy have very long wavelengths compared with the atomic spacings and move through the crystal undisturbed. More energetic electrons have wavelengths \( \lambda \) nearly equal to the atomic spacing \( a \), and these electrons can be diffracted according to Bragg's law (see Chapter 4), \( \lambda = 2a \sin \theta \). This equation can be put in the more convenient form \( k = \pi /a \sin \theta \), where the wave number, \( k = 2\pi /\lambda \), is used instead of \( \lambda \) as a measure of the energy. Figure 3-8 is a schematic illustration of diffraction for a general value of \( \lambda \) (or \( k \)) and the appropriate \( \theta \), and it shows graphically the important fact that the \( z \)-component of \( k \) has the critical value \( k_z = \pi /a \) when diffraction occurs. Similar diffraction by the horizontal planes in Fig. 3-8 occurs when \( k_x = \pi /a \).

The above information on the necessary conditions for diffraction of electrons is summarized in Fig. 3-9 in the representation called the Bril- louin zone for the two-dimensional diffraction problem being considered. A point in this diagram, such as the one indicated in the figure, is to be interpreted as follows. It represents an electron having an energy de-
Fig. 3-8. Diffraction by a square lattice of an electron of wavelength $\lambda$ moving at the critical angle $\theta$ for which Bragg reflection occurs. The electron is described in terms of its wave number, $k = 2\pi/\lambda$.

The energy of free electrons, such as those considered in the Sommerfeld theory, would depend only on the wave number, and increasing energy values would plot as circles such as those shown near the center of the Brillouin zone. However, an important result of the treatment of this problem by zone theory is the prediction that the energy contours become distorted in the vicinity of the boundaries of the Brillouin zones and that the energy suddenly increases as a boundary is crossed in any direction. In Fig. 3-9 the (first) Brillouin zone is just filled by the valence electrons, and therefore this material is a nonconducting substance (an electrical insulator). The reason for this behavior is more easily seen when the data of Fig. 3-9 are presented in the form of an $N(E)$ curve. The energy levels predicted by the zone theory are conveniently shown by $N(E)$ curves that are an elaboration of the parabolic curve of Fig. 3-6. Figure 3-10 is an example of this type of representation of the energy levels sketched in Fig. 3-9. The $N(E)$ curve is parabolic out to 3 ev. Beyond this value the energy contours in Fig. 3-9 begin to be seriously distorted, there is an increased number of electronic states in a given energy interval, and consequently the $N(E)$ curve rises. At 6 ev the energy contours first touch the zone boundaries; therefore, for energies higher than this the $N(E)$ value falls because the area available for additional energy states is limited to the corners of the zone. The $N(E)$ value falls to zero at the energy for the corners of the zone, which is somewhat below 9 ev. The second zone in Fig. 3-9 extends from the first zone to a second bound-
Fig. 3-9. The energy levels in the first Brillouin zone for a square lattice. Two energy levels are shown in the empty second zone.

Fig. 3-10. \(N(E)\) curves for an insulator corresponding to the Brillouin zones of Fig. 3-9. The shaded area indicates that there are just sufficient valence electrons to fill the first zone.
FIG. 3-11. Possible $N(E)$ curves for electrical conductors. (a) The valence electrons in a monovalent metal fill only half the energy levels of the first Brillouin zone. (b) In a divalent metal the first zone is nearly full and the lower energy levels of the second zone are occupied.

ary that is determined by Bragg reflection from planes at 45° in Fig. 3-8 (see Problem 11). For an insulator the energies of the lowest levels in the second zone are considerably higher than the energies of the upper levels in the first zone, Fig. 3-10.

The $N(E)$ curve of Fig. 3-10 represents a nonconductor because it fulfills two conditions. First, it has just enough valence electrons to completely fill one (or more) zones. The quantitative theory shows that this condition is easily fulfilled, since the number of states in each zone corresponds to two electrons per atom; therefore any substance with an even number of valence electrons might be an insulator. The four valence electrons in diamond, for example, just fill the first two zones in this excellent insulator. The second condition requires that the higher, unoccupied zone be separated from the lower, filled zone by a large energy gap. This gap in diamond is 7 ev. Under these two conditions it is clear that an applied voltage cannot cause a current. Because there are no unoccupied states in the filled zone, the electrons cannot increase their velocity in the direction of the voltage since this would require an increase in energy. Also, ordinary voltages are not sufficient to cause an electron to cross the large energy gap separating the lower and upper zones.

In good electrical conductors at least one, and usually both, of the above conditions are lacking. Figure 3–11 is a schematic $N(E)$ curve for a monovalent metal in which conduction occurs within the energy levels of the lower unfilled zone. In this case it is unimportant whether the

* Strictly speaking, the quantity involved is the number of electrons per primitive cell in the crystal structure (see Chapter 4). The primitive cell contains one atom except in special cases such as "defect crystals" in which some lattice sites are not occupied.
second zone overlaps the first, as shown here, or is separated from it as in Fig. 3-10. Substances having an even number of valence electrons, such as magnesium, which has two, can be conductors of electricity only if the lower and higher energy bands overlap in the manner shown schematically in Fig. 3-11(b). The first Brillouin zone can still accommodate two electrons per atom. However, in this case there is an overlap of the energies in the upper part of the first zone with those in the lower part of the second zone (see Problem 12). Consequently the total energy is lower when the electrons only partially fill the energy levels in the first zone and occupy the lower portion of the second zone. Unlike the situation in Fig. 3-10, unfilled energy states are readily available in this arrangement and therefore electrical conduction is possible.

In addition to the concepts of Bragg reflection and \( N(E) \) curves, there is one other useful tool in this area of electronic energies—the so-called effective mass of an electron, \( m^* \). Using this quantity it is possible to retain the same type of equation to describe the behavior of electrons that interact strongly with the periodic structure of the lattice as is used for the free electrons of the Sommerfeld theory. For example, Eq. (3-14) for the permissible energy states can be written

\[
E_n = n^2 \frac{\hbar^2}{2m^*},
\]

by merely substituting \( m^* \) for \( m \). Essentially, by attributing the mass \( m^* \) to an electron that is influenced by a periodic potential, its behavior can be described by the simple theory derived for a uniform potential. Thus, for free electrons \( m^* = m \), but for other conditions \( m^* \) can be larger or smaller than \( m \), or it can even be negative.

The zone theory is often referred to as the band theory because it can be considered as describing a band (range) of energies occupied by the valence electrons of a metal. It may be desirable to distinguish between energy bands that arise from different types of electrons, especially as in the case of semiconductors (see Chapter 7) where the bands are separated by an energy gap. This distinction between energy bands is quite clear in the approach to band theory that is based on the “tight-binding approximation” in which it is assumed that a given valence electron is bound to a given ion.† Thus, in the case of magnesium, for example, the energy levels are sharp in the free atom, as shown in Fig. 3-5(a). However, it can be shown that the broadening illustrated in Fig. 3-12 must occur as an assembly of magnesium atoms is (imagined to be) brought closer and closer

† In the zone theory discussed earlier in this section the “free-electron approximation” was made; i.e., it was assumed that the electrons were free of any particular ion.
Nuclear Theory

By far the largest number of reactions and properties of general interest involve principally the valence electrons. Since these electrons are relatively loosely bound to the atom, the energies needed to influence them are low, on the order of 20,000 calories per gram molecular weight. This is roughly equal to one electron volt of energy per atom. A second type of reaction, such as that involved in the production of x-rays, requires the removal of electrons from the inner orbits of the atom. The energies necessary for this purpose range up to thousands of electron volts. Finally, changes that occur in the nucleus of the atom involve energies on the order of a million electron volts. These nuclear reactions are the basis of nuclear power, a field in which metallurgy is vitally important.

Structure of the nucleus. Two kinds of particles, protons and neutrons, can be considered to make up the atomic nucleus. Attractive forces, the
natures of which are not completely understood, overcome the force of repulsion between the positively charged protons and cause the volume of the nucleus to be very small compared with that of the entire atom. The constitution of a given nucleus is described by two integers: \( Z \), its charge, which is equal to the number of protons, and \( A \), its mass number, which is equal to the sum of its protons and neutrons. The magnesium nucleus, for example, is represented by the symbol \( _2^{25}\text{Mg} \). All magnesium atoms are identical chemically; that is, they all have the same number of protons and therefore the same number of electrons. However, three stable isotopes of this element exist, \( _{12}^{24}\text{Mg} \), \( _{13}^{25}\text{Mg} \), and \( _{13}^{26}\text{Mg} \), which differ in the number of neutrons present in the nucleus. There is only a limited range of masses over which a given element is stable. For example, the magnesium isotopes \( _{13}^{24}\text{Mg} \) and \( _{12}^{27}\text{Mg} \) decompose within a few minutes. Much attention is devoted to the production and disintegration of these unstable isotopes, and the following law governing their useful life is widely used:

\[
N = N_0 e^{-\lambda t},
\]

where \( N \) is the number of unstable atoms remaining after the time \( t \) has elapsed, \( N_0 \) is the number of unstable atoms present initially, \( e \) is the base of the natural logarithms, and \( \lambda \) is the decay constant for a particular isotope. The half-life, \( T \), is defined as the time during which half of a given number of unstable atoms decompose, and it is related to \( \lambda \) by the equation

\[
T = \frac{\log 2}{\lambda}.
\]

Various time units, from seconds to years, are used for \( T \) and \( \lambda \), depending on the stability of the isotope.

Nuclear reactions. The principal energy-producing reactions are of course the fusion of two light nuclei to form a heavier nucleus and the fission of a very heavy nucleus into fission products. An example of the latter reaction is the fission of uranium-235 by a neutron,

\[
{_{92}^{235}\text{U} + {_{0}^{1}}\text{n} \rightarrow \text{fission products} \left(\text{such as } _{88}^{238}\text{Ba}\right) + (1 \text{ to } 3){_{0}^{1}}\text{n},}
\]

in which 200 Mev (million electron volts) of energy are released. It will be shown later that the metallurgical problems in nuclear engineering largely arise from two features of this reaction: (1) the energetic fission products and radiation, and (2) the necessity for conserving as many as
NUCLEAR REACTIONS

Table 3-1
LIST OF ATOMIC ENTITIES

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Mass</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>$\beta^-$</td>
<td>$9.11 \times 10^{-28}$ gram</td>
<td>$-4.80 \times 10^{-10}$ eau</td>
</tr>
<tr>
<td>Positron</td>
<td>$\beta^+$</td>
<td>$9.11 \times 10^{-28}$ gram</td>
<td>$+4.80 \times 10^{-10}$ eau</td>
</tr>
<tr>
<td>Proton</td>
<td>$^1p$</td>
<td>$1.67 \times 10^{-24}$ gram</td>
<td>$+4.80 \times 10^{-10}$ eau</td>
</tr>
<tr>
<td>Neutron</td>
<td>$^0n$</td>
<td>$1.68 \times 10^{-24}$ gram</td>
<td>0 eau</td>
</tr>
<tr>
<td>Deuteron</td>
<td>$^1d^2$</td>
<td>(proton + neutron)</td>
<td></td>
</tr>
<tr>
<td>Alpha particle</td>
<td>$^2a^4$</td>
<td>(2 protons + 2 neutrons)</td>
<td></td>
</tr>
<tr>
<td>Beta particle</td>
<td>$^2\beta$</td>
<td>(electron)</td>
<td></td>
</tr>
<tr>
<td>Gamma ray</td>
<td>$^\gamma$</td>
<td>(electromagnetic radiation of short wavelength)</td>
<td></td>
</tr>
</tbody>
</table>

Possible of the neutrons produced (about 2.5 on the average) both for causing additional fission reactions and for breeding new fissionable material.

Less violent nuclear reactions lead to the production of unstable nuclei. These reactions are produced by bombardment of the various elements with alpha particles, protons, deuterons, neutrons, and gamma rays (see Table 3-1). Neutron bombardment may result in the important neutron capture type of reaction, which is illustrated by the following example:

$$^{47}\text{Ag}^{107} + ^0n^1 = ^{47}\text{Ag}^{108} + \gamma.$$ 

The stable nucleus $^{47}\text{Ag}^{107}$ absorbs a neutron and releases energy in the form of gamma radiation. The silver isotope $^{47}\text{Ag}^{108}$ thus produced is unstable and decomposes with emission of an electron:

$$^{47}\text{Ag}^{108} = ^{46}\text{Cd}^{108} + \beta^-.$$ 

The loss of a unit of negative electricity coincides with an equal gain in positive charge by the nucleus. A second example of nuclear reactions is the following:

$$^{24}\text{Cr}^{52} + ^0n^1 = ^{23}\text{V}^{52} + ^1p^1.$$ 

The chromium nucleus captures a neutron and changes into a vanadium isotope with emission of a proton. The unstable vanadium atom decomposes in accordance with Eq. (3-16), with a half-life of four minutes. The
decomposition reaction is

\[ ^{23}\text{V}^\text{62} = ^{24}\text{Cr}^\text{62} + \beta^- \].

In this instance the electron is emitted with an energy of 2 Mev.

A convenient measure of the likelihood that a metal will absorb a neutron is given by its nuclear cross section. This method pictures the probability of interaction of a neutron with a given nucleus as depending on the "size" of the nucleus expressed in units of barns, defined as \(10^{-24}\) cm\(^2\). Table 3-2 shows the great range in the cross sections of various metals. Rare metals, such as zirconium and boron, occupy a prominent position in nuclear engineering because of their unusual cross sections.

**Table 3-2**

**Absorption Cross Sections of Several Metal Atoms for Thermal Neutrons**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Cross section, barns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>0.009</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.059</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.18</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.22</td>
</tr>
<tr>
<td>Iron</td>
<td>2.4</td>
</tr>
<tr>
<td>Copper</td>
<td>3.6</td>
</tr>
<tr>
<td>Nickel</td>
<td>4.5</td>
</tr>
<tr>
<td>Manganese</td>
<td>12.6</td>
</tr>
<tr>
<td>Hafnium</td>
<td>115</td>
</tr>
<tr>
<td>Boron</td>
<td>750</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2400</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>44,000</td>
</tr>
</tbody>
</table>

**Metals in nuclear engineering.** The principal nuclear fuels, uranium and plutonium, and the fertile material, thorium, are often used in metallic form in nuclear reactors. Used in this way the metals are subjected to severe thermal stresses and to internal bombardment by fission products and other particles. The resulting distortion and growth of the metal, especially for uranium, may be so severe as to limit its useful life to a time much shorter than that required for optimum "burnup" of its fissionable material. One of the remedies for this behavior involves alloying the nuclear fuel with aluminum or zirconium to provide a more stable matrix and to facilitate the removal of heat.
Nonfissionable metals have many uses in a reactor. One of the most critical is as a protective cladding for reactor fuel elements. The two principal functions of the cladding metal are to prevent corrosion of the chemically reactive fuel element by the coolant (water, air, or liquid metal) and to capture radioactive fission products and thus prevent contamination of other portions of the reactor. In addition to corrosion resistance, the ideal cladding material should have a low cross section, good thermal conductivity, and a high melting point. Aluminum is used in low-temperature reactors; zirconium can be used at higher temperatures and in contact with a liquid sodium coolant to about 1000°F; stainless steel has excellent corrosion properties but is distinctly inferior to zirconium or aluminum in its tendency to absorb neutrons. Another use of metals in which low cross section is of primary concern is for structural members within the reactor. Zirconium alloys of adequate high-temperature strength have been developed for this purpose. It is noteworthy that a special restriction is placed on the choice of alloying elements in this case, since alloying elements of high cross section cannot be used. Several factors have prevented extensive structural application of beryllium and magnesium, whose cross sections are especially low; corrosion behavior is one of the important factors for both of these metals.

Nuclear reactors are regulated and shut down through the action of control rods that can absorb the neutrons required to maintain a chain reaction. The principal requirement of a control-rod material is a high cross section, but unfortunately the best elements from this standpoint have serious engineering disadvantages. Gadolinium is extremely rare, and even hafnium, which is obtained as a by-product in the refining of zirconium, is too expensive for most applications. The use of cadmium metal has been restricted because of its low melting point. Metallic boron does not have desirable mechanical properties, but various boron compounds and alloys are widely used. A 2%-boron steel that can be forged or rolled is a commercial control-rod alloy.

Not only must metals for nuclear engineering have satisfactory nuclear properties and adequate engineering strength, they must also operate with utmost dependability in the presence of potentially damaging radiation. Three types of danger from radiation must be considered. The first is the development of unstable, long-lived isotopes in some atoms during irradiation. The best known example is the creation of Co\(^{60}\) in cobalt, but manganese has a similar objectionable behavior and consequently is maintained at a low level in steels for nuclear applications. Another possible action of radiation is to cause unusual chemical reactions. For example, some types of corrosion that are not observed under normal conditions can occur in the presence of radiation. The third effect of radiation is to change the mechanical and physical properties of metals, a
phenomenon called radiation damage. An important mechanism of this phenomenon may be visualized as a high-energy neutron striking a "knock-on" atom and displacing it from its normal position in the lattice. The first atom may in turn produce secondary knock-ons, and even higher knock-ons are possible. Intense local heating, termed thermal spike, also accompanies this process. The effects of radiation damage are more pronounced in soft, annealed metals than in metals that have been hardened, for example, by cold-working. These effects include increases in yield strength, tensile strength, and hardness, and impairment of ductility, impact strength, and creep strength.

Radioactive tracers. Unstable (radioactive) atoms behave like stable atoms of the same element in most respects, but the location of the unstable atoms is easily determined because of their occasional decomposition. It is possible to add a small number of unstable atoms to an ordinary piece of metal and to follow certain changes in the metal by means of these "tagged" atoms. This procedure is called a radioactive tracer technique. It has been used, for example, to prove that the atoms making up a piece of copper are continuously moving through the piece of metal, a phenomenon called self-diffusion. Other applications have included the study of steelmaking reactions, wear resistance, heat treatments, and oxidation.

References


1. Consider the hypothetical experiment in which a microscope is used to measure the position and momentum of an electron moving in the x-direction. To minimize the disturbance of the electron, only a single photon of light is used to illuminate it (Fig. 3-13), but if this photon is to enter the microscope objective of half-aperture angle \( \theta \), it must be scattered at an angle \( \alpha \) that lies in the range \( 90^\circ - \theta \) to \( 90^\circ + \theta \).

![Figure 3-13](image)

(a) The resolving power of a microscope is \( \lambda/(2 \sin \theta) \); that is, distances cannot be measured more accurately than to this limit. Show that \( \lambda/(2 \sin \theta) \) is the value of \( \Delta x \) in Eq. (3-1) in this instance.

(b) The impact of the photon changes the momentum, \( p \), of the electron (Compton effect). If the electron is initially at rest, its momentum in the x-direction after impact is approximately \( (h/\lambda)(1 - \cos \alpha) \), where \( \alpha \) is the angle at which the photon is scattered. Evaluate \( p \) for the two extreme values of \( \alpha \).

(c) Since the same image of the electron would be seen in the microscope for any value of \( \alpha \) in the range \( 90^\circ - \theta \) to \( 90^\circ + \theta \), show that \( \Delta p \)

(Eq. 3-1) is \( \Delta x \) or \( \lambda \) and that therefore \( \Delta x \times \Delta p = \hbar \).

(d) Show that even if we were satisfied with only a rough measure of the position of an electron in an atomic system, for example, \( \Delta x = 10^{-8} \text{ cm} \), which is about the radius of an atom, the accompanying uncertainty in velocity would be very large. Use \( p = mv \), where \( m \) is the rest mass of the electron.

2. Theory demands that every particle have associated wave properties. Why then does a billiard ball, for example, appear to move in a straight line? [Use Eq. (3-2) and consider that a billiard ball is a "particle" that weighs about 200 grams.]

3. An intense beam of green light (\( \lambda = 5000 \text{ A} \)) is insufficient to eject a core electron from magnesium metal, although this can be accomplished by a very weak beam of x-rays having a wavelength of 1 \( \text{ A} \). Show that quantum physics explains this apparent anomaly. [Use Eq. 3-1 and recall that \( v = c/\lambda \), where \( c \) is the velocity of light.]

4. Derive Eq. (3-4) for the electrical potential energy \( W \) of an electron of charge \( -e \) when it is separated a distance \( r \) from a nucleus of charge \( +e \). It is helpful to recall the analogous derivation for the gravitational potential energy of a mass \( m \) grams at a height of \( h \) cm. In general, \( W \) is defined as the work required to take a body from the reference position (where \( W = 0 \) by convention) to the final position. Therefore, since the gravitational force on a mass \( m \) is \( mg \), where \( g \) is the acceleration due to gravity,

\[
W = \int_0^h F \, dz = \int_0^h mg \, dz = mgh.
\]
In setting up the analogous integral for electrical potential energy, it should be noted that the conventional reference position, where $W = 0$, is infinite separation of the charges; therefore the integration is from $\infty$ to $r$, the final distance of separation. Also, while the electron is moving from $\infty$ toward $r$, a positive force of $e^2/r^2$ must be exerted on it to maintain the required equilibrium condition at each instant.

5. In obtaining a useful expression for the total energy $E$ by adding the potential energy $W$ and the kinetic energy $K$, it is necessary to have both $W$ and $K$ expressed in terms of the same quantities. The expression for potential energy, $W = -e^2/r$, is satisfactory, but it is desirable to change the usual expression for kinetic energy, $K = \frac{1}{2}m v^2$, into a form involving $e$ and $r$. (a) The Bohr theory pictures an electron moving in a circular orbit of radius $r$ because the force of electrostatic attraction due to the nucleus just equals the centrifugal force required to keep the electron in its circular orbit. Equate the expressions for these two forces and then rearrange the resulting equation so that one side of the equation is the quantity $\frac{1}{2}mv^2$. The other side of the equation is then the desired expression for $K$. (b) Add the appropriate expressions for $W$ and $K$ to obtain the expression for $E$ as a function of $r$, Eq. (3-6). (c) Plot $E$ versus $r$ for a range of $r$ values from 0.1 to 10 Å. Convert the $E$ values from ergs to electron volts for this plot.

6. Apply Eq. (3-3) to determine the frequency of the quantum of radiant energy given off when the electron in an excited hydrogen atom falls from energy state $E_2$ to $E_1$. Recalling the relation $\Delta \nu = c$, where $c$ is the velocity of light, calculate the corresponding wavelength of the radiation.

7. Since momentum, $p = mv$, and kinetic energy, $K = \frac{1}{2}m v^2$, both depend on the two quantities $m$ and $v$, it is possible to obtain an expression for $p$ that involves $K$. (a) Rearrange the equation $K = \frac{1}{2}mv^2$ so that one side of the equation involves only the quantity $mv$ and the other side involves $K$ and $m$, but not $v$. Since $mv$ can be replaced by $p$, show that this is the desired relation between $p$ and $K$. (b) Recalling the relation $E = K + W$, obtain the expression for $p$ that is used in Eq. (3-9).

8. The production of x-rays involves the inner, completed groups of electrons in an atom; the $1s$ electrons are especially important. The first step in the process is to eject one of these electrons (from the $1s$ level, for example). This is usually accomplished by bombarding the "target" metal with a beam of high-energy electrons; see Fig. 4-12. The vacant $1s$ level is quickly occupied by one of the other electrons in the atom, most probably by one that falls from the $2p$ level. (a) Use a diagram similar to Fig. 3-2(b) to show qualitatively the change in energy accompanying a $2p \rightarrow 1s$ transition in iron. (b) Calculate the difference in energy between the $2p$ and $1s$ levels in iron from the fact that the wavelength of the x-ray produced by this transition is 1.933 Å. (c) Explain what a transition element is. (b) Why may a transition element show unusual behavior in alloys?

9. (a) Apply Eq. (3-3) to determine the frequency of the quantum of radiant energy given off when the electron in an excited hydrogen atom falls from energy state $E_2$ to $E_1$. Recalling the relation $\Delta \nu = c$, where $c$ is the velocity of light, calculate the corresponding wavelength of the radiation.

10. An electron beam of which of the following velocities would be most strongly diffracted by a crystal having periodic spacings of 3 Å separation: (a) $2 \times 10^{10}$, (b) $2 \times 10^{8}$, (c) $2 \times 10^{6}$ cm/sec? (Recall that appre-
ciable diffraction occurs only when the wavelength of the beam and the spacing of the grating are of the same order of magnitude.

11. Prove that the boundaries of the second Brillouin zone shown in Fig. 3-9 are correct. Since these boundaries are determined by reflections from planes at 45° in Fig. 3-8, it is convenient to use coordinates $x'$ and $y'$ that are rotated 45° relative to the $x$- and $y$-axes. The same method can then be used as for the first zone except that the spacing of the planes is $a/\sqrt{2}$ rather than $a$.

12. Determine approximate values for the two energy levels in the second zone of Fig. 3-9 that would give an $N(E)$ curve similar to Fig. 3-11(b).

13. Why is it unsatisfactory to explain electrical conduction entirely on the basis of free electrons?

14. From the data given for the vanadium isotope: (a) determine the time constant $\lambda$, (b) calculate the fraction of a sample of this isotope that would remain after 24 hours.
CHAPTER 4

CRYSTAL STRUCTURE

Crystals have a wonderful diversity and elegance in their phenomena that make the properties of other substances dull and monotonous in comparison.

VOIGT

INTRODUCTION

Metals are aggregates of atoms. Metallic properties, therefore, depend not only on the nature of the constituent atoms, which were considered in the previous chapter, but also on the manner in which the atoms are assembled. It is customary to describe assemblies of atoms as being in the solid, liquid, or gaseous states. The properties of liquid and gaseous metals are more conveniently discussed in a later chapter, after the characteristics of crystalline, solid metals are understood.

The essential, crystalline nature of metals is seldom apparent in final products, such as girders, automobile fenders, or door knobs, but the properties of the individual crystals in a metal are responsible for its ultimate engineering usefulness and they strongly influence the entire processing of the metals. The photographs in Fig. 4-1 show a few of the striking effects that arise because of the crystalline nature of metals. External "crystal" faces similar to those seen on mineralogical specimens of quartz, galena, etc., also develop on metals under suitable conditions. The attractive crystals of magnesium in Fig. 4-1(a) were grown slowly by deposition from vapor in a commercial sublimation process. Even when the crystal planes cannot be seen on the surface of a metal crystal they can sometimes be clearly revealed, as in Fig. 4-1(b), by cleavage along an important crystal plane. This zinc crystal was cooled in liquid nitrogen and was then easily cleaved by the pressure of a knife blade. Action of similar crystal planes can be seen in the "slip" process that occurs when metals are deformed, Fig. 4-1(c).

The three previous illustrations involved single crystals; a more subtle example of crystalline effects in metals is given for an ordinary polycrystalline alloy in Fig. 4-1(d). The large grain that occupies most of this photomicrograph was originally a single crystal. The parallel sets of bands were produced when a second, darker constituent formed on certain crystal planes of the original crystal. It will be explained below why there are several sets of equivalent crystal planes in typical metal crystals.
Some liquids when cooled become more and more viscous and eventually become as rigid as a piece of window glass. Since the random distribution of atoms characteristic of the liquid state still persists, such undercooled liquids are called amorphous substances to distinguish them from true solids. What then, if not rigidity of form, is the criterion of the solid state? It is this: the atoms of a solid are arranged in a regular three-dimensional pattern called a crystal structure. Although all true solids possess a crystal structure, there is a wide range of properties within the solid state. A large part of this variation is the result of differences in the type of
binding of the atoms in the various kinds of solids. While it is convenient to discuss the four types of binding separately, it is more exact to consider that one of the types of binding predominates in a given instance, with the others playing less important roles.

Metallic binding. As its name signifies, metallic binding is the principal force holding together the atoms of a metal. This type of binding results when each of the atoms of the metal contributes its valence electrons to the formation of an electron cloud that pervades the solid metal. A schematic picture of the metal ions and of the electron cloud is given in Fig. 4-3(a). The conduction of electricity and the principal conduction...
of heat are produced by the free movement of these electrons through the metal. Since the negative electron cloud surrounds each of the positive ions that make up the orderly three-dimensional crystal structure, strong electrical attraction holds the metal together. A characteristic of metal binding is the fact that every positive ion is equivalent. Thus, the metal can behave in a ductile fashion under stress because a group of positive ions break their binding at one location, slip to a new position, and re-establish their bonds. This aspect of the plastic deformation of metals is considered in detail in Chapter 9.

Ideally, a symmetrical ion is produced when a valence electron is removed from the metal atom. As a result of this ion symmetry, metals tend to form highly symmetrical, close-packed crystal structures. Figure 4-2(a) shows a representative portion of the crystal structure of copper with the copper ions drawn as spheres in contact and with the electron cloud omitted. Since a crystal structure is made up of a unit that is repeated, this basic group of ions or atoms, the unit cell, is of principal interest and is shown in Fig. 4-2(b). In Fig. 4-2(c) the unit cell is represented in the ordinary diagrammatic fashion with the positions of the centers of the ions indicated by small spheres. Not all metals have structures as simple as copper, and the appearance of more complex, less symmetrical structures is evidence that metallic characteristics are being replaced by those of other solid types.

**Van der Waals binding.** The rare gases and molecules like methane, CH₄, which have no valence electrons available for crystalline binding, obtain a weak attractive force for this purpose as a result of polarization of their electric charges. Polarization is separation of the centers of positive and negative charges in an electrically neutral atom or molecule as it is brought close to its neighbors. Its neighbors also become polarized. A schematic picture of such polarization is given in Fig. 4-3(d). The resulting weak electrical attraction between neighboring atoms or molecules is the van der Waals force. It can overcome the disrupting effect of thermal motion of the atoms and molecules only at low temperatures; therefore the so-called molecular crystals produced by this type of binding are weak and many of them melt at temperatures far below 0°C.

**Ionic binding.** The elementary picture of electrostatic attraction between one sodium ion and one chlorine ion as a result of the transfer of the valence electron of the sodium atom to the chlorine atom must be slightly modified for an understanding of ionic binding in solids. Figure 4-3(b) is a schematic illustration of ionic binding showing that this type of binding is caused by electrical attraction between alternately placed positive and negative ions. A portion of the crystal structure of sodium chloride
The nature of the four types of binding in solids. (a) Metallic binding. (b) Ionic binding. (c) Covalent binding. (d) Van der Waals' binding. Is shown in Fig. 4–4(a). Here each ion has as nearest neighbors six ions of opposite charge. Another type of crystal structure characteristic of ionic solids is that of cesium chloride, Fig. 4–4(b).

No electronic conduction of the kind found in metals is possible in ionic crystals, but weak ionic conduction occurs as a result of the motion of the individual ions. When subjected to stresses, ionic crystals tend to cleave (break) along certain planes of atoms rather than to deform in a ductile fashion as metals do.
Covalent or homopolar binding. Many elements that have three or more valence electrons are bound in their crystal structures by forces arising from the sharing of electrons. The nature of this covalent binding is shown schematically in Fig. 4-3(c). To complete the octet of electrons needed for atomic stability, electrons must be shared with $8 - N$ (8 minus $N$) neighboring atoms, where $N$ is the number of valence electrons in the given element. Diamond is a typical example of the covalent or homopolar crystal produced by this type of binding, and Fig. 4-5(a) shows that each carbon atom has four nearest neighbors, corresponding to the $8 - N$ rule applied to its four valence electrons. Bismuth has five electrons in its
outer shell and requires three additional electrons to achieve a stable configuration. Figure 4-5(b) shows how the crystal structure, which is of the arsenic type, permits a given atom in this case to share valence electrons with three nearest neighbors. High hardness and low electrical conductivity are general characteristics of solids of this type.

**Space Lattices and Crystal Systems**

The crystal structures shown above illustrate the essential characteristic of solids, that is, regularity in arrangement of atoms. This regularity affects almost all the properties of metals, and therefore it is important to be able to describe it quantitatively. Although there is a limitless number of possible crystal structures, the science of crystallography has developed a convenient system of classifying these structures, starting from a few basic concepts. The concepts needed for effective work with the crystal structures found in metals are considered here.

**Space lattice.** When discussing crystal structure it is usually assumed that the structure continues to infinity in all directions. In terms of the conventional crystal (or grain) of iron one hundredth of an inch in size, this may appear to be an absurd assumption, but when it is realized that there are $10^{18}$ iron atoms in such a grain the approximation to infinity seems much closer. The fundamental definition of regularity of distribution of atoms in space is that of a space lattice. A distribution of points (or atoms) in three dimensions is said to form a space lattice if every point has identical surroundings. What a boring, repetitious place an infinite space lattice would be for a hypothetical flea-like creature! As he hopped from one point to the next he would see exactly the same endless vista.

A portion of a general space lattice is shown in Fig. 4-6(a). Because of the regularity in distribution of the points that compose a lattice, the essential geometry can be described by three lattice vectors, $a$, $b$, and $c$ (Fig. 4-6b). These vectors describe the unit cell that is outlined in the corner of the space lattice, Fig. 4-6(a). The geometry of a space lattice is completely specified by the lattice constants (vector lengths) $a$, $b$, and $c$, and the interaxial angles $\alpha$, $\beta$, and $\gamma$. There are only fourteen possible arrangements of points that satisfy the definition of a space lattice, and fewer than half of these are important in metallic structures. Figure 4-7 shows the unit cells of six of the more common space lattices found in metals and alloys.

Although a space lattice is fundamentally a distribution of points in space, it is convenient to connect these points by lines (axes) like those shown in Fig. 4-6(a) and to describe the space lattice in terms of the geometric figure formed by these lines. For example, there are three dif-
Fig. 4-6. (a) A portion of a space lattice, with a unit cell outlined. (b) Description of the unit cell in terms of the lattice vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \). The lattice constants \( a, b, c \), and the interaxial angles \( \alpha, \beta, \gamma \) are shown. (From *Elements of X-ray Diffraction* by B. D. Cullity.)

Different distributions of points that are conveniently described by a cubic network of axes, that is, by three equal axes at right angles to each other. The *simple cubic* space lattice, having points lying only at the intersections of the network of axes, is not an important space lattice in metals. The *body-centered cubic* and the *face-centered cubic* space lattices are common in metals and are shown in Fig. 4-7. These lattices have points at the cube center and at the centers of the cube faces, as well as at the corners of the cubic unit cell. In cubic crystals the lattice constant has the same value \( a \) in all three directions in the crystal, but in other cases, such as in orthorhombic crystals, the lattice constant may have three different values \( a, b, c \) in the three directions in the crystal.
Crystal structure. The crystal structures of some metals are simply atoms placed at the points of a space lattice; the face-centered cubic structure of copper is an example. Sodium chloride, Fig. 4-4(a), is a more complicated crystal structure. It might at first appear that this structure is simple cubic, but further consideration reveals that the points corresponding to a simple-cubic space lattice are not identical, since two adjacent points are occupied by a sodium ion and by a chloride ion. Actually, the space lattice in this case is face-centered cubic and each lattice point is associated with the same structural unit, a sodium ion plus a chloride ion. In Fig. 4-4(a) the sodium ions may be considered to mark the points...
of a space lattice, with each lattice point occupied by a sodium ion and, for example, the chloride ion to its right.

The close-packed hexagonal structure, which characterizes magnesium and a number of other pure metals, is a similar example of a group of atoms at a lattice point. Figure 4-8(a) shows how a cell with hexagonal symmetry can be visualized within a set of four unit cells of the simple hexagonal space lattice, Fig. 4-7. However, magnesium atoms do not occupy merely the points of this space lattice but also the intermediate positions that are shown in the sketch of the close-packed hexagonal crystal structure, Fig. 4-8(b). As in the NaCl structure, a pair of atoms (connected by a dashed line in the figure) can be associated with a point in the space lattice. Figure 4-8(c) gives an explanation for the preference of atoms for the close-packed structure, in terms of the packing of spheres. The simple hexagonal lattice corresponds to the placing of the upper layer of atoms, A, directly on the lower A layer (layer B is not shown). Visualization of this stacking in terms of marbles shows that it tends to be unstable; marbles in the upper layer would slip down into the valleys in the lower layer. Three compatible valley positions are indicated in the lower A layer. In contrast to this unstable arrangement, the close-packed hexagonal structure (Fig. 4-8b) corresponds to the occurrence of the intermediate layer of atoms, B, in such a position that the valleys are occupied, both in the lower and the upper A layers. Figure 4-8(d) shows the compact structure that results from this kind of packing.

For some purposes there is an advantage in describing crystal structures using a primitive cell, a unit cell with lattice points at corners only. For example, the lattice in Fig. 4-6(a) is built up of primitive cells. The unit cells of the body-centered cubic and face-centered cubic space lattices, Fig. 4-7, are evidently not primitive cells, since there are centered lattice points as well as corner ones. However, in Problem 5 it is shown that rhombohedral primitive cells can be used as alternative descriptions of these lattices. A principal advantage in using primitive cells in these two cases is the fact that each cell contains one atom. Figure 4-6(a) can be used to justify this statement. (Show that each of the eight corner atoms of a given cell is shared by a total of eight cells.) Similarly, it can be verified that there are two atoms per cell in the body-centered cubic and close-packed hexagonal structures and four atoms per cell in the face-centered cubic structure. The primitive cell for the close-packed hexagonal structure is the simple hexagonal unit cell, Fig. 4-8(a).

A logical extension of the use of lattice vectors, Fig. 4-6(b), is the classification of the fourteen space lattices by crystal system, according to the relative lengths of the vectors (or axes) and the interaxial angles, Table 4-1. For example, three of the fourteen space lattices can be described by the simple system of equal axes at right angles (cubic crystal
Fig. 4-8. Important features of the close-packed hexagonal crystal structure. (a) Simple hexagonal space lattice. (b) Close-packed hexagonal crystal structures. (c) Exploded view of the packing of spheres in the close-packed hexagonal structure. (d) Assembled view of the close-packed hexagonal crystal structure.
### Table 4-1

**Classification of the Space Lattices by Crystal System**

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Axial lengths and interaxial angles</th>
<th>Space Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>Three equal axes at right angles</td>
<td>Simple cubic</td>
</tr>
<tr>
<td></td>
<td>( a = b = c, \alpha = \beta = \gamma = 90^\circ )</td>
<td>Body-centered cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>Three axes at right angles, two</td>
<td>Simple tetragonal</td>
</tr>
<tr>
<td></td>
<td>equal ( a = b \neq c, \alpha = \beta = \gamma = 90^\circ )</td>
<td>Body-centered tetragonal</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Three unequal axes at right angles</td>
<td>Simple orthorhombic</td>
</tr>
<tr>
<td></td>
<td>( a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ )</td>
<td>Body-centered orthorhombic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Base-centered orthorhombic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face-centered orthorhombic</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>Three equal axes, equally inclined</td>
<td>Simple rhombohedral</td>
</tr>
<tr>
<td></td>
<td>( a = b = c, \alpha = \beta = \gamma \neq 90^\circ )</td>
<td></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>Two equal axes at 120°, third axis</td>
<td>Simple hexagonal</td>
</tr>
<tr>
<td></td>
<td>at right angles ( a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ )</td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>Three unequal axes, one pair not</td>
<td>Simple monoclinic</td>
</tr>
<tr>
<td></td>
<td>at right angle ( \alpha \neq b \neq c, \alpha \neq \gamma \neq 90^\circ \neq \beta )</td>
<td>Base-centered monoclinic</td>
</tr>
<tr>
<td>Triclinic</td>
<td>Three unequal axes, unequally</td>
<td>Simple triclinic</td>
</tr>
<tr>
<td></td>
<td>inclined and none at right angles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( a \neq b \neq c, a \neq \beta \neq \gamma \neq 90^\circ )</td>
<td></td>
</tr>
</tbody>
</table>

This geometrical simplicity is the reason that the face-centered cubic array of points is ordinarily described using cubic axes. However, it is noteworthy that there are many ways of erecting systems of axes for a given space lattice; the primitive cell for the face-centered cubic space lattice uses the inclined axes of the rhombohedral system, for example. Two other concepts are widely used in classifying more complex crystal structures. The thirty-two point groups used in describing minerals are based on the external symmetry of crystals; the sixfold symmetry of hexagonal quartz crystals is an example. Consideration of the possible ways...
Table 4-2
CRYSTAL-STRUCTURE AND X-RAY DATA FOR A NUMBER OF METALS

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal structure</th>
<th>Lattice constant, A</th>
<th>(K)</th>
<th>(\lambda)</th>
<th>Absorption edge, A</th>
<th>(\mu A) Mass absorption coefficient, radiation being absorbed, A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>B.C.C.</td>
<td>4.05</td>
<td>8.32</td>
<td>7.04</td>
<td>2.74</td>
<td>5.30</td>
</tr>
<tr>
<td>Chromium</td>
<td>B.C.C.</td>
<td>2.88</td>
<td>2.887</td>
<td>2.07</td>
<td>13.7</td>
<td>30.4</td>
</tr>
<tr>
<td>Cobalt</td>
<td>C.P.H.</td>
<td>(c = 4.07) (a = 2.51)</td>
<td>1.769</td>
<td>1.60</td>
<td>21.8</td>
<td>41.6</td>
</tr>
<tr>
<td>Copper</td>
<td>F.C.C.</td>
<td>2.62</td>
<td>1.536</td>
<td>1.38</td>
<td>26.4</td>
<td>49.7</td>
</tr>
<tr>
<td>Gold</td>
<td>F.C.C.</td>
<td>4.06</td>
<td>0.181</td>
<td>0.153</td>
<td>1.04</td>
<td>55.7</td>
</tr>
<tr>
<td>Iron</td>
<td>B.C.C.</td>
<td>2.87</td>
<td>1.933</td>
<td>1.74</td>
<td>19.9</td>
<td>38.3</td>
</tr>
<tr>
<td>Lead</td>
<td>F.C.C.</td>
<td>4.95</td>
<td>0.166</td>
<td>0.140</td>
<td>0.95</td>
<td>74.4</td>
</tr>
<tr>
<td>Magnesium</td>
<td>C.P.H.</td>
<td>(c = 5.21) (a = 3.21)</td>
<td>9.87</td>
<td>9.50</td>
<td>2.27</td>
<td>4.36</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>B.C.C.</td>
<td>3.15</td>
<td>0.710</td>
<td>0.618</td>
<td>70.7</td>
<td>20.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>F.C.C.</td>
<td>3.52</td>
<td>1.050</td>
<td>1.48</td>
<td>25.0</td>
<td>47.4</td>
</tr>
<tr>
<td>Platinum</td>
<td>F.C.C.</td>
<td>3.92</td>
<td>0.184</td>
<td>0.158</td>
<td>1.07</td>
<td>64.2</td>
</tr>
<tr>
<td>Silver</td>
<td>F.C.C.</td>
<td>4.09</td>
<td>0.809</td>
<td>0.484</td>
<td>3.69</td>
<td>14.8</td>
</tr>
<tr>
<td>Tin</td>
<td>B.C.T.</td>
<td>(c = 3.18) (a = 5.83)</td>
<td>0.491</td>
<td>0.424</td>
<td>3.15</td>
<td>17.4</td>
</tr>
<tr>
<td>Titanium</td>
<td>C.P.H.</td>
<td>(c = 4.68) (a = 3.28)</td>
<td>2.75</td>
<td>2.50</td>
<td>11.8</td>
<td>22.7</td>
</tr>
<tr>
<td>Tungsten</td>
<td>B.C.C.</td>
<td>3.16</td>
<td>0.210</td>
<td>0.178</td>
<td>1.31</td>
<td>54.8</td>
</tr>
<tr>
<td>Zinc</td>
<td>C.P.H.</td>
<td>(c = 4.85) (a = 2.56)</td>
<td>1.453</td>
<td>1.38</td>
<td>28.3</td>
<td>64.8</td>
</tr>
</tbody>
</table>

B.C.C. = body-centered cubic  
F.C.C. = face-centered cubic  
C.P.H. = close-packed hexagonal  
B.C.T. = body-centered tetragonal  
\(A = 10^{-8}\) centimeter
of placing the point groups on the various space lattices leads to the concept of space groups, of which there are 230. Fortunately, it is possible to specify most metal structures merely by a space lattice and one or more lattice constants. The crystal structures of a number of common metals are given in Table 4-2.

Miller indices. Special planes and directions within metal crystal structures play an important part in plastic deformation, hardening reactions, and other aspects of metal behavior. A qualitative picture of lattice planes is given by Fig. 4-9. However, the quantitative descriptions needed for many purposes are best supplied by sets of numbers that identify given planes of atoms; for example, the vertical and horizontal planes in Fig. 4-9(a) are [100] type planes, while the vertical planes in Fig. 4-9(b) are (110) planes. These numbers are the Miller indices of the planes and can be used directly in x-ray and other analyses. The three steps used in determining the indices of a given plane will be illustrated with the aid of Fig. 4-10.

1. Determine the intercepts of the plane on the three crystal axes. These intercepts are expressed in terms of number of axial lengths from the origin:

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
<td>1</td>
<td>intercept</td>
</tr>
</tbody>
</table>

2. Take the reciprocals of these numbers: $\frac{1}{2}, \frac{1}{3}, 1$.

![Fig. 4-9. Two views of a portion of a simple cubic lattice. The (100) planes are the prominent vertical planes in (a), while the (110) planes are the prominent vertical planes in (b). (By permission from Introduction to Physical Metallurgy by L. R. VanWert. McGraw-Hill, 1936.)](image-url)
3. Reduce the reciprocals to the smallest integers that are in the same ratio:

\[
\begin{align*}
3 & \quad 2 & \quad 6 \\
\end{align*}
\]

or \((326)\)

Thus the position of the plane of atoms shown in Fig. 4-10 is specified by the Miller indices \((326)\). It should be noted that these indices give only geometrical information about the crystal planes and say nothing about the distribution or kinds of atoms in the plane. On the other hand, a set of Miller indices such as \((326)\) describes not merely a single crystal plane but the entire array of planes parallel to the plane on which the three-step analysis was carried out. For example, a plane having intercepts 4, 6, and 2 would be parallel to the plane shown in Fig. 4-10, and it can be verified that its indices would also be \((326)\). Figure 4-9(a) shows the physical necessity for this identical numbering of parallel planes, since the planes are exactly equivalent.

It was convenient to choose the plane shown in Fig. 4-10 for the above analysis because it passed through lattice points on each of the three axes; however, such a plane may not be the first plane out from the origin in the given set of parallel planes. For example, in Fig. 4-11(d) it is not the first but the second plane that passes through lattice points on both the \(x\)- and \(y\)-axes. When the location of the first plane in a set is required, it can be determined from the fact that its intercepts on the \(x\), \(y\), and \(z\)-axes are \(a/h\), \(b/k\), and \(c/l\), where \(a\), \(b\), and \(c\) are the axial lengths (lattice constants) and \(h\), \(k\), and \(l\) are the Miller indices of the general plane \((hkl)\).
Fig. 4-11. Some of the simpler crystal planes in cubic crystals. Other designations of these planes are (a) octahedral, (b) dodecahedral, and (c) cubic. In (d) the relation of the [210] direction to the (210) plane is shown.
For example, in Fig. 4–11(d) \( h = 2, k = 1, \) and \( l = 0, \) so that the intercepts of the first plane are \( a/2, a, \) and \( x, \) respectively. The intercept \( x \) for the \( x \)-axis signifies that the plane is parallel to this axis.

The more common planes in cubic crystals are shown in Fig. 4–11, together with their Miller indices. Since the space lattice of atoms is considered to be infinite, and since the origin can be made to coincide with any one of the atoms, it is evident that there is no physical difference between planes such as \( (100) \) and the \( (100) \) planes that happen to be on the other side of the arbitrary origin. (Analysis of planes passing through the origin is unprofitable.) Similarly, \( (010) \) planes are equivalent to \( (100) \) planes and, in fact, could be made to have the latter indices by merely choosing the coordinates in a different manner. Families of such equivalent planes are of sufficient interest to have a special designation, and the symbol \( (100) \) stands for the family of planes \( (100), \) \( (100), \) \( (010), \) \( (010), \) \( (001), \) and \( (001), \) with similar definitions for other families of planes.

A direction in a crystal is indicated by bracketed indices, e.g. \([210]\), and in the cubic system the direction is always perpendicular to the plane having the same indices, Fig. 4–11(d). More generally, a line in a given direction, such as \([210]\), can be constructed in the following manner. Draw a line from the origin through the point having the coordinates \( x = 2, y = 1, z = 0, \) in terms of axial lengths. This line and all lines parallel to it are then in the given direction. Note that reciprocals are not involved in obtaining the Miller indices of directions. A family of equivalent directions, such as \( [100], [100], [010], [010], [001], \) and \( [001], \) is designated as \( (100). \)

In the case of hexagonal crystals two equivalent systems of indices are in use. The usual Miller indices are referred to the axes shown in Fig. 4–8(a) and have the customary three numbers. However, Fig. 4–8(b) shows that hexagonal symmetry suggests the use of four axes, the \( c \) axis plus three \( a \) axes at 120° intervals. The intercepts of a crystal plane on these four axes leads to the four-number Miller-Bravais indices. The two systems of indices are simply related: if \( (hkI) \) are the Miller indices, then the Miller-Bravais indices are \( (hkil), \) where \( t = -(h + k). \) For example, it can easily be verified that the \( (110) \) plane in Fig. 4–8(a) would be described as the \( (1120) \) plane in terms of the axes in Fig. 4–8(b).

Methods for Studying Crystal Structures

Interesting structural features of metals range in magnitude from the nucleus of a single atom to large blowholes or similar macroscopic flaws in final metal products. The appropriate techniques for studying these structures are, of course, quite varied. (Sonic methods of flaw detection, microscopic study of grain size, and visual observation of metal fractures
are some of the techniques to be discussed later.) Since the atomic spacings in crystals are only a few angstrom units, the most generally useful tools for studying crystal structure make use of radiation (or particles) having a similar, very short wavelength. X-rays are most widely used for this purpose, but beams of electrons or neutrons are also used for special purposes. A brief introduction to these three techniques follows.

X-ray techniques. The very short wavelength radiation known as x-rays has basically the same nature as visible light. While light rays can be produced by transitions of valence electrons between various energy states, x-rays are generated only by transitions involving inner (core) electrons. Figure 4-12 shows the principle of operation of an x-ray tube, in which high-speed electrons knock out inner electrons from the atoms of the target metal. X-rays are generated when electrons from outer levels fall into vacant positions in the inner levels. It will be recalled that the nature of this process was considered in the previous chapter, especially in Problem 8. Of principal importance are the $K_a$ characteristic x-rays, examples of which are given in Table 4-2 for some common metals. However, Fig. 4-13 shows that there is also a $K_{eta}$ characteristic radiation and a weaker white radiation, so called because it covers a range of wavelengths like those for ordinary white light instead of just a few characteristic

![Figure 4-12. The operation of an x-ray tube with a molybdenum target at 35,000 volts.](image-url)

![Figure 4-13. The range of wavelengths produced when molybdenum metal is the target of an x-ray tube operating at 35,000 v.](image-url)
values. Under some conditions it can be seen that \( K_n \) is actually a closely spaced doublet.

Bragg's law. Since the wavelength of x-rays is about equal to the distance separating the atoms in solids, diffraction effects are produced when a beam of x-rays strikes a crystalline substance. Although the basic explanation of such a diffraction effect involves the concept of each atom acting as a center of wave propagation, it is more convenient for many purposes to consider entire planes of atoms as mirrors reflecting the incident beam. This view assumes that the atoms form a perfect, infinite lattice, but it is quite satisfactory for many applications. In Fig. 4-14 the horizontal lines represent the cross sections of crystal planes of the set

![Diagram](image-url)

**Fig. 4-14.** The reflection of an x-ray beam by the \((hkl)\) planes of a crystal. In (a) no reflected beam is produced at an arbitrary angle of incidence. At the Bragg angle, \( \theta \), the reflected rays are in phase and reinforce one other, (b). Figure (c) is similar to (b) except that the wave representation has been omitted.
of parallel planes having, in general, Miller indices \((hkl)\). When a beam of x-rays with wavelength \(\lambda\) strikes this set of crystal planes at some arbitrary angle, there will usually be no reflected beam because the rays reflected from the various crystal planes of the set must travel paths of different lengths. Therefore, although the incident rays are in phase, the reflected rays are out of phase and cancel one another, Fig. 4-14(a). There is one particular degree of "out-of-phaseness" that does not have this destructive effect. If each ray is out of phase with the preceding one by exactly one wavelength (or exactly two, etc.), then there will be a reflected beam consisting of rays that are effectively in phase again, Fig. 4-14(b). The angle at which this reflection occurs is known as the Bragg angle, \(\theta\).

Figure 4-14(c) shows that the condition for the existence of the reflected beam is that the distance \(MPN\) be equal to an integral number of wavelengths; that is,

\[ n\lambda = MPN, \]

where \(\lambda\) is the wavelength and \(n\) can have the values 1, 2, 3, etc. Both \(MP\) and \(PN\) are equal to \(d \sin \theta\), where \(d\) is the interplanar spacing of the \((hkl)\) planes. Therefore the condition for the production of a reflected x-ray beam is

\[ n\lambda = 2d \sin \theta. \]

This equation is known as Bragg's law. Although for a given substance \(n\) and \(d\) ordinarily have only a few different values, both \(\lambda\) and \(\theta\) can be varied continuously over a wide range. The various x-ray diffraction techniques differ according to whether \(\lambda\) or \(\theta\) is varied. The Laue method is shown in Fig. 4-15. A narrow (collimated) beam of white x-rays is caused to strike a stationary single crystal of the metal to be studied.

![Fig. 4-15. The Laue method of x-ray diffraction. The reflected spots are visible only after the film has been developed in the usual manner.](image)
Each of the planes in the crystal can select the wavelength that satisfies Bragg's law and can reflect this portion of the x-ray beam. Each of the reflected spots indicated on the film in Fig. 4-15 is produced by a different set of planes. The principal metallurgical uses of the Laue method are the determination of crystal orientation and the detection of imperfections in metal crystals.

The rotating crystal method uses characteristic (constant wavelength) x-radiation but the diffracting single crystal is rotated, and so values of θ are obtained that cause reflections to be produced. This method is used mostly for crystal structure determinations.

The powder method. This method uses an x-ray beam of constant wavelength and a specimen consisting of thousands of tiny crystals. The random orientations of the individual crystals ensures the required variation in angle, and hundreds of reflected beams are produced. As the name powder method suggests, the multicrystal sample is often prepared by reducing larger crystals to powder, but an ordinary piece of metal wire can also be used, since it consists of a large number of very small crystals. Figure 4-16 shows the procedure used in obtaining a typical diffraction pattern from a powder specimen. A narrow x-ray beam strikes the specimen and is diffracted as cones of radiation. The reason for this behavior can be understood by first considering the reflections produced by the crystal planes that have the largest interplanar spacing d. Bragg's law shows that these planes will yield reflections at the smallest angle possible for this substance (using the given x-ray wavelength λ). The Bragg angle θ of these reflections will have some definite value; it is about 15° in Fig. 4-16. However, the angle between the x-ray beam and the reflections is 2θ, as shown in Fig. 4-14(c). The crystal planes in question will produce reflections for any orientation around the x-ray beam provided the beam strikes their surfaces at the Bragg angle. Since many of the tiny crystals in a powder specimen are suitably oriented, the cone of reflection having a semi-apex angle of 2θ is generated as shown in Fig. 4-16. Similar reasoning can be used to explain the production of the remaining cones of reflected radiation by additional sets of crystal planes having progressively smaller spacings. However, since θ cannot be greater than 90°, it can be concluded from Eq. (4-2) that crystal planes having an interplanar spacing less than λ/2 cannot yield a reflection. Each cone of reflected radiation is made up of many reflections from individual crystals, and it is necessary to record only a representative portion of each cone on the x-ray film. Ordinarily two portions of each cone are recorded in order to make it easier to obtain the desired measurements.

Two principal kinds of information can be obtained from a powder diffraction pattern: the positions of the reflected beams, which are determined by the size and shape of the unit cell, and the intensities of the reflected
beams, which are determined by the distribution and kinds of atoms in
the unit cell. For simplicity, the present treatment will be restricted to
diffraction patterns of pure metals that crystallize in the cubic system. It
will then be necessary to consider only the positions of the reflected beams
to determine the space lattice and the lattice constant that correspond
to the diffraction pattern. This analysis is made easier by use of the fol-
lowing relation between $d$, the spacing of the $(hkl)$ plane, and $a$, the
lattice constant of the cubic crystal (see Problem 9):

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \quad (4-3)$$

It is conventional to incorporate the order of reflection $n$ in the Miller
indices, so that second-order reflection from the (100) plane is considered
as first-order reflection from the (300) plane. Such higher-order planes
may be fictitious in the sense that they need not have physical existence,
but they are used conveniently and correctly in most x-ray analyses.
**Table 4-3**

Reflecting Planes for the Three Cubic Space Lattices

<table>
<thead>
<tr>
<th>Reflecting plane (hkl)</th>
<th>$Q^2 = h^2 + k^2 + l^2$</th>
<th>Simple cubic</th>
<th>Body-centered cubic</th>
<th>Face-centered cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>1</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(110)</td>
<td>2</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(111)</td>
<td>3</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(200)</td>
<td>4</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(210)</td>
<td>5</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(211)</td>
<td>6</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(220)</td>
<td>8</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(300) (221)</td>
<td>9</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(310)</td>
<td>10</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(311)</td>
<td>11</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(222)</td>
<td>12</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(320)</td>
<td>13</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(321)</td>
<td>14</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(400)</td>
<td>16</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(410) (322)</td>
<td>17</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(411) (330)</td>
<td>18</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(331)</td>
<td>19</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(420)</td>
<td>20</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(421)</td>
<td>21</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>(332)</td>
<td>22</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* Indicates the occurrence of reflection.

Bragg’s law, Eq. (4-2), can be put into a form useful for the analysis of powder diffraction patterns of cubic crystals by substituting Eq. (4-3) for $d$ and including the order of reflection $n$ in the indices of the reflecting plane. The law then becomes

$$\lambda = \frac{2a}{\sqrt{h^2 + k^2 + l^2} \sin \theta}.$$  \hspace{1cm} (4-4)

The square root can be eliminated by squaring both sides of this equation. Letting $Q^2 = h^2 + k^2 + l^2$ and rearranging the factors, the significant result is

$$Q^2 \left( \frac{x^2}{a^2} \right) = Q^2 = \sin^2 \theta.$$ \hspace{1cm} (4-5)
where $C$ is a constant. That is, the squares of the sines of the angles at which reflections occur are in the ratio of certain whole numbers. This relation among the $\theta$ values can be used to determine the crystal lattice of the metal that produces a given diffraction pattern, since the possible $Q^2$ values are different for the three cubic space lattices (Table 4-3). Each reflecting plane $(hkl)$ has a corresponding value of $Q$. However, not all values of $Q$ can occur in the analysis of diffraction patterns from most space lattices, since certain reflections cannot appear because of destructive interference produced by body- or face-centered atoms. For example, reflection from the (100) plane in the body-centered cubic lattice cannot occur because the body-centered atoms form intermediate planes that produce reflected waves exactly out of phase with those from the corner atoms.

To illustrate the use of Eq. (4-5) in solving a diffraction pattern, film (d) in Fig. 4-17 will be analyzed. The first step, that of determining the diffraction angle $\theta$ associated with each line in the pattern, can be carried out using an equation derived with the aid of Fig. 4-18. The angle that the reflected beam makes with the exit beam is $2\theta$. Expressed in radians, $2\theta = \frac{s}{r}$, where $s$ is measured on the flattened film and is one-half the distance between the two arcs of the cone of reflected radiation; $r$ is the radius of the camera. It is more convenient to express $\theta$ in degrees and to measure $2\theta$ directly as the distance between the two arcs of a given cone of reflected radiation. Therefore the expression for $\theta$ is usually written

$$\theta = \frac{s}{2r} \times \frac{360}{2\pi} = 14.32 \frac{2s}{r} \text{ degrees}. \quad (4-6)$$

The value of $2\theta$ measured for each line of the pattern in Fig. 4-17(d) and the corresponding $\theta$, $\sin \theta$, and $\sin^2 \theta$ can be tabulated conveniently as follows:

<table>
<thead>
<tr>
<th>Line</th>
<th>$2\theta$, cm</th>
<th>$\theta$, degrees</th>
<th>$\sin \theta$</th>
<th>$\sin^2 \theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.19</td>
<td>23.6</td>
<td>0.400</td>
<td>0.1600</td>
</tr>
<tr>
<td>2</td>
<td>6.09</td>
<td>34.4</td>
<td>0.565</td>
<td>0.3192</td>
</tr>
<tr>
<td>3</td>
<td>7.77</td>
<td>43.8</td>
<td>0.692</td>
<td>0.479</td>
</tr>
<tr>
<td>4</td>
<td>9.42</td>
<td>53.1</td>
<td>0.800</td>
<td>0.640</td>
</tr>
<tr>
<td>5</td>
<td>11.23</td>
<td>63.3</td>
<td>0.880</td>
<td>0.776</td>
</tr>
<tr>
<td>6</td>
<td>13.90</td>
<td>78.4</td>
<td>0.980</td>
<td>0.960</td>
</tr>
</tbody>
</table>

These six lines result from the first six planes that can cause reflection (Table 4-3). Depending on the space lattice of the unknown metal that produces the diffraction pattern, these first six planes may have $Q^2$ values
Fig. 4-17. Simplified sketches of x-ray diffraction patterns obtained from wires of four different metals using a 5.08 cm diameter camera and cobalt Kα radiation, λ = 1.78Å.
FIG. 4-18. The relation between the angle of reflection, \( \theta \), from a crystal plane and the distance \( \delta \) measured on the film.

of 1, 2, 3, 4, 5, 6 (simple cubic), 2, 4, 6, 8, 10, 12 (body-centered cubic), or 3, 4, 8, 11, 12, 16 (face-centered cubic). But Eq. (4-5) shows that the ratio of the \( Q^2 \) values is the same as the ratio of the \( \sin^2 \theta \) values. Therefore, the space lattice of the unknown metal can be determined from the ratio of \( \sin^2 \theta \) values. In the pattern being considered the \( \sin^2 \theta \) values are seen to be very nearly in the ratio 1:2:3:4:5:6. However, the diffraction pattern is that of a pure metal, and the true ratio of \( Q^2 \) values is almost certainly 2:4:6:8:10:12, inasmuch as a simple cubic lattice is almost unknown in pure metals. From this ratio it can be concluded that the metal has a body-centered cubic space lattice.

The next step is to determine the lattice constant \( a \). Writing each value of \( \sin^2 \theta \) in the form of Eq. (4-5) gives

<table>
<thead>
<tr>
<th>Line</th>
<th>( \sin^2 \theta )</th>
<th>( Q^2 \times C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1600</td>
<td>2 \times 0.0600</td>
</tr>
<tr>
<td>2</td>
<td>0.3192</td>
<td>4 \times 0.0798</td>
</tr>
<tr>
<td>3</td>
<td>0.479</td>
<td>6 \times 0.0798</td>
</tr>
<tr>
<td>4</td>
<td>0.640</td>
<td>8 \times 0.0800</td>
</tr>
<tr>
<td>5</td>
<td>0.797</td>
<td>10 \times 0.0797</td>
</tr>
<tr>
<td>6</td>
<td>0.960</td>
<td>12 \times 0.0800</td>
</tr>
</tbody>
</table>

Since \( C \) is equal to \( \lambda^2/4a^2 \) (Eq. 4-5), and since in this case the wavelength used is \( \lambda = 1.786 \Delta \), the value of \( a \) is given by

\[
a = \frac{\lambda}{2\sqrt{C}} \quad a = \frac{1.786}{2 \times 0.2826} = 3.15 \text{ A.}
\]
Fig. 4-19. The diffractometer method of x-ray diffraction. (Courtesy General Electric Company.) (a) An x-ray diffractometer. (b) Record of diffraction angles for a tungsten sample obtained by use of a diffractometer with copper radiation.
Table 4-2 shows that tungsten is the body-centered cubic metal that has a lattice constant of 3.16 Å, and therefore tungsten is the pure metal that produces the diffraction pattern of Fig. 4-17(d).

Analyses of this type are used for many purposes, for example, to determine what kinds of solid phases (what kinds of crystal structures) are present in a given alloy. If two different kinds of crystals coexist, as in many industrial materials, each diffraction pattern appears on the film independently of the other. Inasmuch as almost all inorganic chemical compounds are crystalline substances, chemical analyses can be made by means of x-ray diffraction. Another important application of x-ray techniques is the investigation of reactions in solid metals that lead to softening, hardening, or to other property changes. The magnitude and condition of stress in metal grains can also be determined by this means.

In addition to photographic techniques, such as the powder method discussed above, there are methods of analysis that detect x-rays by the use of counter tubes. An x-ray diffractometer, Fig. 4-19(a), measures the intensity of the beam (counts per second) diffracted from a specimen over a range of angles and can be arranged for automatic recording of the data on a chart like that shown in Fig. 4-19(b) for a powder specimen. The $\theta$ values so obtained can then be analyzed in the same manner as in the photographic method. The same instrument can be arranged to serve as an emission spectrometer for chemical analysis utilizing the characteristic x-ray spectra of the elements. In this method the spectra are excited by very energetic x-rays, and the resulting characteristic wavelengths are determined from their diffraction by a crystal in the instrument.

Electron and neutron diffraction. It will be recalled from Chapter 3 that de Broglie waves are associated with moving particles. These waves are diffracted in much the same way as x-rays, and Bragg's law applies. However, there are sufficient dissimilarities between x-ray diffraction and diffraction of the two principal particles, electrons and neutrons, that the three techniques complement one another and permit a variety of approaches to problems in crystal structure.

Electron diffraction. Figure 4-20(a) shows a typical arrangement for obtaining characteristic patterns of crystalline substances by the use of a beam of electrons. Electrons from a heated filament are given the desired velocity by being accelerated by a potential of 50,000 volts. After the characteristics of the electron beam have been improved through the action of two magnetic lenses, the beam is then allowed to strike the specimen and produce a diffraction pattern on the photographic plate. The wavelength associated with electrons accelerated by 50,000 volts, as determined by the relation $\lambda = h/mv$ (Eq. 3-2), is 0.0356 Å, about
one-twentieth that of x-rays. Thus, although Bragg’s law also holds for electron diffraction, the diffraction angle is very much smaller than in the case of x-rays. Another characteristic of an electron beam is the ease with which it is absorbed. The entire diffraction apparatus must be operated in a good vacuum, and transmission specimens can be only a millionth of an inch in thickness. A transmission pattern for gold is shown in Fig. 4–20(b). The use of reflection specimens avoids the difficulties of preparing thin sections. When the electron beam is caused to graze the surface of a specimen, the diffraction pattern produced is that characteristic of only a thin surface layer about 100 atoms deep. This behavior is useful in investigating surface films such as those formed during the corrosion of metals. More generally, electron diffraction can be used like x-rays to identify substances and to obtain information on the grain size, the state of stress, and the orientation of crystal grains.

**Neutron diffraction.** In contrast to x-ray and electron diffraction, both of which are important industrial techniques, neutron diffraction is still in the experimental stage. Some of the practical problems in the use of this new method are apparent in the sketch of a typical experimental ar-
rangement, Fig. 4–21. A nuclear reactor is needed for the intense initial source of neutrons. However, these neutrons are white radiation containing many wavelengths and for most purposes the characteristic radiation needed is obtained by reflection from a monochromator, often a single crystal of lead. The intensity of the initial neutron beam is reduced by a factor of about $10^3$ by this operation, and after further diffraction by the sample the final beam is quite weak. An efficient, well-shielded counter is required for adequate analysis of this beam using the spectrometer technique that was described for x-rays.

Neutron diffraction has advantages over the other two techniques because of differences in the source of diffraction. The nucleus causes most of the diffraction of neutrons, while electrons are primarily responsible for diffraction of x-rays and electron beams. Since the number of electrons increases uniformly with atomic number, the diffracting power of atoms for x-rays and electrons exhibits a similar increase. Two consequences of this fact are especially noteworthy. Light elements, such as hydrogen and carbon, have little diffracting power compared with heavier elements and so it is difficult to study structures such as metal hydrides containing both heavy and light atoms. A second problem arises in studying structures made up of atoms whose atomic numbers are nearly the same. For example, iron and cobalt have nearly identical scattering powers.
for x-rays, so it is difficult to determine by x-rays the positions in the crystal structure occupied by each kind of atom.

In contrast to the regularity in scattering power for x-rays, the various elements show a random distribution in neutron-scattering power. The following representative values are from the reference by Bacon.

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative neutron-scattering power</th>
<th>Relative x-ray-scattering power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.8</td>
<td>1</td>
</tr>
<tr>
<td>Deuterium</td>
<td>5.4</td>
<td>1</td>
</tr>
<tr>
<td>Beryllium</td>
<td>7.7</td>
<td>4</td>
</tr>
<tr>
<td>Carbon</td>
<td>5.4</td>
<td>6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>3.6</td>
<td>12</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1.5</td>
<td>13</td>
</tr>
<tr>
<td>Titanium</td>
<td>1.8</td>
<td>22</td>
</tr>
<tr>
<td>Iron</td>
<td>11.4</td>
<td>26</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1.0</td>
<td>27</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>5.5</td>
<td>42</td>
</tr>
<tr>
<td>Tungsten</td>
<td>2.7</td>
<td>74</td>
</tr>
</tbody>
</table>

These values show clearly that iron and cobalt atoms can be distinguished readily by neutron diffraction. Also, since light atoms such as hydrogen and beryllium have neutron-scattering powers that are comparable to those of heavy atoms, neutron diffraction is a useful tool for studying metal hydrides, beryllides, and the like. In addition to the effect of the nucleus, an important contribution to the neutron-diffraction pattern is made by the electrons in unfilled shells in magnetic substances. An example of this phenomenon will be given in Chapter 7.

**Imperfections in Crystal Structures**

The perfectly regular crystal structures that have been considered up to now are called ideal crystals to distinguish them from the more or less imperfect real crystals that compose engineering alloys. The concept of an ideal crystal structure is adequate for explaining the structure insensitive properties of metals discussed at the beginning of Chapter 3. Also, the ideal structure is the framework within which the various types of imperfections exist. Thus, a knowledge of conventional, ideal crystal structures is an essential first step in understanding metallic behavior, but an adequate treatment of structure-sensitive properties requires additional information about real crystals. The two most important structural defects of real crystals are vacant lattice sites or vacancies and the...
extended discontinuities in internal structure that are called dislocations. Before discussing these defects in detail, however, it is desirable to survey briefly the various imperfections that are known to exist in real crystals.

**Types of imperfections.** Even an otherwise completely regular lattice of atoms has its atoms displaced from their ideal locations by thermal vibrations. The following data show the magnitude of this effect at room temperature.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Frequency of vibration, ( \nu ), ( \text{l/sec} )</th>
<th>Average amplitude of vibration, ( \AA )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>( 4 \times 10^{12} )</td>
<td>0.5</td>
</tr>
<tr>
<td>Aluminum</td>
<td>( 7 \times 10^{12} )</td>
<td>0.2</td>
</tr>
<tr>
<td>Copper</td>
<td>( 6 \times 10^{12} )</td>
<td>0.15</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>( 7 \times 10^{12} )</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The frequency of vibration is almost independent of temperature, but the amplitude increases with increasing temperature. For copper, the amplitude near room temperature is about one-half the value near the melting point and about twice the value near 0°K. Since the atoms interact with one another, they tend to vibrate in synchronism; that is, groups of atoms tend to move in the same direction, somewhat as waves on the ocean. However, the wave motion of these elastic displacements in a crystal is constrained by the periodic spacing of the atoms to have wavelengths that are simple multiples of the atomic spacing. This concept is analogous to that used in the Sommerfeld theory in Chapter 3 and leads to a similar quantizing effect. Here the term phonon is used to describe one of the quantized elastic waves. Advanced treatments of effects due to thermal vibrations of crystal lattices are conveniently made in terms of collisions of phonons with impediments such as other phonons or electrons.

A somewhat similar imperfection in ideal crystal structures is the exciton, which has been used to explain photoconductivity and luminescence. In suitable structures a valence electron may absorb sufficient radiant energy to cross the energy gap between its full Brillouin zone and an upper unfilled zone. The energy state left vacant in this process can be treated as a positively charged hole (see Chapter 7), which remains in the vicinity of the excited electron because of coulomb attraction. This electron-hole combination is called an exciton. As the exciton moves through the lattice its energy is transferred from place to place, and finally the energy is released on recombination of the electron and hole. The phenomenon of semiconductivity, which also involves electrons and holes, will be treated in Chapter 7.
In contrast to the foregoing imperfections that can exist in a perfect array of atoms in a lattice, there are various structural imperfections in the lattice itself. These are conveniently classified as point defects, line defects, and surface defects. The point defects, which are the simplest of the three, are shown in Fig. 4-22. The vacancy, Fig. 4-22(a), and the interstitial atom or interstitialcy, Fig. 4-22(b), are evidently inverse phenomena that can occur in combination as a Frenkel defect, Fig. 4-22(c).
An impurity atom, Fig. 4-22(d), disturbs the perfection of the lattice whether it occurs on a lattice point as the substitutional impurity shown here or as an interstitial impurity similar to Fig. 4-22(b).

In contrast to these isolated point defects, there can be continuous paths of defective structure running through a crystal, that is, line defects. A simple example of this type of imperfection is the edge dislocation sketched in Fig. 4-25(a). In a later discussion of dislocations (Chapter 12), it will be shown how various types of boundaries in metal structures are formed by the aligning of many dislocations to create internal surfaces, such as the grain boundaries. Still another class of imperfections, which were considered in connection with radiation damage, are the various transient effects produced by radiation from nuclear reactors.

Vacancies. In view of the strong interatomic forces that bind atoms in a crystal structure, it is strange that a perfect, continuous array of atoms should not be the most stable arrangement. Yet there is much experimental evidence, particularly the diffusion phenomena discussed in Chapter 11, indicating that a significant number of lattice positions are vacant. Furthermore, it can be shown by the following thermodynamic reasoning that lattice vacancies are in fact a stable feature of metals at all temperatures above absolute zero. If the process of forming vacancies is considered to be a chemical reaction similar to the reduction reactions discussed in Chapter 2, it will be recalled that the reaction tends to occur provided a reduction in free energy accompanies the reaction, Eq. (2-4).

The molar free-energy change, \( \Delta F \), for the formation of \( N_1 \) mol fraction of vacancies is

\[
\Delta F = N_1 \Delta H - T \Delta S,
\]

(4-8)

where \( \Delta H \) is the molar heat of reaction accompanying the formation of vacancies, and where the corresponding entropy change \( \Delta S \) is conveniently assumed to be due only to configurational entropy, which is discussed below. It can be seen that the configurational-entropy term is essential in explaining the existence of vacancies, for if \( \Delta S \) were zero Eq. (4-8) would become

\[
\Delta F = N_1 \Delta H.
\]

(4-9)

The argument of Problem 12 can be used to estimate the value of \( \Delta H \), which is about 20,000 cal/mol for typical metals. Thus in the absence of configurational entropy \( \Delta F \) would increase during vacancy formation and vacancies would not be stable. The configurational entropy, which plays an important role in a number of other metallurgical problems also, is easily understood as arising from simple mixing. The common observation that a drop of ink quickly
spreads throughout a glass of water is a typical example of the tendency of the particles of a system to become randomly distributed. This tendency is expressed quantitatively for simple mixtures by the useful equation

\[ \Delta S = - R (N_1 \ln N_1 + N_2 \ln N_2), \]  

(4-10)

where the gas constant \( R \) is approximately 2 cal/mol·deg and \( N_1 \) and \( N_2 \) are the mol fractions of the two particles that have been mixed together. The meaning of this equation can be illustrated by Fig. 4-23, showing the dissolving of a vacancy by an initially perfect lattice. In a pure metal all the atoms are the same, and so there is only one distinguishable configuration in Fig. 4-23(a). In Fig. 4-23(b), on the other hand, the vacant lattice site is distinguishable from the occupied sites and a different configuration is produced when the vacancy is at each of the individual lattice sites. Thus, the randomness of the system is greatly increased by the addition of a single vacancy.

If \( N_1 \) and \( N_2 \) in Eq. (4-10) refer to vacancies and atoms, respectively, the value of \( \Delta S \) is zero for Fig. 4-23(a), since \( N_1 = 0 \) and \( \ln N_2 = \ln 1 = 0 \). In Fig. 4-23(b), on the other hand, \( N_1 \) is greater than zero and \( N_2 \) is less than one, so that \( \Delta S \) has a finite, positive value.

The equilibrium number of vacancies can easily be determined starting from the equation

\[ \Delta F = N_1 \Delta H + RT(N_1 \ln N_1 + N_2 \ln N_2), \]

obtained by combining Eqs. (4-8) and (4-10). As the mol fraction of
vacancies increases from zero, $\Delta F$ decreases and passes through a minimum at the equilibrium value of $N_1$. This value can be found by setting the derivative of $\Delta F$ with respect to $N_1$ equal to zero:

$$\frac{d\Delta F}{dN_1} = \Delta H + RT \ln \frac{N_1}{N_2} = 0. \quad (4-11)$$

Solving this equation for the equilibrium fraction of vacancies, $N_1$, gives

$$N_1 = e^{-\Delta H/RT}, \quad (4-12)$$

since $N_2$ is very nearly unity. Using the value $\Delta H = 20,000$ cal/mol for copper, the fraction of vacant lattice sites at various temperatures can be calculated to be:

<table>
<thead>
<tr>
<th>Temperature, °K</th>
<th>Fraction of lattice sites that are vacant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (absolute zero)</td>
<td>0</td>
</tr>
<tr>
<td>300 (room temperature)</td>
<td>$3 \times 10^{-15}$</td>
</tr>
<tr>
<td>1000 (an average temperature for heat treatments)</td>
<td>$4 \times 10^{-5}$</td>
</tr>
<tr>
<td>1350 (just below the melting point)</td>
<td>$6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Dislocations. Consider the contrast in strength between the following metal crystals, both of which are in the "soft" metallurgical condition.

<table>
<thead>
<tr>
<th>Type of crystal</th>
<th>Effective strength, lb/in²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal &quot;whiskers&quot;</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Ordinary crystals</td>
<td>100 to 1000</td>
</tr>
</tbody>
</table>

Metal "whiskers" are filaments only about $10^{-4}$ inch in diameter that can be produced under special conditions. They are believed to be virtually perfect crystals, and their strengths are those expected in such a crystal lattice (see Problem 13). Thus metals should be very strong, and the question to be answered is why are ordinary metals so weak? The answer is found in the occurrence in the crystal structure of extended defects called dislocations. Convincing experimental evidence for the existence of dislocations is provided by the electron micrograph of a metallo-organic crystal at 1,500,000 diameters magnification shown in Fig. 4-24. The characteristic structural feature is seen to be the incomplete plane of molecules. Figure 4-25 is a schematic illustration of one
type of dislocation, an edge dislocation, in a simple cubic lattice with atoms at the lattice points. The location of a typical edge-type dislocation in the interior of a crystal is indicated by a conventional dislocation line in Fig. 4-25(a), and it can be seen that the crystal structure is regular except in the vicinity of the dislocation.

Figure 4-25(b) shows how a dislocation can produce permanent deformation of a lattice under the action of a relatively small force. When a force tends to shear the upper portion of the crystal to the right as shown, the plane of atoms above the dislocation can easily establish bonds with the lower plane of atoms to its right, with the result that the dislocation moves one lattice spacing. The atomic distribution is again similar to the initial configuration and so the slipping of atom planes can be repeated. This step-by-step motion of a dislocation can occur under a force one-thousandth that required to shear a perfect crystal structure. Figure 4-25(c) shows the final, permanent deformation of the crystal structure that results when the dislocation reaches the surface of the crystal. If a large number of dislocations move in succession along the same slip plane, the accumulated deformation becomes visible, as in Fig. 4-1(c).

A dislocation can be described in a number of ways. One of the most general descriptions is in terms of the slip plane, the plane along which a dislocation moves. Figure 4-25(b) shows that the dislocation divides the crystal into a portion (to the left) that has slipped along the slip plane and a portion that has not yet slipped. An edge dislocation may also be visualized as resulting from the insertion of an extra half-plane of atoms above (or below) the dislocation line. By definition, the dislocation in Fig. 4-25(b) is a positive dislocation. A negative dislocation has the extra half-plane below the dislocation line.

A quantitative description of dislocations is given by the Burgers vector, \( \mathbf{b} \), illustrated in Fig. 4-26. This vector is defined using the Burgers circuit, which is an atom-to-atom path that makes a closed loop in a dislocation-free part of the crystal lattice, Fig. 4-26(a). Now if the same Burgers
Fig. 4-25. The motion of an edge dislocation and the production of a unit step of slip at the surface of the crystal. (a) An edge dislocation in a crystal structure. (b) The dislocation has moved one lattice spacing under the action of a shearing force. (c) The dislocation has reached the edge of the crystal and produced unit slip.

Circuit is made to encircle a dislocation, Fig. 4-26(b), the loop does not close. The vector needed to close the loop (the vector from the end of the Burgers circuit to its starting point) is the Burgers vector describing the dislocation. This vector is conveniently specified using the lattice parameters of the crystal structure as its components: a, 0, 0, in the case of Fig. 4-26(b) for the choice of x-direction shown. A more concise representation...
FH. 4-26. Description of a dislocation in terms of its Burgers vector. (a) A Burgers circuit in dislocation-free material. (b) The same Burgers circuit passing through dislocation-free material, but encircling a dislocation of unit Burgers vector, \( \mathbf{b} \).

of the same vector is \( l[100] \), where the numbers in the brackets give the components of the vector as the number of lattice distances along each of the three coordinate axes; the number in front of the brackets indicates the length of the Burgers vector as a multiple of the given vector.

An important characteristic of a dislocation is the fact that it cannot end inside the crystal. Evidently a dislocation can end at a grain boundary or at a surface of the crystal; for example, the front plane of atoms in Fig.
Fig. 4-27. The relation between an edge dislocation and a screw dislocation.
(a) The conversion of an edge dislocation to a screw dislocation, $S-O$, at a point $O$ within a crystal. (b) A view of (a) along $S-O$, showing the spiral surface around a screw dislocation.
might be the surface of this crystal. It is possible for a dislocation to change its character inside a crystal, as shown in Fig. 4-27(a). Here an edge dislocation is converted to a screw dislocation at point $O$; in this case the screw dislocation is shown ending at the surface of the crystal. It is also possible for components of edge and screw dislocations to join together to form a closed dislocation loop within the crystal. The material within the loop is visualized as having slipped on the specified slip plane relative to the material around it.

The term screw dislocation is used because of the spiral surface formed by the atomic planes around the screw-dislocation line. This characteristic is shown in Fig. 4-27(b). When a Burgers circuit is used to determine the Burgers vector of a screw dislocation, the vector is found to be parallel to the dislocation line rather than perpendicular to it as in the case of an edge dislocation. This result can be understood from a study of Fig. 4-27, since the slipped region (which has a given Burgers vector) is bounded in the direction of slipping by the edge dislocation, while the screw dislocation is $90^\circ$ to this direction.

**Multiplication of dislocations.** The number of dislocations in a metal is determined as the number of dislocation lines that cut through one square centimeter of surface, and is called the dislocation density. The value for soft crystals is about $10^8$, corresponding to an average distance between dislocations of a few thousand atoms. Brief consideration will show that if each dislocation produced only unit slip, Fig. 4-25, this relatively small number of dislocations could not produce macroscopic slip of the kind shown in Fig. 4-1(c). For this reason several mechanisms have been proposed to explain how dislocations might multiply and thus increase their effectiveness a thousandfold. Figure 4-28 describes the operation of the Frank-Read spiral mechanism for slipping on the indicated slip plane. It should be noted that the initial condition requires that the dislocation $OA$ leave the slip plane at $O$, for example, in the perpendicular direction, $OB$. Figure 4-28(a) shows how this arrangement might be produced by prior slip on portions of two intersecting slip planes; the two dislocation lines separate the slipped regions from the unslipped region.

If a uniform force is applied to the upper portion of the crystal, as indicated in Fig. 4-28(b), additional slip will tend to occur on the horizontal slip plane by motion of the dislocation $OA$. However, this force system does not cause slip on the vertical plane, and therefore $OB$ remains fixed and anchors $OA$ at the point $O$. The uniform force tends to produce the same velocity at every point along the dislocation line $OA$, so that in a given time a portion near $O$ completes a larger angular circuit than a portion farther out; consequently, the dislocation tends to assume a spiral form. The region of the lattice swept over by the dislocation experiences unit slip in the direction of the applied force, and at the rear of the crystal
The Frank-Read spiral mechanism for the multiplication of dislocations. (a) Initial condition, with the dislocation line $AO$ leaving the slip plane at $O$. (b) A uniform force tending to shear the top half of the crystal causes $AO$ to begin sweeping over the slip plane. (c) The end of the spiral has completed one revolution and is ready to repeat the process.

The slip can be seen as a unit step of the kind shown in Fig. 4-25(c). A later stage in the rotation of $OA$ is shown in Fig. 4-28(c), where the end of the spiral has just completed one revolution and has produced unit steps at both the front and rear surfaces of the crystal. The end of the spiral is now in position to again sweep over the crystal, the inner portions of the spiral having already begun the second revolution.

A similar mechanism of dislocation multiplication produces complete dislocation loops from the Frank-Read source shown in Fig. 4-29. The essential initial condition in this case is the presence in the slip plane of a length of dislocation line $O-O'$ pinned at both ends. In Fig. 4-29(a) the pinning is pictured as occurring in the same way as in Fig. 4-28(a). When a uniform force is applied to the upper portion of the crystal, the dislocation line bows outward and produces slip in the semicircular region shown.
Fig. 4-29. The Frank-Read mechanism for the production of complete dislocation loops. (a) Initial condition, with the dislocation line $O-O'$ leaving the slip plane at $B$ and at $B'$. (b) A uniform force tending to shear the top half of the crystal causes $O-O'$ to begin sweeping over the slip plane by bowing outward. (c) As the dislocation line continues to expand it spirals about $O$ and $O'$. (d) Further expansion of the dislocation line brings the two spiral sections together. (e) As the two sections join they produce an outer loop that continues to expand and an inner line similar to $O-O'$ in (a). (f) The outer loop produces a unit step as it leaves the surface of the crystal; $O-O'$ begins the cycle again.
in Fig. 4-29(b). Continued movement of the dislocation line causes spiraling about points $O$ and $O'$, Fig. 4-29(c). Further growth of the slipped region brings the two sections of the spiral together, Fig. 4-29(d), and their coalescence produces an outer loop around the entire slipped region and an inner dislocation line $0-O'$, Fig. 4-29(e). This line is essentially the same as the initial dislocation line in Fig. 4-29(a), and under the continued action of the uniform force it will begin another cycle. The completed loop continues to expand across the slip plane, Fig. 4-29(f), and in this case would soon produce a unit step along the entire front and rear surfaces of the crystal.

Partial dislocations. In the preceding discussion of dislocations it has been convenient to use the simple cubic lattice to illustrate the concepts involved. Actually, this structure is rarely encountered among metals; the most common structures are the body-centered cubic, face-centered cubic, and close-packed hexagonal. In these more complex structures the relation between macroscopic slip and the movement of dislocations involves a new factor, the splitting of a dislocation into partial dislocations. The behavior of face-centered cubic metals is typical and is discussed here as an illustration of the essential phenomena involved. The slip planes in this structure are $\{111\}$ type planes, Fig. 4-30(a), which have the same hexagonal-type packing of atoms as the basal plane in the close-packed hexagonal structure, Fig. 4-7. The slip directions in both structures are the three equivalent directions of closest spacing shown in Fig. 4-30(b); these are $(10\overline{1})$ directions in face-centered cubic metals. An important difference between the close-packed hexagonal and face-centered cubic structures is the mode of stacking of the hexagonal-type planes. In Fig. 4-8 it is seen that the close-packed hexagonal structure is created by the alternation of planes $A$ and $B$, which differ only in their relative positions. Figure 4-30(b) shows that the face-centered cubic structure can be visualized as a similar alternation of three planes, $A$, $B$, and $C$, that also differ only in relative position. It should be noted that the atoms in a given plane, say plane $B$, form triangular figures. If the center of a given triangle is occupied by an atom in plane $A$, which is below plane $B$, then the centers of the three adjacent triangles are occupied by atoms in plane $C$, which is above plane $B$.

When the details of the unit slip process on the $(111)$ plane in the $(10\overline{1})$ direction are considered, Fig. 4-30(c), it is found that a hump tends to bar the path in this direction, but that a combination of two valley routes results in the same net motion. Since a dislocation whose Burgers vector is $b$ permits slip of amount $b$ to occur, it follows that unit slip in the face-centered cubic lattice is associated not with a dislocation in the $(10\overline{1})$ direction, but with the two partial dislocations in $(112)$ directions. If $l(10\overline{1})$ is the vector from the origin out to the point whose lattice co-
Fig. 4-30. Description of the mechanism of the slip process in face-centered cubic metals. (a) Three adjacent (111) planes in the face-centered cubic lattice. The [101] slip direction is shown. (b) A view of (a) perpendicular to the (111) planes, showing the relative positions of the A, B, and C planes. The three (101) slip directions are shown. (c) Unit slip of an atom in the slip direction by two alternate routes. (d) Description of the vectors involved in unit slip in the slip direction.
ords are $x = 1$, $y = 0$, and $z = -1$, in terms of axial lengths in the lattice, and if $\frac{1}{2}[112]$ is an analogous vector, then Fig. 4-30(d) shows that slip from one position to an adjoining equivalent position, given by the vector $\frac{1}{2}[112]$, actually occurs by the combination $\frac{1}{2}[112] + \frac{1}{2}[2\bar{1}]$. This concept is expressed concisely by the "reaction" for the dissociation of the first dislocation:

$$\frac{1}{2}[10\bar{1}] \rightarrow \frac{1}{2}[112] + \frac{1}{2}[2\bar{1}].$$

(4-13)

The two partial dislocations have their lowest energy when they are separated by about ten atomic distances. In the space between them the lattice is not strictly face-centered cubic, since the alternation of layers has been disturbed in the manner shown schematically in Fig. 4-31. This figure represents seven layers of (111) planes in which the atoms are indicated by a letter ($A$, $B$, or $C$) designating the relative position of the given atom. Starting at the left of the figure the lattice is face-centered cubic up to the first partial dislocation. At this point the positions of the atoms in the portion of the lattice above the slip line are changed. Specifically, the layer immediately above the slip line changes from $C$ positions to $B$ positions, since the $A$ positions are excluded. When the second partial dislocation is reached, this layer of atoms changes in position again and necessarily goes back to $C$ positions. The lattice at the right of the second partial dislocation again has the symmetry of the face-centered cubic lattice. However, it is seen that the region along the slip plane between the two partial dislocations has the $ABAB$ pattern characteristic of the close-packed hexagonal structure and has a higher energy than the parent lattice.
The preceding treatment of dislocations has emphasized the basic structural characteristics of this type of imperfection. Other aspects of dislocation theory will be discussed in later chapters in connection with its use in explaining the behavior of metals and alloys.

REFERENCES

Problems

1. Use two labeled sketches to show schematically the differences between (a) the binding of atoms in a solid metal such as sodium, and (b) the binding of atoms in a solid nonmetal such as sodium chloride.

2. The force of electrostatic attraction accounts for most of the binding energy in ionic crystals such as NaCl. This fact can be demonstrated by a rough comparison of the experimentally observed heat of formation, which is about 8 ev per molecule of NaCl, with the electrostatic binding energy of a single chloride ion and a single sodium ion. Use Eq. (3-4) to calculate the latter value for the actual spacing of the ions in the crystal, 2.81 Å. Although only order-of-magnitude agreement can be expected from this crude approximation, quantitative agreement is obtained from calculations based on a more realistic model of the crystal structure of NaCl.

3. According to the 8 - \( N \) rule, how many nearest neighbors does antimony have? (Use Fig. 3-4. Antimony is element number 51 in the periodic table.)

4. Show that there are five two-dimensional plane lattices corresponding to the fourteen three-dimensional space lattices. (Hint: the least obvious of the five is analogous to the hexagonal space lattice, Fig. 4-7.)

5. (a) Sketch the primitive cell for the face-centered cubic structure within a cubic unit cell. The cell is rhombohedral with \( \alpha = 60^\circ \) and lattice constants \( 1/\sqrt{2} \) those of the cubic cell. (b) The lattice vectors of the rhombohedral primitive cell for the body-centered cubic structure are conveniently drawn from the center atom out to three nonadjacent corner atoms. This makes \( \alpha = 109.5^\circ \) and the lattice constants \( \sqrt{3}/2 \) those of the cubic cell. Your sketch of this primitive cell will extend outside a single body-centered unit cell.

6. Sketch planes that have the following Miller indices: (a) (001), (b) (110), (c) (111).

7. Indicate the following directions in the corresponding sketches of Problem 6: (a) [210], (b) [111], (c) [101].

8. (a) Use Bragg's law, Eq. (4-2), to determine whether the (001) plane of the grain of iron (Fig. 4-32 on the following page) will produce an x-ray reflection when copper \( \text{K}_\alpha \) radiation is used. Since iron is body-centered cubic, reflections from [100] type planes can occur only for even values of \( n \), Table 4-3. The crystal axes of the grain of iron coincide with the \( z \)-, \( y \)-, and \( x \)-axes in the figure. (b) Make similar analyses for the (100) and (010) planes.

9. The value of \( d \), given by Eq. (4-3), can be determined as the perpendicular distance between the origin and the first plane in the set of (hkl) planes. Sketch the first (464) plane on a set of coordinate axes; recall that the intercepts are \( a/h \), \( a/k \), and \( a/l \). Erect the perpendicular from the origin to this plane; its length is \( d \) and it makes angles \( \alpha_1 \), \( \alpha_2 \), and \( \alpha_3 \) with the three coordinate axes. Now, show that Eq. (4-3) follows from the geometrical relation \( \cos^2 \alpha_1 + \cos^2 \alpha_2 + \cos^2 \alpha_3 = 1 \).

10. From an analysis of the diffraction patterns, identify the metals that produced patterns (a), (b), and (c) of Fig. 4-17.
11. Show by means of qualitative sketches the essential difference between diffraction patterns that would be produced by (a) a mechanical mixture of 50% copper powder with 50% nickel powder; (b) an alloy of 50% copper and 50% nickel. [Note: This alloy is discussed in Chapter 6 and is shown to consist of only one crystal structure, a solid solution in which copper and nickel atoms occupy lattice points at random.]

12. A vacancy (Schottky defect) is considered to be formed by removing an atom from a lattice position within the crystal and placing it on the surface of the crystal. If $z$ represents the number of nearest neighbors that an atom has, then $z$ bonds are broken in removing the atom and about $z/2$ bonds are re-formed when the atom is placed in a surface position. The heat of reaction for the formation of a vacancy can be estimated from the heat of vaporization, since all the atoms have their bonds broken when a mass of metal is vaporized. (a) Show that an average of only $z/2$ bonds are broken per atom in the vaporization process. (b) Express the heat of formation of a mol of vacancies, $\Delta H$, in terms of the molar heat of vaporization, $\Delta H_{\text{vap.}}$.

13. An estimate of the strength of a perfect crystal lattice can be made using two representative planes in a perfect lattice, for example the two central planes in Fig. 4-25(c), which are subjected to opposing shearing forces. As the shearing force is increased, the upper plane will be displaced to the right relative to the lower plane. It can be shown that the maximum shearing force is reached at a displacement of $a/4$, where $a$ is the spacing of atoms in the slip direction, and that slip then occurs to the next equivalent position of the two planes of atoms. Assume that the initial, elastic resistance to shear, given by the equation $\tau = G\gamma$ [see Eq. 8-11], is valid out to the maximum shear, $\gamma = \frac{a}{4}$. Taking $G = 10^7$ lb/in² as a typical value of the shear modulus, show that the maximum shear stress estimated in this way is in the range of values observed for metal "whiskers."

14. (a) Starting from the same atom as in Fig. 4-26(b), trace a different Burgers circuit that also encircles the dislocation. For example, we might start our circuit by going...
back at a 45° angle into the body of the crystal and then continuing in such a manner that our circuit would form a closed loop if it were made in a perfect crystal. Show that the Burgers vector obtained for our inclined circuit is the same as that for the simple circuit used in the figure. (b) Trace a Burgers circuit around the screw dislocation in Fig. 4-27(b) to verify that the Burgers vector is the same as that for the edge dislocation associated with the same slipped region.
CHAPTER 5
PHASES IN METAL SYSTEMS

"With what bodies gold will incorporate
by simple colliquefaction and with what not?
And in what quantity it will incorporate; and
what kind of body the compound makes?"
FRANCIS BACON (1627)

INTRODUCTION

The crystalline state considered in the previous chapter is an important
mode of aggregation of metal atoms. However, assemblies of metal atoms
can also exist in the other two states of matter, the liquid and vapor
states. In this chapter a study will be made of several characteristics of
the three states that determine not only their direct commercial applica­
tions but also the important equilibria among them. The latter subject
is considered in Chapter 6.

A further refinement in the concept state of matter is needed for discus­
sing the assemblies of atoms that are encountered in metallurgical systems.
Consider a metal specimen in the solid state that consists of 50 percent
iron atoms and 50 percent copper atoms, Fig. 5-1(a). These atoms do not
form a homogeneous solid under equilibrium conditions; rather, they
form two different solids, one rich in iron and the other rich in copper.
Since it is convenient to distinguish between these two solids, it is con­
tventional to label them with the first two letters of the Greek alphabet, $\alpha$
and $\beta$. Each of the distinguishable solid states is then called a phase, and
one speaks of the $\alpha$-phase and the $\beta$-phase. The nature of the boundary
that separates two phases is considered in detail in a later section.

Two or more different kinds of metal atoms will usually form a homo­
geneous solution in the liquid state. This behavior is shown for a 50%
Fe-50% Cu alloy in Fig. 5-1(b). Here also it is conventional to use the
word phase rather than state and to speak of the liquid phase. In a few
instances, such as that of the 50% Zn-50% Pb alloy shown in Fig. 5-1(c),
two (or more) liquid phases exist at equilibrium. The usual nomenclature
in this case is simply to use $L_1$ (liquid 1) and $L_2$ (liquid 2). All gases are
completely miscible in one another and metal vapors are no exception
to this rule. Figure 5-1(d) shows the vapor phase in which the 50%
Pb-50% Zn alloy can exist under suitable conditions of temperature and
pressure.
Fig. 5-1. The distributions of atoms in solid, liquid, and vapor phases of alloys. (a) Two solid phases formed in a 50% Fe-50% Cu alloy. (b) The liquid phase formed by a 50% Fe-50% Cu alloy. (c) Two liquid phases formed in a 50% Zn-50% Pb alloy. (d) The vapor phase formed by a 50% Zn-50% Pb alloy.

**ONE-COMPONENT SYSTEMS**

Before considering in some detail the phases that constitute metal systems, it will be helpful to understand the nature of the equilibrium relations among these phases. The relations are relatively simple for a one-component system, that is, a system consisting of a single, pure metal. It is convenient to consider only this simple system now and to postpone the treatment of more complex equilibria to Chapter 6.

**Equilibrium diagram.** How does one put a metal into the liquid condition for casting? Or into the vapor phase for purification? Obviously, one or more external conditions must be altered, and of these the temperature and pressure are of greatest importance. Although it is possible to change haphazardly the temperature and pressure of a metal until the desired effect is produced, it is much more satisfactory to choose the optimum conditions from data collected by previous workers. Fortunately, these data are not spread in long columns through many journals, but are concisely presented in a single diagram for each metal.
Figure 5-2 is the one-component diagram for magnesium. This diagram shows what phases are present as a function of the temperature and pressure. In this case the three phases that can exist correspond to the three states of matter—vapor, liquid, and solid. The interpretation of equilibrium diagrams is made easy by the following rule: only points in the diagram have physical significance. Since the variables are temperature and pressure, evidently a point is determined by a temperature and a pressure. In Fig. 5-2 the point $A$ is at pressure $p_A$ and at temperature $T$. Since $A$ is in the field of the diagram labeled liquid, magnesium metal held long enough at pressure $p_A$ and temperature $T$ for equilibrium to be established will be entirely liquid. Similarly, magnesium metal at pressure $p_B$ and temperature $T$ will be a mixture of liquid and vapor. The temperature and pressure of the triple point will cause solid, liquid, and vapor to be in equilibrium. When two or more phases coexist, the relative amount of each phase cannot be determined from this diagram.

An elementary principle of chemistry states that every liquid or solid tends to be in equilibrium with a particular pressure of its vapor. How then, it may be asked, can there be a completely liquid region in the one-component diagram? Will not vapor exist in equilibrium with the liquid at point $A$ in Fig. 5-2? The explanation lies in the manner in which the one-component system is determined, Fig. 5–3. Only the metal being investigated is contained in the cylinder that exerts pressure on the system; even air is excluded. If the external pressure is equal to the vapor pressure of the liquid metal at the given temperature, both liquid and vapor exist in equilibrium in the cylinder. This is the condition at point $B$, Fig. 5–2, and is shown schematically in Fig. 5–3(a). However, if the external pres-
sure is greater than the vapor pressure of the liquid metal, the piston is forced down, the vapor condenses, and only the liquid phase remains. This is the condition at point A, Fig. 5-2, and is shown schematically in Fig. 5-3(b). An entirely different situation exists if magnesium metal is held at temperature \( T \) in contact with air at one atmosphere pressure (760 mm of mercury), Fig. 5-3(c). Of the total pressure of one atmosphere, only the partial pressure \( p_B \) is supplied by magnesium vapor. In this instance the significant pressure for most purposes is that of the vapor, not that of vapor and air combined.

Just as the line separating the liquid and vapor areas of the diagram in Fig. 5-2 gives the vapor pressure of the liquid metal as a function of temperature, so the corresponding line for the solid gives the vapor pressure of the solid. It is significant that a solid metal need not melt on being heated. For example, if magnesium is held in a vacuum of 1 mm of mercury and is heated to slightly over 600°C, the metal will completely vaporize without the formation of any liquid. Moderate pressures above that of the triple point have little effect on the melting point of a metal, and the line separating the solid and liquid regions is almost vertical.

The phase rule. In the study of equilibrium diagrams it is not surprising that one can use that powerful tool for analysis of equilibrium, thermodynamics. Among the many applications of thermodynamics in this field, by far the best known is the phase rule of Willard Gibbs, which defines the number of phases that can be in equilibrium.

What are the prerequisites for equilibrium? Generally they are constancy of temperature, pressure, and chemical potential* in each of the coexisting phases. The vapor pressure often can be considered a measure of the chemical potential; thus to be in equilibrium the liquid and vapor

---

* Each component in each phase has a chemical potential.
phases of a pure metal must have the same vapor pressure and must be at the same temperature and pressure. Gibbs has shown that such conditions of equilibrium can exist only if the following relation is satisfied:

\[ P + F = C + 2, \]

(5-1)

where \( P \), \( F \), and \( C \) represent the number of phases, of degrees of freedom, and of components in the given system. (The degrees of freedom are the number of such variables as temperature, pressure, or concentration that can be changed independently without changing the number of phases present.)

The application of the phase rule to the one-component diagram for magnesium, Fig. 5-4, will show the significance of its terms. In this case there is only one component, magnesium, and in general the number of components is equal to the number of metals present in the system being considered. At point 1 in Fig. 5-4 there is only one phase present, gaseous magnesium; therefore at this point the phase rule becomes

\[ P + F = C + 2, \]

\[ 1 + F = 1 + 2, \]

\[ F = 2. \]

That is, there are two degrees of freedom. Two of the variables can be changed independently without causing a change in the number of phases. Thus, the temperature and the pressure may be varied separately without losing the vapor phase.

* A useful though irreverent mnemonic version of this equation is

Police Force = Cops + 2.
The situation at point 2 is significantly different. Since the liquid and vapor phases exist in equilibrium at this point, there are two phases present and the phase rule yields

\[ P + F = C + 2, \]
\[ 2 + F = 1 + 2, \]
\[ F = 1. \]

We may ask how there can be only one degree of freedom when it is evident that both temperature and pressure must change in order to proceed from point 2 to point 2', where the two phases continue to exist. The answer is that only one of the variables can be changed independently. To increase the pressure without losing either of the phases originally present, the temperature must also be raised exactly the proper amount. Similarly, the temperature can be changed arbitrarily but the two phases will continue to exist only if the pressure is also varied by a specific, not an independent, amount. Only one of the variables, therefore, can be independently changed at point 2 if two phases are to remain. A similar analysis shows that there are zero degrees of freedom at point 3, the triple point, in Fig. 5-4.

The phase rule and much of the other information on one-component systems can be applied to the multicomponent alloys that are of greater commercial interest. Of course, the presence of a second component metal makes it possible to vary the chemical compositions of the phases as well as the temperature and pressure.

The Vapor Phase

Of the three states of aggregation of metal atoms, the vapor state is the simplest to treat. As was pointed out above, even in many-component systems there is only a single vapor phase. Also, the vapors formed by metal atoms are essentially the same as the more common gases; they have low density, are transparent, and obey the gas laws, although under most conditions they are monatomic in contrast to such diatomic gases as oxygen and nitrogen. The large interatomic distances in the vapor phase, Fig. 5-1(d), effectively isolate each atom so far as interchange of electrons is concerned. Therefore, it follows from the theory discussed in Chapter 3 that metal vapors do not show ordinary electrical conductivity.

An important aspect of the vapor phase in many commercial processes is the metal vapor that tends to be in equilibrium with every solid or liquid metal. The method for determining vapor pressures for a pure metal from its one-component diagram was described above, and it can be seen from the trend of the solid-vapor line in Fig. 5-2.
Table 5.1
Vapor Pressure Data for Some of the Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Liquid*</th>
<th>Solid*</th>
<th>Triple point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Aluminum</td>
<td>-19.150</td>
<td>1.023</td>
<td>12.36</td>
</tr>
<tr>
<td>Calcium</td>
<td>-9.840</td>
<td>1.21</td>
<td>12.575</td>
</tr>
<tr>
<td>Chromium</td>
<td>-20.050</td>
<td>1.0</td>
<td>13.36</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-17.450</td>
<td>1.21</td>
<td>13.21</td>
</tr>
<tr>
<td>Copper</td>
<td>-19.710</td>
<td>1.27</td>
<td>13.27</td>
</tr>
<tr>
<td>Iron</td>
<td>-10.130</td>
<td>0.985</td>
<td>11.16</td>
</tr>
<tr>
<td>Lead</td>
<td>-7.550</td>
<td>1.41</td>
<td>12.79</td>
</tr>
<tr>
<td>Magnesium</td>
<td>-3.240</td>
<td>3.04</td>
<td>19.44</td>
</tr>
<tr>
<td>Manganese</td>
<td>-3.305</td>
<td>0.705</td>
<td>10.555</td>
</tr>
<tr>
<td>Mercury</td>
<td>-18.000</td>
<td>-0.705</td>
<td>10.555</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>-14.260</td>
<td>-1.055</td>
<td>12.23</td>
</tr>
<tr>
<td>Nickel</td>
<td>-22.110</td>
<td>-0.875</td>
<td>10.35</td>
</tr>
<tr>
<td>Silver</td>
<td>-6.620</td>
<td>-1.255</td>
<td>12.34</td>
</tr>
</tbody>
</table>

that vapor pressures tend to be very low at room temperature. However, at higher temperatures the vapor pressure may be great enough that significant evaporation can occur.

The following equation permits the calculation of the vapor pressure of a liquid metal as a function of temperature:

\[
\log p = \frac{A}{T} + B \log T + CT + D,
\]

(5-2)

where \( \log \) is the logarithm to the base 10, \( p \) is the vapor pressure in mm of mercury, \( T \) is the absolute temperature in degrees Kelvin, and \( A, B, C, \) and \( D \) are constants for a given liquid metal (Table 5-1). This is the equation of the line that separates the liquid area from the vapor area in Fig. 5-2.

The corresponding line between the solid and vapor areas is expressed by a similar equation, in which the primed constants \( A', B', C', \) and \( D' \) are used (Table 5-1). This second equation gives the vapor pressure of the solid metal. The line separating the solid and liquid areas is essentially vertical. Few one-component diagrams are given in the literature, but from the triple-point temperatures and pressures listed in Table 5-1 and from vapor pressure data it is easy to construct a usable diagram. Frequently the triple-point pressure alone gives enough information for many purposes, for example, determining the possibility of melting chromium in a good vacuum (see Problem 5-4).

Kinetic theory. The picture of the vapor phase as an assembly of individual atoms, Fig. 5-1(d), can easily be developed into a quantitative description of important aspects of the behavior of the gas phase. A simplified treatment of kinetic theory is used here for that purpose. Consider that there are \( n \) atoms, each of mass \( m \), in a cubic container \( l \) centimeters on an edge. It is convenient to assume that all the atoms are moving with the average velocity \( u \), that one-third of them are moving parallel to each of the coordinate axes, and that collisions of the atoms with one another can be neglected. The pressure exerted by the gas on a wall of the container is created by collisions of the atoms with the wall. Since an atom moves \( u \) centimeters each second, it will cover the distance \( l \) a total of \( u/l \) times per second and it will strike a given wall \( u/2l \) times per second. A total of \( n/3 \) atoms are assumed to move in the direction perpendicular to this wall, so that the total number of collisions per second is \( nu/2l \).

To determine the force \( F \) exerted on the wall by these collisions, it is convenient to use Newton's law \( F = ma \) in the form \( F = (d/dt)(mu) \), where \( mu \) is the momentum. At each collision the momentum of an atom is changed from \( +mu \) to \( -mu \), since the direction of its velocity is assumed
to be completely reversed in an elastic impact with the wall. Therefore
the total momentum change per second is \( \frac{nmu^2}{3l} \). But this is \( \frac{d}{dt} \)
\( (mu) \), the rate of change of momentum, and it follows that \( F = \frac{nmu^2}{3l} \).
Since the pressure \( P \) is the force per unit area,
\[
P = \frac{nmu^2}{3l}.
\]

It is convenient to work with a gram atomic weight of the gas, \( M = N\mu \),
where \( N \) is Avogadro's number, since the volume \( l^3 \) is then the usual molar
volume \( V \). Equation (5-3) then becomes
\[
P = \frac{Mu^2}{3}.
\]

Metal vapors can be assumed to obey the ideal gas law so that, \( PV = RT \)
and Eq. (5-4) can be written
\[
u = \sqrt{\frac{3RT}{M}}.
\]

Examples of the use of this equation are given later in connection with
nucleation and rates of evaporation.

**The Liquid Phase**

Liquid metals are of commercial interest for two reasons. First, most
metals are produced and refined in the liquid state and are later sub-
jected to a casting process as a step in their fabrication. Second, there
have been a number of direct engineering applications of molten metals;
their use as cooling media in nuclear power production is an example.
The properties that must be considered in working with metal liquids are
similar to those of other liquids, for example hydrodynamic properties
and surface tension, which are considered below. A key to understanding
the properties and behavior of liquids is provided by a knowledge of the
structure of this type of phase.

**Structure.** As in the case of solid crystalline phases, the structure of
a liquid can be studied by diffraction techniques, such as x-ray diffraction.
It is found that the diffraction pattern contains not the sharp lines char-
acteristic of crystals but rather a few wide diffuse bands. This result
indicates that although the atoms of the liquid do not have the long-range
order of a crystalline substance, there is a tendency toward packing of the
neighboring atoms around a given atom in the liquid. A quantitative in-
terpretation of a diffraction pattern is made by considering that diffraction
is caused by the number of atoms \( (4\pi r^2 \rho) \, dr \) in each spherical shell of thick-
Fig. 5-5. Atomic distribution curve for liquid sodium calculated from x-ray diffraction data. The upper drawing explains the two maxima in the curve in terms of "shells" of neighboring atoms around the reference atom. The dashed curve represents a uniform distribution of atoms, and the vertical lines show the positions and numbers of neighboring atoms in solid sodium.

If the number of nearest neighbors (the coordination number) of the reference atom is determined from the area under the curve out to the minimum point, it is found to be 10.6. Since sodium is body-centered
cubic, the coordination number of the solid is only 8, although the vertical lines in Fig. 5-5 show that there are six additional atoms only slightly beyond the eight nearest neighbors. The face-centered cubic and close-packed hexagonal metals have a higher coordination number (12) in the solid state, but their liquid structures are about the same as that of liquid sodium. Thus, the structures of liquid metals show more similarity than do the structures of solid metals. This similarity is reflected in the properties of liquid metals, where much greater uniformity is exhibited than in the case of solid metals.

Since the atoms of a liquid metal are about as closely packed as the atoms in the solid, the interactions of the valence electrons are similar to those considered for solid metals in Chapter 3. For example, the nature of electrical conductivity is essentially the same, although the conductivities are about 50 percent lower in the liquid phase for most metals. In a few metals like antimony and bismuth the breakdown of the usual Brillouin zone structure on melting greatly affects the electrical conductivity and causes it to be higher in the liquid metal. These two metals also experience a decrease in volume on melting, whereas the usual behavior is an increase of a few percent. The extra volume in the typical liquid metal is pictured as being occupied by the counterpart of vacancies in solid metals. However, the vacancies are thought to be smaller in liquids (only about one-sixth of an atomic volume) and correspondingly more numerous.

Properties of liquid metals. The mobility of atoms in liquid metals can be expressed as a diffusion coefficient, in the manner described for solid metals in Chapter 11. The mobility is of course much greater than that for solid metals, and it is found that all liquid metals have comparable values.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature, °C</th>
<th>Viscosity, centipoise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>700</td>
<td>3.0</td>
</tr>
<tr>
<td>Copper</td>
<td>1200</td>
<td>3.2</td>
</tr>
<tr>
<td>Iron</td>
<td>1600</td>
<td>6.2</td>
</tr>
<tr>
<td>Iron—3.4% carbon</td>
<td>1300</td>
<td>8.9</td>
</tr>
<tr>
<td>White cast iron—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.4% carbon</td>
<td>1300</td>
<td>2.4</td>
</tr>
<tr>
<td>Steel (above melting range)</td>
<td>approx. 3</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>680</td>
<td>1.2</td>
</tr>
<tr>
<td>Zinc</td>
<td>500</td>
<td>3.7</td>
</tr>
</tbody>
</table>
ranging slightly above $10^{-5}$ cm$^2$/sec. The viscosity is related to the diffusion coefficient and shows a similar narrow range of values, Table 5-2. Fluidity is of much interest in the casting of metals and is usually studied in terms of the distance in inches a liquid alloy will flow in a standard groove mold before solidifying. This flow distance depends on several factors in addition to viscosity, and therefore it is sometimes called casting fluidity. Although oxide films and dissolved gases are complicating variables, usually fluidity increases linearly with temperature and decreases with initial additions of alloying elements. The data for the aluminum-silicon system given in Fig. 6-15 illustrate a typical variation of casting fluidity with alloy composition.

The fluidity of liquid alloys during casting operations or in engineering equipment is governed by the usual laws of hydrodynamics. For example, hydraulic pressure can be obtained from a head of liquid metal for use in forcing the metal to fill difficult mold sections. The Reynolds number concept also applies and can be used to predict whether flow will be laminar or turbulent under given conditions. Actually, the flow of metal in castings is usually turbulent, but there appears to be an upper limit where increasing turbulence is detrimental. An unusual aspect of metal casting is the fact that the flow of metal in the initial stages of filling the mold is largely dependent on the momentum of the liquid stream entering the mold.

The surface tension $\gamma$ of liquid metals is an important example of interfacial tensions, which are discussed more fully below. Table 5-3 shows:

### Table 5-3

**Surface Tensions of Liquid Metals and Other Liquids**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Temperature, °C</th>
<th>Surface tension $\gamma$, dynes/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>750</td>
<td>520</td>
</tr>
<tr>
<td>Aluminum and oxide film</td>
<td>700</td>
<td>840</td>
</tr>
<tr>
<td>Copper</td>
<td>1200</td>
<td>1160</td>
</tr>
<tr>
<td>Iron</td>
<td>1000</td>
<td>1360</td>
</tr>
<tr>
<td>Lead</td>
<td>350</td>
<td>453</td>
</tr>
<tr>
<td>Magnesium</td>
<td>681</td>
<td>563</td>
</tr>
<tr>
<td>Mercury</td>
<td>20</td>
<td>465</td>
</tr>
<tr>
<td>Zinc</td>
<td>600</td>
<td>770</td>
</tr>
<tr>
<td>Fused salts</td>
<td>400 to 930</td>
<td>35 to 180</td>
</tr>
<tr>
<td>Water</td>
<td>20</td>
<td>74</td>
</tr>
</tbody>
</table>
that the surface tension of metals is about ten times greater than that of common liquids such as water. An interesting application of surface tension is the action of capillary attraction that draws liquid metal, such as a solder or braze, upward against the force of gravity into a narrow space between two pieces of metal. Assuming that the liquid “wets” the solid metal, the equation that applies is

\[ h = \frac{2\gamma}{\rho gd} \]  

where \( h \) is the rise of the liquid in cm, \( \rho \) is the density of the liquid in gm/cm\(^3\), \( d \) is the space between the pieces of metal in cm, and \( g \) is the acceleration due to gravity (980 cm/sec\(^2\)). If the spacing is 0.01 cm, as in brazing practice, copper at 1200°C will rise:

\[ h = \frac{2 \times 1160}{980 \times 8.9 \times 0.01} = 26.6 \text{ cm}. \]

This macroscopic effect has spoiled many a delicate design.

**Solid Phases**

Many kinds and distributions of solid phases are found in metallurgical systems. The underlying cause of this variety is the crystalline nature of these phases, which was discussed in Chapter 4. However, several additional aspects of crystal structure will be studied here that profoundly affect the actual microstructures found in commercial metals and alloys.

**Allotropy or polymorphism.** Many of the metallic elements exist in alternate crystalline forms depending on the external conditions of temperature and pressure. This phenomenon is called *allotropy* or *polymorphism*. Under the usual condition of atmospheric pressure each allotropic form of a metal exists at equilibrium over a range of temperatures, as shown for iron in Fig. 5-6. The iron atoms are at the points of a body-centered cubic space lattice at temperatures below 1670°F. If this piece of iron is heated above 1670°F the atoms proceed to form a different solid phase, a phase in which the iron atoms are at the points of a face-centered cubic lattice. A second allotropic change in iron occurs on heating the iron above 2552°F. The face-centered cubic phase then becomes unstable and changes to a body-centered cubic phase. Almost all the properties of a metal change when the metal transforms from one allotropic form to another, but the change of principal commercial importance is the apparently trivial one of a decrease in the solubility of solid iron for carbon.
when the iron changes from the gamma to the alpha form. This effect forms the basis of steel hardening and will be studied in detail later.

An allotropic change is a phase change. The solid metal changes from one crystalline form to another, from one phase to another phase. In a more easily recognized phase transformation, the change from the liquid to a solid phase, two phenomena are observed: (1) supercooling and (2) liberation of the heat of reaction. Both these effects are also associated with phase transformations in the solid state.

Supercooling, the delay of a phase change to a temperature below the equilibrium temperature for such change, is especially pronounced in solid-state transformations. While liquids usually supercool a few degrees before solidifying, solids may be cooled to tens or hundreds of degrees
below the equilibrium temperature before transformation to the new phase occurs. The consideration of equilibrium diagrams will not be complicated by constant reference to supercooling, but its importance in many commercial heat treatments will be emphasized later.

The heat effects that accompany phase transformations in the solid state are small compared with those associated with the solidification of liquid metal. For example, 64.9 calories are liberated when a gram of liquid iron solidifies, while only 3.6 calories are liberated by a gram of iron when it changes from the gamma to the alpha form. However, even this small heat of transformation is detectable, and thermal analysis is often used to study solid-state transformations as well as solid-liquid reactions. This technique consists basically in detecting departures from the normal cooling (or heating) curve of a substance and interpreting these as evidence for absorption or evolution of heat during phase transformations.

Although the allotropic change in iron is of most importance industrially, there are two other examples of allotropy that deserve attention. One of these is the change in titanium from close-packed hexagonal to the body-centered cubic structure at temperatures above 885°C. It will be shown in Chapter 6 that the technology of titanium alloys is vitally affected by this transformation. A second important example of allotropy is that in uranium. The low-temperature phase \( \alpha \) is orthorhombic and exists up to 668°C. From 668 to 774°C uranium exists as the complex, tetragonal \( \beta \) structure containing 30 atoms per unit cell, while above 774°C a body-centered cubic lattice is the stable phase. When uranium is forged or rolled in the \( \alpha \)-phase condition there is a strong tendency toward the development of preferred orientation of crystal axes similar to that sketched in Fig. 8-5. Crystals of \( \alpha \)-uranium behave in an unusual manner on being heated in that they contract in one direction and expand strongly in the other two directions. The combined effects of preferred orientation and nonuniform thermal expansion can cause such severe distortion of a uranium specimen that it may grow to many times its original size. This difficulty is largely overcome if the preferred orientation is eliminated by heating the uranium into the temperature range where the \( \beta \)-phase forms and then rapidly cooling to re-form randomly oriented grains of the \( \alpha \)-phase.

Grain boundaries. Although the vapor phase and liquid phase of a pure metal are continuous and typically uniform from point to point, the solid phase is usually divided into grains that are separated by grain boundaries. Each grain represents a portion of the solid phase with a given orientation of the crystal axes, and in passing from one grain to the next the orientation changes abruptly across the grain boundary. If a specimen
consists of a single grain, a metal single crystal, it has lower energy than in the usual polycrystalline form. Thus, the existence of small grains in ordinary metals is not a requirement of equilibrium but rather a consequence of the mechanism by which the grains are formed. This fact will be illustrated later for the solidification of a molten metal.

It is convenient to begin the consideration of grain boundaries with the simple case in which the misorientation of the two neighboring grains can be described as a "tilting" of one with respect to the other. A tilt boundary of this kind is shown in Fig. 5-7(a). This figure indicates that the boundary between the two grains can be quite well matched provided an extra plane of $\text{atoms}$ is inserted at intervals $D = b/\theta$, where $b$ is the spacing of the planes and $\theta$ is the angle of tilt of the two grains (see Problem 6). The extra planes form edge dislocations at the positions indicated, and thus a boundary of this kind can be considered as an array of dislocations.

Evidence for the correctness of this picture is given by the photomicro-

---

**FIG. 5-7.** The nature of tilt boundaries in metals. (a) A tilt boundary as a succession of added crystal planes. The corresponding edge dislocations are indicated. (After Burgers.) (b) Photomicrograph of a tilt boundary in germanium showing the regularly spaced dislocations (X1000). (Courtesy F. L. Vogel, Jr., Bell Telephone Laboratories.)
FIG. 5-8. Variation of grain-boundary energy with misorientation angle, $\theta$, for tilt boundaries in silver. (After Aust.)

Figure 5-8 shows this behavior in silver. For other metals the value of $\theta_m$ ranges from 12 to 30$^\circ$. Most grain boundaries are not low-angle tilt boundaries but are more complex. It is believed that their grain-boundary energy is approximately equal to $\gamma_m$, which in silver is on the order of 500 ergs/cm$^2$.

Grain boundaries are an example of interfacial boundaries, which also include boundaries between two different phases (e.g., solid and liquid) or between phases that differ in composition, as in the case of the liquids described in Fig. 5-9. All boundaries have the common characteristic that they represent regions of high energy, and the system attempts to minimize the energy by decreasing the area of the interface. This property of an interface is conveniently represented by the surface tension, which is the force per unit length of interface acting parallel to the interface in a direction that tends to decrease its area. In Problem 7 it is shown that the surface tension is equal to the surface energy and has equivalent units. The effect of surface tension on the equilibrium of liquid phases is shown in Fig. 5-9. If one liquid phase is completely surrounded by another, Fig. 5-9(a), it will tend to assume a spherical shape, since this shape minimizes the interfacial area. However, if the same liquid phase lies between two other liquids, Fig. 5-9(b), then the geometry of the interfaces is determined by the three interfacial tensions $\gamma_{12}$, $\gamma_{23}$, and $\gamma_{31}$ existing between the pairs of liquid phases. These tensions can be pictured as exerting forces on the periphery of the lens-shaped volume of liquid 2. The angles $\theta_1$, $\theta_2$, and $\theta_3$ between the three pairs of interfaces are those existing when the tensions are balanced in the manner shown by the graph of a low-angle boundary in germanium, Fig. 5-7(b). Each of the etch pits formed at a dislocation, and the spacing of the etch pits, is exactly as predicted.

Since the energy of a crystal lattice is increased by the presence of a dislocation, an additional energy $\gamma$ is associated with unit area of grain boundary. For low-angle grain boundaries this energy increases with the angle $\theta$ up to a maximum value $\gamma_m$ at $\theta_m$ according to the equation

$$\frac{\gamma}{\gamma_m} = \frac{\theta}{\theta_m} \left( 1 - \ln \frac{\theta}{\theta_m} \right).$$

(5-7)
Fig. 5-9. Equilibrium of interfaces among immiscible liquid phases. (After C. S. Smith.) (a) The interfacial tension favors a sphere in this case. (b) Three interfacial tensions may create a lens-shaped volume. (c) This mechanical analogy shows how the tensions are balanced at definite angles.

mechanical analogy of Fig. 5-9(c). The following relation then applies:

\[
\frac{\gamma_{12}}{\sin \theta_2} = \frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{31}}{\sin \theta_2}.
\] (5-8)

This equation can be applied when three grains meet to form a boundary in a solid metal. Since all the boundaries then have the same surface tension, the three angles should be equal when equilibrium has been established. Statistical studies of grain geometry in pure metals have verified this conclusion. Figure 5-10 shows the occurrence of 120° angles in annealed iron.

Another important example of interfacial equilibrium is that occurring on a solid surface, for example, the equilibrium shown in Fig. 5-11 in-
Fig. 5-10. Polygonal grains in annealed iron, showing the tendency for three grain boundaries to meet at 120° angles (X250). (Courtesy C. S. Smith, Institute for the Study of Metals, University of Chicago.)

Fig. 5-11. Equilibrium of interfacial tensions for a spherical cap of liquid phase in contact with a solid and a vapor. (a) Spherical cap of liquid on a solid surface. (b) Section through the liquid cap showing the equilibrium of the interfacial tensions.

Volving a liquid phase and a vapor phase. Under the conditions shown the liquid tends to form a spherical cap with a contact angle $\theta$ determined by the equilibrium of the horizontal components of the three interfacial tensions,

$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos \theta.$$  \hspace{1cm} (5-9)

The vertical component of the liquid-vapor interfacial tension is balanced by elastic forces that it sets up in the solid. Surface-tension values for the interface between the liquid phase and an inert vapor phase are given in Table 5-3. Representative values of other types of interfacial tensions are listed in Table 5-4.

The dislocation model of a low-angle grain boundary suggests the following picture of an ordinary grain boundary. For a distance of an atom
Table 5-4

INTERFACIAL TENSIONS OF PURE METALS

<table>
<thead>
<tr>
<th>Metal</th>
<th>Type of interface</th>
<th>Interfacial tension, ergs/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>Solid-vapor</td>
<td>500</td>
</tr>
<tr>
<td>Silver</td>
<td>Solid-vapor</td>
<td>1130</td>
</tr>
<tr>
<td>Gold</td>
<td>Solid-vapor</td>
<td>1350</td>
</tr>
<tr>
<td>Copper</td>
<td>Solid-vapor</td>
<td>1650</td>
</tr>
<tr>
<td>Lead</td>
<td>Solid-liquid</td>
<td>30</td>
</tr>
<tr>
<td>Silver</td>
<td>Solid-liquid</td>
<td>120</td>
</tr>
<tr>
<td>Gold</td>
<td>Solid-liquid</td>
<td>130</td>
</tr>
<tr>
<td>Copper</td>
<td>Solid-liquid</td>
<td>150</td>
</tr>
<tr>
<td>Silver</td>
<td>Grain boundary</td>
<td>500</td>
</tr>
<tr>
<td>Copper</td>
<td>Grain boundary</td>
<td>600</td>
</tr>
<tr>
<td>Copper</td>
<td>Twin boundary</td>
<td>25</td>
</tr>
</tbody>
</table>

or two near the center of the boundary, the lattice structure is severely distorted, with the atoms greatly displaced from their normal positions. For some additional distance from the grain boundary, the lattice is elastically strained and is therefore at higher energy than the main volume of the grain. Thus, the grain boundary is thought to be a region of transition between the differently oriented crystal lattices of the two neighboring grains. The interface between two different solid phases is believed to be essentially the same as a grain boundary.

A special type of grain boundary in a pure metal is the twin boundary, shown in Fig. 9-5. The two portions of lattice separated by a twin boundary have a special orientation relationship that permits easy transition from one lattice to the other, and therefore the energy of a twin boundary is low. Similar orientation relationships can also occur between two different phases. The corresponding boundaries are called coherent boundaries in this case, and their energies are also relatively low.

Grain boundaries and other interfacial boundaries have important effects on the properties of metals. Since the motion of dislocations through the lattice is the principal mechanism by which a metal deforms, it is understandable that the disturbed grain-boundary region impedes deformation by interfering with the motion of dislocations. Other effects of grain boundaries on deformation and fracture of metals are considered in Chapter 9. Chemical reactions of various kinds take place preferentially at grain boundaries; examples of this behavior will be met later in treat-
ments of corrosion and precipitation of a second solid phase. Diffusion along grain boundaries is also much faster than within grain itself. Because of the altered structure and higher energy of the grain-boundary region, the concentration of impurities is different in grain boundaries than in the body of grains. The more significant behavior occurs when the concentration is higher in the grain boundaries, in which case the impurity is said to be positively adsorbed. This type of adsorption is thought to be responsible for some properties of grain boundaries.

Types of solid phases. Pure metals are the simplest examples of solid phases, but several other kinds of phases are commonly found in metallurgical systems. When a second element dissolves in a solid metal the resulting phase is called a solid solution, by analogy with the familiar aqueous solutions such as sugar in water. However, a solute atom may occupy two alternate types of position in the lattice of the matrix (solvent) metal, as shown in Fig. 5-12. If the two atoms are of comparable size, the solute atom will substitute at random for one of the matrix atoms in the crystal lattice, Fig. 5-12(a). This kind of structure is called a substitutional solid solution. There are a few relatively small atoms that can be accommodated in the interstices between the matrix atoms (Fig. 5-12b) to form an interstitial solid solution. Examples of these two kinds of solid solution will be given in Chapter 6, and it will be found that no sharp dividing line exists between a pure metal and its solid solution.

Substitutional solid solutions. In the course of an alloy development it is frequently desirable to increase the strength of a given alloy by adding a metal that will form a solid solution. Unfortunately, if an alloying element is chosen at random it is likely to form an objectionable intermediate phase instead of a solid solution. Largely through the work of Hume-Rothery, a number of general rules governing the formation of substitu-
TYPES OF SOLID PHASES

Tional solid solutions are available to aid in the proper choice of such alloying elements. These rules can be summarized as follows.

1. **Relative size factor.** If the sizes of two metallic atoms (given approximately by their lattice constants) differ by less than 15 percent, the metals are said to have a *favorable* size factor for solid-solution formation. So far as this factor is concerned, each of the metals will be able to dissolve appreciably (on the order of 10 percent) in the other metal. If the size factor is greater than 15 percent, solid-solution formation tends to be severely limited and usually is only a fraction of one percent.

2. **Chemical affinity factor.** The greater the chemical affinity of two metals, the more restricted is their solid solubility. When their chemical affinity is great, two metals tend to form an intermediate phase rather than a solid solution.

3. **Relative valency factor.** If the alloying element has a different valence from that of the base metal, the number of valence electrons per atom, called the electron ratio, will be changed by alloying. Crystal structures are more sensitive to a decrease in the electron ratio than to an increase. Therefore, a metal of high valence can dissolve only a small amount of a lower valence metal, while the lower valence metal may have good solubility for the higher valence metal.

4. **Lattice-type factor.** Only metals that have the same type of lattice (face-centered cubic, for example) can form a complete series of solid solutions. Also, for complete solid solubility the size factor must usually be less than 8 percent. Copper-nickel and silver-gold-platinum are examples of binary and ternary systems exhibiting complete solid solubility.

A qualitative estimate of the solid solubility of one metal in another can be obtained by considering these four factors. It should be noted that an *unfavorable* relative size factor alone is sufficient to limit solid solubility to a low value. If the relative size factor is *favorable*, then the other three factors should be considered in deciding on the probable degree of solid solubility. It must be emphasized that numerous exceptions to these Hume-Rothery rules are known.

X-ray studies have revealed several important features of the structure of actual solid solutions. In a solution of two atoms of different size, Fig. 5-13, the tendency toward close packing causes a typical atom to be somewhat displaced from the ideal lattice site. This distortion of the lattice can be evaluated quantitatively as the average (root mean square) static displacement of the atoms and has been found to be about 0.1 Å for systems in which the two atoms differ in size by 10 to 15 percent.

The size of an atom in a pure metal is ordinarily determined as the distance from the center of a given atom to the center of a nearest-neighbor atom (see Problem 8). The corresponding distance, \( r_{AA} \) for example, can also be determined in a solid solution from suitable x-ray data. The re-
PHASES IN METAL SYSTEMS

FIG. 5-13. The static displacement of atoms in a solid solution. (After Averbach.) (a) Atoms of uniform size at the points of a crystal lattice. (b) $A$ and $B$ atoms in a solid solution are displaced from the average lattice sites.

FIG. 5-14. Results of x-ray studies of the gold-nickel solid solutions. (a) The short-range order coefficient. (b) The sizes of the atoms in solution. (After Flinn, Averbach, and Cohen.)
results of a study of this kind are shown in Fig. 5-14(b) for gold and nickel, which can dissolve completely in each other over the entire range of compositions. It is seen that the size of the gold atom decreases from its size in pure gold as the fraction of nickel atoms in the alloy increases. The nickel atoms show a corresponding change.

When the distribution of $A$ and $B$ atoms in a solid solution is completely random, the probability $p_A$ that a given neighbor of a $B$ atom is an $A$ atom is just the fraction $X_A$ of $A$ atoms in the alloy. That is, $p_A/X_A = 1$. The amount $\alpha$ by which this ratio differs from unity in a given case is a useful measure of the departure of a solid solution from randomness:

$$\alpha = 1 - (p_A/X_A),$$

(5-10)

where $\alpha$ is the short-range order coefficient. There are two possible departures from $\alpha = 0$, the value for a random solution. If $B$ atoms group themselves preferentially around other $B$ atoms, then $p_A$ is less than $X_A$ and $\alpha$ is positive. This behavior is called clustering in the solid solution. On the other hand, if a given $B$ atom is preferentially surrounded by $A$ atoms, $\alpha$ is negative and the solid solution is said to show short-range ordering. The curve of Fig. 5-14(a) shows that the degree of ordering varies with composition in the gold-nickel system and that in this case even the maximum departure from a random distribution is not large.

**Interstitial solid solutions.** The four elements hydrogen, carbon, nitrogen, and boron have such small atomic diameters that they can occupy the empty spaces (interstices) in the crystal lattices of many metals, Fig. 5-12(b). Such interstitial solid solutions usually have a limited composition range and are generally considered of secondary importance, but there are a few instances worthy of special attention. The interstitial solution of carbon in iron constitutes the basis of steel hardening and is discussed in Chapter 14. Very small amounts of hydrogen introduced into steels during acid pickling (cleaning), plating, or welding operations cause a sharp decrease in ductility, known as hydrogen embrittlement. Interstitial nitrogen is useful not only in the nitriding process (to be discussed later) but also as an important factor in maintaining 18 Cr-8 Ni stainless steel in the austenitic condition (Chapter 10).

In some alloys both interstitial and substitutional solid solutions are formed to an appreciable extent. For example, a chromium-nickel steel contains interstitially dissolved carbon and substitutionally dissolved chromium, nickel, and minor elements.

**Intermediate phases.** When an alloying element is added to a given metal in such amount that the limit of solid solubility is exceeded, a second phase appears with the solid solution. This second phase may be
the (primary) solid solution of the alloying element. The aluminum-silicon system (Fig. 6-13) is an example of this behavior. When the solubility of aluminum for silicon is exceeded, the silicon-rich beta phase appears with the aluminum-rich alpha phase. More often the second phase that appears is an intermediate phase, such as the Mg$_2$Pb compound in the lead-magnesium diagram, Fig. 6-24. It is convenient to classify the possible intermediate phases into categories determined by their structures.

**Interstitial compounds.** When the solubility of an interstitially dissolved element is exceeded, an intermediate phase is produced in which these elements are again at interstitial positions. Compounds of this type, such as TaC, TiN, WC, TiH$_2$, Mn$_2$N, and Fe$_3$C, have high hardnesses and melting points, and they are useful in steels and in cemented carbides.

**Valency compounds.** Two chemically dissimilar metals tend to form compounds showing ordinary chemical valence. As would be expected from the ionic or covalent binding characteristic of these compounds, their properties are essentially nonmetallic; moreover, they are brittle and have poor electrical conductivity. Examples of valency compounds are Mg$_2$Si, Mg$_2$Pb, and AlSb.

**Electron phases.** The intermediate phases that appear at definite compositions in certain binary equilibrium diagrams have been shown to depend on the ratio of electrons to atoms at those compositions. Consider a monovalent base metal like copper, which is face-centered cubic. The initial electron ratio is then one electron per atom. If a divalent alloying metal, such as zinc, is added to the base metal, the electron ratio increases. For example, at 50 atomic percent zinc, the electron ratio is three electrons to two atoms, or 1.50. At this ratio a body-centered cubic beta phase appears. A complex cubic gamma phase appears at a ratio of 1.62, and a close-packed hexagonal epsilon phase appears at 1.75. The essentially metallic nature of these phases is indicated by the electronic character of their binding and by the fact that each phase exists over a range of compositions. The copper-zinc diagram in Fig. 6-45 shows the electron phases beta, gamma, and epsilon in addition to the primary solid solutions, alpha and eta.

**Ordered phases.** The extension of a primary solid solution over a large composition range is sometimes interrupted by the occurrence of an ordered form of that solid solution, Fig. 6-28. Such an ordered phase is roughly similar in mechanical and physical properties to the (disordered) solid solution from which it forms. A fuller treatment of order-disorder transformations is given in Chapter 13.

**Phase Transformations**

Metallurgical processes often involve the transformation of a metal from one phase to another; examples are the change from one solid phase
to another during heat treatment, and the solidification of a liquid alloy in a casting process. Although the character of a given phase transformation depends on the natures of the two phases involved, every transformation can be considered to be dependent on two factors: (1) a thermodynamic factor that determines whether the transformation is possible and (2) a kinetic factor that determines whether the transformation will proceed at a practical rate. Much of the following discussion is devoted to the effect of the thermodynamic and kinetic factors on the initial stage of transformation, that is, the nucleation of a stable volume of the new phase. However, these two factors also control the subsequent growth of the nuclei that completes the process of phase transformation.

It will be recalled from Eq. (2-4) that the Gibbs free energy $\Delta F$ is a useful measure of the tendency for a reaction to occur. To see how this concept can be applied to phase transformation, consider the solidification of 1 cm$^3$ of liquid zinc.* At the melting point of zinc, $T_0$, the liquid phase and the solid phase are in equilibrium and there is no tendency for the transformation to occur; that is,

$$\Delta F = \Delta H - T_0 \Delta S_v = 0,$$

$$\Delta S_v = \frac{\Delta H}{T_0} \quad (5-11)$$

If it is assumed that $\Delta H_v$ and $\Delta S_v$ do not vary with temperature, then the free-energy change accompanying the solidification of liquid zinc at any temperature $T$ can be determined as

$$\Delta F_v = \Delta H_v - T \Delta S_v$$

$$= \Delta H_v \left( \frac{T_0 - T}{T_0} \right), \quad (5-12)$$

where the value of $\Delta S_v$ given by Eq. (5-11) has been used. Since 170 calories of heat are given off during the solidification of 1 cm$^3$ of zinc, $\Delta H_v = -170$ and $\Delta F_v$ is negative (that is, the solidification reaction is possible) provided the temperature $T$ is less than the melting point $T_0$.

It is well known that a reaction such as solidification does not occur at temperatures only infinitesimally below the equilibrium temperature; rather, an appreciable supercooling is required before a practical rate of reaction is produced. This behavior is a result of the mechanism by which phase transformations occur. Before continuing with the treatment of the liquid-to-solid transformation, it is convenient to consider the simpler, related question of the formation of drops of liquid from the vapor phase.

* A subscript $v$ is used on the quantities $\Delta F_v$, $\Delta H_v$, etc., in the following treatment as a reminder that they refer to 1 cm$^3$ (unit volume) of material.
Vapor-liquid transformations. Consider a volume of vapor phase under conditions such that the formation of liquid is thermodynamically possible; that is, $\Delta F$ is negative for this reaction. Now, if a drop of liquid of radius $r$ is to form, an interface must be created between the liquid and the surrounding vapor. Since $\gamma$ is the energy required to create one square centimeter of interface, the over-all change in free energy, $\Delta f$, that accompanies the formation of a spherical drop of liquid within the vapor is

$$\Delta f = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta F^*$$  \hspace{1cm} (5-13)

The first term in this expression is always positive but the second term will be negative when $\Delta F^*$ is negative for the phase transformation being considered. Since the terms contain $r^2$ and $r^3$, respectively, they vary with increasing radius of the drop in the manner shown in Fig. 5-15; the $r^3$ term is smaller initially but becomes greater for larger values of $r$. Thus the sum $\Delta f$ goes through a maximum at some critical radius $r^*$, whose value (see Problem 10) is

$$r^* = \frac{2\gamma}{\Delta F^*}$$  \hspace{1cm} (5-14)
VAPOR-LIQUID TRANSFORMATIONS

The corresponding value of $\Delta f$ is

$$\Delta f^* = \frac{16\pi r^3}{3(\Delta F)^2}. \quad (5-15)$$

The drops of liquid described by the curve of $\Delta f$ versus $r$ arise because of random collision of two atoms to form a pair, the addition of a third atom to the group in another collision, and so on through successive collisions. Thus at any instant there will tend to be drops of the whole range of sizes, and it can be shown that in each cm$^3$ of vapor the number of drops of radius $r^*$ is

$$n^* = n e^{-\Delta f^*/kT}. \quad (5-16)$$

where $n$ is the number of atoms per cm$^3$ in the vapor phase and $k$ is Boltzmann’s constant. Drops of radius $r^*$ or greater differ from smaller drops in that the addition of one more atom to these larger drops is accompanied by a decrease in the free energy of the drop below the maximum value $\Delta f^*$. Thus a drop larger than $r^*$ will grow spontaneously, and for this reason it is called a nucleus. Drops smaller than $r^*$ will tend to decrease in size and can grow only if they are subjected to the proper combination of chance collisions. These drops are called embryos.

Since the number of critical nuclei $n^*$ is given by Eq. (5-16), the rate of formation of stable nuclei can be determined from the rate at which these nuclei are struck by an additional vapor atom. If $z$ is the number of vapor atoms striking one cm$^3$ per second, then the rate of nucleation per cm$^3$/sec, $I_w$, is

$$I_w = z \times n^* s(r^*)^2, \quad (5-17)$$

since the second factor is the area of critical-nucleus surface available for collision. Using the value of $z$ obtained from kinetic theory (see Problem 11) and the value of $n^*$ from Eq. (5-16), we find that the rate of nucleation is

$$I_w = \frac{nP4\pi (r^*)^2}{\sqrt{2\pi mkT}} e^{-\Delta f^*/kT} \quad (5-18)$$

where $P$ is the pressure of the vapor phase and $m$ is the mass of each atom.

When appropriate values are used in Eq. (5-18), it is found that extremely large amounts of supercooling would be required to obtain a practical rate of nucleation of drops in the volume of the vapor. This process is called homogeneous nucleation. In practice, before homogeneous nucleation has a chance to occur, drops of liquid form on foreign material that serves as a nucleation catalyst. Suitable materials for this purpose are the walls of the container or dust particles in the vapor. The
Fig. 5-16. Screw dislocations in the growth of crystals. (Electron micrograph courtesy H. F. Kay, University of Bristol.) (a) and (b) A screw dislocation produces a "step" in the crystal structure, at which additional atoms can attach themselves. The resultant growth causes the step to assume a spiral form. (c) Growth spiral in a single crystal of paraffin. The step is one molecule high (×28,000; reproduced at two-thirds size).
mechanism of the catalytic action is similar to that described in the following section for heterogeneous nucleation in the freezing of a liquid.

The formation of a solid phase directly from the vapor is similar to the formation of a liquid, but here there is a problem not only in promoting nucleation but also in causing growth to continue. Assuming that a stable crystallite has been produced by heterogeneous nucleation, further growth occurs by the addition of atoms from the vapor to incomplete crystal planes. If the crystal were perfect this process would soon lead to the development of atomically smooth crystal surfaces on which an additional plane of atoms could form only with great difficulty. The presence of a screw dislocation in the growing crystallite avoids this problem, since a "step" is then a permanent feature of the crystal face (Fig. 5-16a) and offers a site for the addition of atoms from the vapor phase (Fig. 5-16b).

Evidence for the existence of screw dislocations in growing crystals is afforded by the spiral growth pattern (Fig. 5-16c) found in many instances.

Other transformations involving the vapor phase are the evaporation of liquid metals and the sublimation of solid metals. These processes are the basis for the commercial refining of many metals, including zinc, magnesium, arsenic, and antimony. Excessive volatilization of alloying elements can sometimes cause difficulty during melting in vacuum or even during vacuum annealing of solid metals. The loss of zinc from brass and the loss of manganese from sheet steel are examples of the latter problem. It is possible to predict the rate of vaporization of a metal into a vacuum by means of the following equation, derived from kinetic theory (see Problem 12):

\[
G = \frac{p}{17.44\sqrt{T/M}}.
\]

where \(G\) is the grams of metal vaporized per cm\(^2\) per sec, \(p\) is the vapor pressure in mm of mercury, \(T\) is the temperature in °K, and \(M\) is the atomic weight of the metal. Since the vapor pressure is the principal factor determining the rate of vaporization, a useful reference point is provided by the fact that usually a vapor pressure of about 2 mm of mercury must be attained to make distillation commercially feasible.

There are two common circumstances that require modification of Eq. (5-19). If the metal being vaporized is in an inert atmosphere rather than in a vacuum, the rate of evaporation is reduced in direct proportion to the pressure of the inert gas. The magnitude of this effect is illustrated by the fact that the rate of evaporation of magnesium at its melting point is reduced by a factor of 100 by the presence of 1 mm of argon. Equation (5-19) must also be modified if it is to be applied to a component of an alloy rather than to a pure metal. As a rough approximation it can be assumed that Raoult's law is valid; namely, that the vapor pressure of a
metal in solution is given by its mol fraction multiplied by its vapor pressure in the pure state, $p^0$ (Table 5-1). By definition, an ideal solution obeys Raoult's law. However, if data on the thermodynamic activities $a$ of a nonideal solution are available, the correct vapor pressure can be calculated as

$$p = ap^0,$$  \hspace{1cm} (5-20)

provided the activities are referred to the pure metal as the standard state. For example, the activity of zinc in brass containing 0.3 mol fraction zinc is only 0.07 at 750°C; hence in this case the true vapor pressure is significantly lower than the value given by the Raoult’s law approximation.

Liquid-solid transformations. The argument used above in developing the equation for homogeneous nucleation in the vapor phase applies in large part to homogeneous nucleation of a spherical nucleus of a solid within a liquid phase. However, in this case the equation corresponding to Eq. (5-17) is

$$I_1 = (n^*m^*)v,$$  \hspace{1cm} (5-21)

where $m^*$ is the number of atoms in the liquid phase that are neighbors of a given critical nucleus; therefore the quantity in parentheses is the total number of atoms that have an opportunity to combine with the number $n^*$ of critical nuclei per cm$^3$. The frequency $v$ with which a typical liquid atom will cross the interface and become part of the solid nucleus is given by the theory of absolute reaction rates as

$$v = \left(\frac{kT}{h}\right) e^{-(\Delta f_a/kT)}$$  \hspace{1cm} (5-22)

where $h$ is Planck's constant and $\Delta f_a$ is the energy barrier posed by the interface. When Eq. (5-16) is used for $n^*$ and if $m^*$ is omitted to compensate for factors neglected in this simplified treatment, Eq. (5-21) becomes

$$I_1 = n \frac{kT}{h} e^{-(\Delta f_a/kT)}$$  \hspace{1cm} (5-23)

where $n$ is the number of atoms per cm$^3$ in the liquid phase and, in this case, $\gamma$ in the expression for $\Delta f_a$ (Eq. 5-15) is the energy of the liquid-solid interface.

The calculation of Problem 13 demonstrates that a metal must be supercooled approximately 100° below its melting point before homogeneous nucleation will occur. Although this type of nucleation can be produced in the laboratory, it is clear that the solidification of most metals does not
occur by this mechanism, since actual supercooling is only several degrees.

As in the case of the vapor phase, heterogeneous nucleation in a liquid
occurs in practice either on a nucleating substance floating in the liquid or
on the walls of the container. The following discussion shows that dif­
ferences in interfacial tensions account for the relative ease of heteroge­
neous nucleation compared with homogeneous nucleation.

If the embryos of the solid phase are assumed to form as spherical caps
on a plane nucleating surface in a manner analogous to that shown in
Fig. 5-11, then the equilibrium among the interfacial tensions is given by
the analog of Eq. (5-9), namely

\[ \gamma_{SL} = \gamma_{aS} + \gamma \cos \theta, \]  

where \( S \) refers to the nucleating surface and \( a \) refers to the solid phase
being formed; \( \gamma \) is equivalent to \( \gamma_{aL} \). There is now another free-energy
term that enters into Eq. (5-13), besides \( \gamma \) and \( \Delta F_v \). As the embryo de­
velops and covers a larger area on the nucleating surface, Fig. 5-17, the
high-energy \( S-L \) interface is replaced by the \( a-S \) interface. Per cm\(^2\)
of growth of the \( a-S \) interface, there is a change in free energy equal to
the difference in the two interfacial energies: \( \gamma_{aS} - \gamma_{SL} \). From Eq.
(5-24) this free-energy change can be evaluated as

\[ \gamma_{aS} - \gamma_{SL} = -\gamma \cos \theta. \]  

When this additional energy term is taken into account Eq. (5-13)
has the form

\[ \Delta F_s = \frac{\pi r^3 \gamma + \pi r^2 \Delta F_v}{3} \left( 2 - 3 \cos \theta + \cos^3 \theta \right) \]  

(5-26)
and the critical values of $r$ and $\Delta f$, are

\begin{align}
  r^* &= -\frac{2Y_0}{\Delta F_v} \sin \theta = r^* \sin \theta, \\
  \Delta f^* &= \Delta f^* \left(\frac{2 + \cos \theta}{1 - \cos \theta}\right)^2.
\end{align}

(5-27) (5-28)

where $r^*$ and $\Delta f^*$ are the values for homogeneous nucleation given by Eqs. (5-14) and (5-15). The equation for the rate of heterogeneous nucleation is obtained by an argument analogous to that used in connection with Eq. (5-23) for homogeneous nucleation:

\[ I_n = n_a \frac{kT}{h} e^{-\left(\Delta f^*/kT\right)}, \]

(5-29)

where $n_a$ is the number of atoms of the liquid adsorbed on 1 cm$^2$ of the solid nucleating surface. It can usually be assumed that a monolayer of liquid atoms are adsorbed on this surface. Problem 14 illustrates how heterogeneous nucleation can explain the small amounts of supercooling that occur in the actual solidification of metals.

Crystal growth. The grains produced by the solidification of a liquid metal have a variety of forms, resulting from the conditions that exist during growth of the grains. For example, an ingot cast in a metallic mold usually has the structure shown in Fig. 5-18, consisting of a fine-grained chill zone at the surface, a region of columnar grains, and a central zone of equiaxed grains. The explanation of this diverse behavior is to be found in three factors: (1) crystallographic features of growth, (2) temperature distribution during freezing, and (3) solute redistribution between the liquid and solid phases during the freezing of an alloy. The solidification of a pure metal will be discussed first, and then the additional effect of alloying will be considered.

When a liquid metal is placed in a cold metallic mold, the liquid near the surface of the mold is quickly cooled below the equilibrium melting temperature $T_m$ and stable nuclei are formed both on the mold wall and in the body of the liquid near the wall. These nuclei grow very rapidly into grains of roughly spherical shape, liberating the large latent heat of fusion. This heat plus the superheat of the liquid metal must be dissipated through the mold wall and the layer of solidified metal. Therefore, the rate of growth of the crystals soon becomes limited by the rate of heat removal rather than by the inherent growth velocity (the latter is extremely large). The temperature distribution in the solidifying metal at this stage is shown in Fig. 5-19(a). The small amount of supercooling in advance of the growing grains does not permit nucleation of new grains, and many of
the grains in the chill zone give way to more favorably oriented grains. These two factors give rise to the columnar structure shown in Fig. 5-19(b). The columnar grains tend to have a characteristic crystal direction as their axis, and they advance uniformly into the liquid. In pure metals the type of solidification shown in Fig. 5-19 continues to the center of the mold.

In the freezing of many alloys an entirely different pattern of supercooling is produced, even though the temperature distribution is similar to that for pure metals. The additional cause of supercooling in this case is the rejection of solute by the freezing solid and the consequent enrich-
ment of the liquid near the growing interface. In the following chapter it will be shown that the enriched liquid then has a lower freezing temperature. Therefore, if the growth of the solid is to continue, the temperature of the liquid in contact with it must be low enough to maintain the necessary amount of supercooling. Fig. 5-20. Since the freezing temperature of the liquid rises with increasing distance from the surface of the solid, it is possible for the amount of supercooling to increase for a distance into the liquid before decreasing to zero. This behavior is called constitutional supercooling, since it involves a change in the constitution (composition) of the liquid.

The initial stage of solidification of an alloy is similar to that for a pure metal (Fig. 5-19b). During the period of columnar growth, however, the solid-liquid interface is not plane but tends to develop protuberances,
Fig. 5-21. This behavior results because the constitutionally supercooled liquid allows portions of each grain to grow rapidly. In the course of this growth a new solute distribution is produced that discourages similar rapid growth by neighboring portions of the grain. Because of the symmetry of the diffusion process which controls the new solute distribution, the protuberances have a uniform spacing. If the amount of supercooling is small, the protuberances are only mounds on the surface of the growing crystal and are revealed as a "cell" structure (Fig. 5-21a) if the liquid is removed. If the thickness of supercooled liquid is large, then the protuberances can grow well in advance of the completely solidified portions, and a dendritic pattern of growth is obtained, Fig. 5-21(b). Under certain conditions of growth a dendrite consists not only of the main axis of growth but also of secondary and higher-order axes that branch off the existing axes. A well-developed dendrite is shown in Fig. 5-21(c).

![Fig. 5-20. Constitutional supercooling in a liquid alloy having an original freezing temperature $T_A$.](image)

![Fig. 5-21. Examples of nonuniform growth fronts in the solidification of metals. (a) Cellular structure in a lead-0.05% tin alloy (X100). (b) Dendritic structure in a lead-0.75% tin alloy (X50). (c) Dendrites that grew in casting of monel metal (X25). (Photographs (a) and (b) courtesy W. A. Tiller, Westinghouse Research Laboratories; (c) courtesy C. W. Mason, Cornell University.](image)
Constitutional supercooling also explains the occurrence of the central, equiaxed grains in Fig. 5-18. The reasoning on which Fig. 5-20 is based leads to the prediction that eventually all the liquid remaining in the central portion of the mold will be supercooled. The degree of supercooling is often great enough to nucleate new grains within the liquid, grains that then grow into the supercooled liquid by the dendritic mode of solidification.

**Solid-solid transformations.** Phase changes that occur within solid alloys are of paramount importance in metallurgical operations and are considered in detail in several later chapters. However, it is useful now to consider the broad aspects of these reactions and to note the new features that are displayed in addition to those already present in the simpler liquid-solid transformation. The new features include strain energy, orientation relationships between the crystal structures of the matrix and of the new phase, and the effect of grain boundaries.

A new solid phase can form within a previously stable solid phase only if the external conditions are changed. Ordinarily the temperature is varied for this purpose, although large changes in pressure are known to be effective in some cases. Pure metals that can exist in alternate allotrop forms can be made to undergo a phase change from one form to another by simply being heated (or cooled) past the temperature of the allotropic change. For example, if a rod of α-iron is heated above 910°C (see Fig. 5-6), grains of γ-iron will nucleate and grow and will eventually replace the original grain structure of α-iron. The term **neocrystallization** may be used to describe this process of forming a new phase in a pure metal. New solid phases are created in all metals by suitable alloying whether the pure metal undergoes an allotropic change or not. Many commercial alloys owe their importance to the fact that the new phase is stable only in a certain range of temperatures, offering the possibility of beneficial heat treatment.

When the conditions are such that a new solid phase forms at a high temperature (where diffusion is rapid) with relatively small supercooling, then the phase transformation is most similar to the formation of a solid phase from a liquid. The interfacial energy is high and nucleation occurs heterogeneously; the grain boundaries usually serve as the nucleation catalyst. The transformed region often grows into the matrix phase as a spherical volume to minimize the area of high-energy interface. The crystal structure of the matrix phase influences the orientation of the particles of the new phase, and there is a tendency for the boundaries of the two phases to have similar atomic spacings and patterns. For example, in the copper-zinc system, when the α-phase forms within the β-phase, Fig. 6-45, a (111) plane of the α-phase is parallel to a (110) plane in the β-phase and a [110] direction in the α-phase is parallel to a [111] direction in the β-
An orientation relation of this kind is often written in the form
\((110)_s \parallel (11)_a\) and \([111]_s \parallel [110]_a\).

Since the new phase usually has a volume different from that of the matrix, there is a tendency for solid-solid phase changes to be accompanied by an increase in strain energy. At high temperatures the attendant strain energy is often low because of yielding by the surrounding matrix but, especially at lower temperatures, strain energy may play a major role in the over-all change in free energy. Calculations have shown that the amount of strain energy produced by the formation of a given volume of second phase depends on the shape of the second-phase particles in the manner shown in Fig. 5-22. Thus, although spherical particles of a given volume have a minimum surface energy, they cause a maximum strain energy, while particles in the form of disks (platelets) minimize the strain energy but create additional surface.

If a solid phase is greatly supercooled below the equilibrium temperature at which a second phase becomes stable, platelet particles may form under conditions that do not require an excessive amount of surface energy. When a second phase maintains atomic matching across the boundary that separates it from the matrix, the boundary is called coherent. The interfacial energies of coherent boundaries are much lower than those of ordinary (incoherent) boundaries, as shown by the data of Table 5–4 for a twin boundary, which is a special type of coherent boundary. However, usually the equilibrium lattice of the second phase does not have the proper geometry to form a coherent interface and a transition lattice having the matching geometry may be nucleated instead. Although the transition lattice is unstable relative to the equilibrium form of the second phase, it may nucleate and grow more rapidly under suitable conditions.
involving large supercooling. The disk-shaped particles may form throughout the grain and are not dependent on the grain boundaries for nucleation sites. At a later stage, the equilibrium phase may form, and the transition phase will then disappear either by re-solution in the matrix or by loss of coherency with the matrix.

During most phase transformations in solids, diffusion occurs to produce a difference in concentration between the two (or more) phases involved. However, at low temperatures, where diffusion occurs slowly, greatly supercooled solids can transform by the martensitic mechanism, in which diffusion may be completely absent. In this type of transformation the second phase has the same composition as the matrix, but it forms a different crystal structure by a shearing action within the matrix. An example of this type of behavior will be considered for steel in Chapter 14.

References

1. (a) Apply the phase rule to the triple point in Fig. 5-4. (b) What change in the condition of the metal corresponds to shifting the pressure-temperature point from the triple point to the liquid region of the diagram?

2. Explain on the basis of electron theory why metal vapors would not be expected to exhibit ordinary electrical conductivity.

3. (a) Sketch a qualitative one-component diagram for nickel, using the data of Table 5-1. (b) Use the diagram of part (a) to determine the vapor pressure of nickel when it is held just above its melting point in an open crucible exposed to air.

4. Gaseous impurities are largely eliminated from some metals by melting them in a vacuum of 0.1 mm of mercury. Would you suggest this procedure for (a) chromium? (b) nickel? (c) copper?

5. Difficulty was encountered with excessive rise of a silver braze at 1000°C in an 0.02 cm space between two copper plates. On the basis of Eq. (5-6), suggest possible changes that might be made to limit the rise to a reasonable amount, say 1.0 cm.

6. (a) For a simple cubic lattice of the kind shown in Fig. 5-7(a), prove that the relation $D = \mu \theta$ is valid for small angles. (b) Show that $b$ is actually the Burgers vector of the dislocations formed along the low-angle boundary.

7. Consider a soap film on the wire frame shown in Fig. 5-23. (a) In which direction does the surface tension act on the movable wire? (b) If the surface tension is 25 dynes/cm (for each of the two surfaces of the soap film), calculate the work that must be done on the soap film to increase its total area by 1 cm² as indicated in the figure. (c) Determine the surface energy of the soap film and show that it is equal numerically to the surface tension. (d) Show that the units ergs/cm² and dynes/cm² are equivalent.

8. Use the data of Table 4-2 on the lattice constant of pure nickel to verify the value shown in Fig. 5-14 for the size of a nickel atom.

9. (a) Use Eq. (5-12) to show that the sign of $\Delta F$ correctly predicts that the reaction Zn(liquid) $\rightarrow$ Zn(solid) is impossible above the melting point of zinc. (b) Considering the value of $\Delta H$ in this case, criticize the naive concept that the heat liberated in a reaction is the driving force for the reaction.

10. (a) Determine the value of $r$ at which $\Delta f$ in Eq. (5-13) attains its maximum value. Recall the use of the derivative of a function in this connection. (b) Determine the maximum value of $\Delta f$. 

\begin{figure}[h]
\centering
\includegraphics[width=0.3\textwidth]{fig523.jpg}
\caption{Figure 5-23}
\end{figure}
11. Obtain an expression for \( z \) in Eq. (5-17), using the results of simplified kinetic theory, Eqs. (5-3) and (5-6). [Equation (5-3) will refer to the number of atoms in 1 cm\(^2\) if \( l \) is set equal to unity.] Note that the number of atoms striking an area of 1 cm\(^2\) can be considered to be the number per cm\(^3\) that are moving in the direction of a given coordinate, multiplied by the distance moved per second (the velocity \( u \)). Compare your result with that obtained by more refined kinetic theory,

\[
z = \frac{p}{\sqrt{2\pi rmkT}}.
\]

12. Use the method of the previous problem to determine the rate of vaporization of a metal in a vacuum. It can be assumed that the number of grams vaporized is equal to the number of atoms striking unit area multiplied by the weight of each atom. Compare your result with that obtained by more refined kinetic theory,

\[
G = \frac{p}{\sqrt{(2\pi RT)M}}.
\]

13. Assuming that \( \gamma \) (liquid-solid interfacial energy) for zinc is 60 ergs/cm\(^2\), and that \( \Delta f_s \) can be neglected in comparison with \( \Delta f_A^* \), calculate the degree of supercooling, \( \Delta T = T_0 - T \), at which the rate of homogeneous nucleation, \( I_0 \), first reaches an appreciable value, say \( 10^{-2} \) nucleus per second per cm\(^2\). \( I_0 \) varies extremely rapidly with change in \( \Delta T \), and suitable assumptions can be used to keep the mathematics quite simple. Recall the conversion 1 cal = \( 4.18 \times 10^7 \) ergs.

14. (a) Under actual conditions liquid zinc does not nucleate homogeneously, as assumed in the previous problem, but heterogeneously. Assuming that the actual supercooling is observed to be 3°C, solve the equation for the rate of heterogeneous nucleation to obtain the corresponding value of \( \theta \). See the previous problem for comments on the mathematical procedure. (b) Make a sketch showing how nucleation occurs in this case.
CHAPTER 6

PHASE DIAGRAMS

"Now it has been deduced from thermo-dynamical principles that there are only a very limited number of ways in which a liquid phase formed by two component (metals) may solidify to one or two solid phases; and this being so, there are a limited number of ways in which a transformation in or between these solid phases may take place."

ROOZEBOOM (1900)

INTRODUCTION

Phase diagrams are concerned with the relations among the phases in metals and alloys. Chapter 5 showed that atoms may combine to form a gaseous phase, a liquid phase, or a solid phase; and of course the properties of these phases strongly influence the properties of a given alloy. However, the behavior of an alloy depends also on the manner in which these phases are related. An alloy composed of two solid phases, for example, can have a variety of properties, depending on the structure built up by these two phases. Two instances of the commercial use of structural changes will help illustrate this point.

Contrary to popular belief, steel is useful not because it is hard but because it is hard and soft. Numerous substances are as hard or harder than steel, but as with the problem of storing the hypothetical universal solvent, it is difficult to form these deformation-resistant bodies into useful shapes. This problem is minimized in steels for the following reason. In one condition at room temperature steel is a mixture of crystals of ferrite and cementite (see p. 200), and the alloy is then soft enough to be machined readily and ductile enough to be formed by bending or pressing operations. However, after the necessary shaping has been accomplished, the soft steel can be caused to pass through changes of phase that render it extremely hard. These changes involve a third solid phase, produced by heating, and its later decomposition during quenching. The iron-carbon diagram, studied in this chapter, is the basis for heat treatments that soften and harden steel. It will be shown to have other uses also.

Aluminum-copper alloys offer a second example of changes in crystalline structure that radically affect metallic properties. Like steels, aluminum-base alloys containing about 5 percent copper are soft and ductile in some
conditions, for example in the presence of crystals of the alpha and theta phases (described in this chapter). After forming operations the alloy can be hardened by means of phase changes. In this instance the changes consist in dissolving the theta phase by heating, and then precipitating this phase again in a finely divided form. When the precipitation hardening of these alloys is studied in a later chapter, it will be shown that simple principles expressed in equilibrium diagrams are the basis of this process.

Phase changes in the solid state are of paramount interest in physical metallurgy, as these examples show, but liquid-solid reactions like those that occur in the solidification of castings are also important. Because the physical picture of a liquid solidifying or of a solid melting is easily grasped, it is convenient to begin using liquid-solid reactions as examples of equilibrium diagrams. The nature of solid-solid reactions can then be understood by analogy. The gas phase does not occur in the usual equilibrium diagrams, since these diagrams are for use at atmospheric pressure, which is high compared with the vapor pressures of metals in the temperature range involved. A type of diagram that does show the behavior of the gas phase is a P-T-X (pressure-temperature-composition) diagram, and it will be helpful to consider a simple example of this diagram to see the relation between one-component (pressure-temperature) diagrams and the usual (temperature-composition) equilibrium diagrams at constant pressure.

**P-T-X Diagrams**

In plotting the one-component diagrams discussed in the previous chapter, pressure and temperature were used as the variables that determined the equilibrium state of the system. When the system consists of two components, there is an additional variable, i.e., composition, and a three-dimensional diagram is needed to permit the plotting of all three variables. The P-T-X diagram for most binary (two-component) alloys is quite complex and few diagrams have been completely investigated. However, when the two metals in a given binary system dissolve completely in each other in both the liquid and solid states, then the P-T-X diagram is similar to a one-component diagram extended along the composition axis, Fig. 6-1(a). Note that a single solid phase, the alpha solid solution, exists in the upper-left portion of the diagram and joins the solid-phase regions of the two one-component diagrams that form the front and back faces of the P-T-X model. The regions occupied by the liquid and vapor phases can be described in a similar manner.

A new feature in the P-T-X diagram is the fact that the two-phase and three-phase equilibria extend over a region rather than being limited to a line or point as in the one-component diagram. This behavior is shown in
Fig. 6-1. Typical pressure-temperature-composition relations for metals A and B that dissolve completely in each other in the liquid and solid states. (a) The $P-T-X$ diagram. (b) A $P-T$ section at the 50% $B$ composition. (c) A $P-X$ section below the triple points of both pure metals. (d) A $T-X$ section at atmospheric pressure.
PHASE DIAGRAMS

the P-T section (at constant composition), Fig. 6-1(b).* It is often useful to have a section at constant temperature through the P-T-X diagram. A P-X section of this kind is shown in Fig. 6-1(c) for a temperature below the triple points of both component metals. By far the most useful section through the P-T-X diagram is the one at constant pressure, at atmospheric pressure in particular. Figure 6-1(d) shows the diagram obtained in this instance. All the equilibrium diagrams considered in the balance of the chapter are T-X diagrams and unless otherwise indicated they refer to a fixed pressure of one atmosphere; the first to be discussed is similar to Fig. 6-1(d).

SOLID-SOLUTION SYSTEMS

Depending on the nature of the two metals involved, several types of binary equilibria can occur. Moreover, a number of different kinds of solidification behavior and solid-state reactions may be combined in a single two-component diagram. The iron-carbon diagram is an important example of such complex reactions and will be considered later in the chapter. Fortunately, the interpretation of even the most complicated diagram is hardly more difficult than understanding each of the types of alloy behavior that it includes. This is true because every separate region of a complex diagram can be treated individually and independently. However, there remains the task of learning to analyze the typical reactions. For this purpose, especially simple two-component diagrams have been chosen for study. Each diagram contains only a single type of reaction; the copper-nickel system, for example, which is considered first, shows only solid-solution freezing.

Solid-solution freezing. We shall use the copper-nickel system as an example of a solid-solution equilibrium diagram. It has been found experimentally that alloys of these two metals form solid solutions when they are cooled from the liquid condition, and the experimental data have been conveniently summarized in the form of an equilibrium diagram (Fig. 6-4). An insight into the significance of the diagram can be obtained by considering the freezing of a number of compositions of copper-nickel alloys. When pure copper in the molten state is slowly cooled under equilibrium conditions, solidification occurs at the freezing point in the manner described in the previous chapter and shown schematically in Fig. 6-2. The occurrence of supercooling and of columnar growth are not considered in this figure.

* Sections of this type are not convenient for reasoning based on the phase rule, since the compositions of the phases in equilibrium are not shown.
SOLID-SOLUTION FREEZING

Fig. 6-2. Time-temperature curve for the solidification of a small crucible of liquid copper.

Fig. 6-3. Time-temperature curve for the solidification of a small crucible of 50% copper, 50% nickel alloy.
The equilibrium solidification of an alloy of 50% copper and 50% nickel* is slightly more involved than the freezing of a pure metal. Complete solidification does not occur at a single temperature but progressively over a small temperature range, and there is an accompanying continuous variation of the chemical compositions of the liquid and of the solid metal. The experimental facts in this case are indicated in the sketch of Fig. 6-3. When the liquid alloy reaches 2400°F, solidification begins with the formation of nuclei of the solid phase, composed of 67% nickel, 33% copper. As the temperature decreases, solidification continues with the growth of the solid phase, often in the form of dendrites. When solidification is about half completed, the composition of the solid phase is 60% nickel, 40% copper, and the liquid phase has changed its composition to 45% nickel, 55% copper. Upon completion of solidification the liquid has disappeared, and the solid phase has the composition of the original liquid phase, namely 50% nickel, 50% copper.

While it is not difficult to see that the liquid must change in composition as the result of the nucleation and dendritic growth of a solid phase relatively richer in the higher melting metal, it may seem incredible that the solid should be able to change its composition from 67% nickel to 50% nickel during the course of equilibrium solidification. The explanation is that although the atoms of a solid have only limited mobility, they can move about in the solid solution. This diffusion of atoms is considered in detail in Chapter 11, and it is shown there that appreciable changes in the composition of solid phases can occur at the high temperatures involved in this case.

The equilibrium diagram for a solid-solution alloy system, Fig. 6-4, summarizes the essential information obtained from time-temperature curves. In this case, data are plotted for a series of alloys ranging in chemical composition from pure copper to pure nickel. For example, the data from the curve for the solidification of pure copper, Fig. 6-2, are given adequately by point A in the equilibrium diagram. This point indicates that when the composition is completely free of nickel (pure copper) the liquid phase changes to the solid phase only at the freezing point of copper. Similarly, the data of Fig. 6-3 are recorded by the points B1 and B2 plotted at the composition 50% nickel. These points fully record the information that the 50% nickel alloy begins to solidify at 2400°F and is completely solid at 2280°F. It will be shown that data on the chemical compositions of phases are also furnished by this diagram. The complete liquidus and solidus lines are constructed by the use of many pairs of points similar to B1 and B2 obtained for other alloy compositions. The

* Compositions are given here in percent by weight. For certain purposes other units are useful, such as atomic percent, volume percent, or grams per cm³. Interconversion among these units is possible.
USES OF THE SOLID-SOLUTION DIAGRAM

liquidus and solidus lines divide the equilibrium diagram into regions where the liquid phase, liquid and solid phases, and solid phase exist. The microstructure of the equilibrium solid-solution phase is identical with that of a pure metal. It is noteworthy that such a structure is single phase, although many grains of the phase exist and are separated by grain boundaries.

Fig. 6-4. The copper-nickel equilibrium diagram. Points A, B₁, and B₂ show how the diagram is constructed from time-temperature curve data.

Fig. 6-5. The equilibrium conditions of a 30% nickel alloy at three different temperatures.

Uses of the solid-solution diagram. Since an equilibrium diagram is merely a concise presentation of experimental data obtained on a given alloy system, it follows that the original data can be obtained again from the diagram. For a specified alloy composition and temperature it is possible, under equilibrium conditions, to tell (1) the phases that are present, (2) the chemical composition of each phase, and (3) the amount of each phase. The procedures for obtaining this information will be illustrated using the alloy of 30% nickel shown by the vertical dashed line in Fig. 6-5.

Prediction of phases. The equilibrium diagram is plotted with temperature as the ordinate and composition as the abscissa. Therefore, specific information can be obtained from it only if a temperature and a composition are specified. Such a pair of values locates a point in the diagram. Points of this kind are used repeatedly in analyzing equilibrium diagrams. For example, the state of the alloy of composition 30% nickel can be determined only with reference to a certain temperature. Thus, when this
alloy is at 2170°F point 2 is determined.

Once the point of interest is located in the diagram, it is easy to ascertain which phase or phases are present. Those phases are present that correspond to the phase field in which the point lies. For example, the 30% nickel alloy at 2170°F (point 1) consists of only one phase, the liquid solution. On the other hand, at 2170°F the same alloy consists of a mixture of liquid solution and solid solution, since point 2 lies in the liquid and solid field of the diagram. At 1850°F (point 3) only the solid-solution phase exists. Evidently a similar analysis can be made for any point (any alloy composition and temperature) in the diagram. For practical purposes, a point on the liquidus or solidus line is usually considered to be in the two-phase field.

Production of chemical compositions of phases. When only a single phase is present, as at points 1 and 3 in Fig. 6-5, it is evident that the chemical composition of the phase must be the same as the composition of the alloy. Since at point 1, for example, the 30% nickel alloy is completely liquid, the chemical composition of the liquid phase is obviously 30% nickel and 70% copper.

When two phases are present, each phase has a different composition, and since neither of these compositions is the same as the composition of the alloy as a whole, it is necessary to consider two additional points in the diagram. If the two phases are to be in equilibrium, they must be at the same temperature; the points representing these phases, therefore, must lie at the temperature of the original point. For example, point 2 is determined by the alloy composition 30% nickel and the temperature 2170°F, but the two phases that exist in the alloy at this temperature are not at point 2 but only somewhere along the horizontal line at 2170°F. The exact points characterizing the liquid and solid phases are given by the intersections of the temperature horizontal with the liquidus and solidus lines, respectively. Thus the composition (and temperature) of the liquid phase in the 30% nickel alloy at 2170°F is given by point 2a (20% nickel, 2170°F), while the solid phase is specified by point 2b (35% nickel, 2170°F). The chemical composition of a given phase is read on the composition axis as indicated by the vertical dashed lines from points 2a and 2b. The horizontal (constant temperature) line connecting the points that represent the two different phases is called a tie line.

In summary, the chemical compositions of the phases that occur in an alloy at a given temperature are determined as follows:

* Considering the manner in which the liquidus and solidus curves are plotted from experimental data, it can be seen that this procedure for obtaining the compositions of the liquid and solid phases is equivalent merely to reobtaining the data that were used in plotting these curves.
1. When only a single phase is present, its composition is the same as that of the alloy.
2. When two phases are present, a horizontal line is drawn through the alloy-temperature point, and their compositions are read at the intersections of this line with the boundary lines of the two-phase field.

It should be noted that it is unnecessary to draw a tie line when the alloy-temperature point lies in a single-phase field.

Prediction of amounts of phases. If the total amount of alloy is known, it is possible to determine the amount of each phase that is present at equilibrium at a given temperature. When the total weight of alloy is 100 pounds or 100 grams the numerical relations are especially convenient, but the same convenience can be retained for any weight of alloy by expressing the amount of each phase as a percentage of the weight of the alloy.

If only a single phase is present, as at point 1 in Fig. 6-5, the weight of the phase must be equal to the weight of the alloy. There is 100% liquid phase present in this instance. If the weight of the alloy is 100 pounds, the amount of liquid phase at point 1 is 100 pounds. If the weight of the alloy is only 2.5 pounds, there is still 100% liquid phase or 2.5 pounds.

When two phases are present, their relative amounts are determined by the relation of their chemical compositions to the composition of the alloy. This is true because the total weight of one of the metals, say metal A, present in the alloy must be divided between the two phases. This division can be represented by the equation

\[
W_o \times \frac{\%A_o}{100} = W_L \times \frac{\%A_L}{100} + W_s \times \frac{\%A_s}{100},
\]

where \(W_o\), \(W_L\), and \(W_s\) are the weights of the alloy, liquid phase, and solid phase, respectively, and \(\%A_o\), \(\%A_L\), and \(\%A_s\) are the respective chemical compositions in terms of metal A. Since the weight of the alloy is the sum of the weight of the liquid phase and the weight of the solid phase, the following relation exists:

\[
W_o = W_L + W_s.
\]

This equation can be used to eliminate \(W_L\) from Eq. (6-1), and the resulting equation can be solved for \(W_s\) to give the expression

\[
W_s = \frac{W_o (\%A_o - \%A_L)}{(\%A_s - \%A_L)}.
\]
Although a similar expression can be obtained for the weight of the liquid phase $W_L$, the weight of the second phase is more easily obtained by means of Eq. (6-2).

Since the weight of each phase is determined by chemical composition values according to Eq. (6-3), it is not surprising that the tie line used in obtaining composition values is also significant in computing the weights of phases. In terms of lengths in the tie line (Fig. 6-5), Eq. (6-3) can be written

$$W_s = W_0 \left( \frac{\text{length of line } 2 - 2a}{\text{length of line } 2b - 2a} \right),$$

where the lengths are expressed in terms of the numbers used for the concentration axis of the diagram. Another characteristic of the tie line with respect to the amounts of the two phases leads to the namelever law for Eqs. (6-3) and (6-4). The relative amount of a given phase is proportional to the length of the tie line on the opposite side of the alloy point of the tie line. Thus, the weights of the two phases are such that they would balance as in Fig. 6-6.

Using Eq. (6-3), we can find the weight of solid-solution phase at point 2 in Fig. 6-5 as follows:

$$W_s = W_0 \left( \frac{30 - 20}{35 - 20} \right),$$

$$W_s = W_0 \times 0.667.$$  

The percentage of solid-solution phase can be determined by use of the equation

$$\text{Percentage of solid} = \frac{W_s}{W_0} \times 100 = \left( \frac{\%A_s - \%A_L}{\%A_s - \%A_L} \right) \times 100.$$  \textit{(6-5)}
At point 2 the percentage of solid phase is
\[ \% \text{solid} = \left( \frac{30 - 20}{35 - 20} \right) \times 100 = 66.7\% . \]
The percentage of liquid phase is the difference between 66.7 and 100\%,
that is, 33.3\%.

Copper-nickel: a typical solid-solution system. The copper-nickel system is not unique in solidifying to produce a single, solid-solution phase. A number of other binary systems show a similar behavior; for example, the silver-gold system involves only solid-solution freezing (see Problem 4). Alloy systems of a given type have a similar pattern of solidification behavior, and characteristic variations in mechanical and physical properties appear with change in chemical composition. A knowledge of these regularities is useful in making rough predictions of the properties of alloys of various compositions even in the more complex equilibrium diagrams. Most of the property changes in a solid-solution system are caused by distortion of the crystal lattice of the base (solvent) metal by additions of the solute metal. A schematic picture of this lattice distortion is given by the sketches of atom distributions in Fig. 6-7. The distortion increases with the amount of solute metal added, and the maximum effect occurs near the center of the diagram, since either metal can be considered as the solvent.

Figure 6-7 shows typical variations in properties of commercial copper-nickel alloys as the chemical composition of the solid solution changes from 100\% copper to 100\% nickel. Such strength properties as hardness and yield strength also pass through a maximum, while the ductility values show a minimum. Properties that are almost unaffected by atom interactions vary more linearly with composition. Examples of such properties of the solid solution are the lattice constant, thermal expansion, specific heat, and specific volume.

Figure 6-7 lists the properties characteristic of alloys under equilibrium conditions, but alloys that solidify at the cooling rates found in comm-

* The solid solutions shown in Fig. 6-7 illustrate the difficulty of giving a solid solution a completely descriptive name. In this case is the complete series of solid solutions based on nickel or on copper? It is difficult to say. Also, the addition of a few percent of a third element would not change the essential nature of the solid solution. Because of these complications, it is customary to use the Greek letters to name the solid solutions in a given equilibrium diagram. In this case there is only one solid solution, and it is called by the first Greek letter, the alpha (α) solid solution. In Fig. 6-12 there are two solid solutions, and they are arbitrarily called the alpha and beta (β) solid solutions.
Fig. 6-7. Typical property variations with change in composition in commercial copper-nickel alloys. The sketches of atom distribution illustrate the lattice distortion produced by solid-solution formation.
FIG. 6-8. Microstructures at X75 of a 30% nickel, 70% copper alloy in the cast and in the homogenized conditions. (Courtesy American Brass Company.)

(a) Cored structure in the cast alloy. (b) Homogeneous structure produced by working and heating.

Commercial casting operations are not in equilibrium. Figure 6-8(a) shows the microstructure of a cast alloy that is 30% nickel, 70% copper. The undesirable, inhomogeneous structure (called coring) that developed in the course of solidification is clearly visible. Note that the dendritic solidification is made evident by the coring. The interior of the dendrite, which solidifies first, differs in chemical composition from that of the outer region, and the etching process* discloses this difference as a slight contrast in appearance under the microscope. In the absence of sufficient time for diffusion in the growing particles of solid alloy, such an inhomogeneous, cored structure is an inevitable result of the mechanism of freezing in solid-solution systems. The equilibrium condition can be approached by prolonged heating of the solidified alloy at a temperature below the melting range. The same homogenization of the cast structure, however, can be produced more quickly by combining plastic deformation of the alloy with the heating, for example by hot-working the alloy, Fig. 6-8(b).

Solid solutions in other equilibrium diagrams. Although only a relatively small number of alloy systems, like copper-nickel, show complete

* Weak chemical solutions, called etching solutions, are used to treat the surface of polished specimens to reveal the microstructure (see also p. 10).
solid solubility, almost all equilibrium diagrams exhibit certain ranges of solid solubility in connection with other types of alloy formation. These limited regions of solid solubility can be analyzed in exactly the same manner as a complete solid-solution diagram, and the property variations correspond to those found at low percentages of the solute metal. Since these limited ranges of solid solubility occur so widely in equilibrium diagrams, the strengthening effects and other property changes associated with them are of industrial importance.

**Eutectic Systems**

Equilibrium diagrams merely record the experimentally observed behavior of alloy systems. While solid-solution formation represents one manner in which a liquid solution of two metals may solidify, the eutectic reaction is an equally prominent solidification mechanism. A useful explanation of various types of phase behavior can be obtained using the free-energy concept, and this approach will be illustrated here for the eutectic reaction.

**Free energy of alloy phases.** It is convenient to begin with a consideration of the liquid phase in a system composed of metals \( A \) and \( B \). From Eq. (2-3) it follows that the free energy \( F \) of a mole of liquid of a given composition can be represented as

\[
F = H - TS
\]

where the enthalpy \( H \) is largely determined by the energies of interaction of the \( A \) and \( B \) atoms in the liquid solution, and the entropy \( S \) is affected primarily by its change due to mixing of the two kinds of atoms, Eq. (4-10). If it is assumed that the two metals form an ideal solution, the enthalpy varies linearly with composition as shown in Fig. 6-9. The entropy of mixing given by Eq. (4-10) goes through a minimum and leads to the curve shown for \(-TS\). The sum of these two curves gives the over-all variation of the free energy of the liquid phase with composition.

The same kind of reasoning can be applied to the solid solution based on metal \( A \). The entropy term still acts to produce a minimum in free energy. However, frequently the enthalpy becomes very high as large percentages of metal \( B \) are (hypothetically) forced into solid solution with metal \( A \). The free-energy curve for the solid solution then has the form shown in Fig. 6-10, dropping to a minimum at small percentages of metal \( B \) and then rising to a very high value as pure \( B \) is approached.
A similar free-energy curve exists for the $\beta$-phase. In Fig. 6-10 it is assumed that the crystal structure of metal $B$ is different from that of $A$.

When we recall that a system tends to exist in a state of lowest free energy, it is clear to us that alloy 1 in Fig. 6-10 will exist as the $\alpha$ solid solution under equilibrium conditions. It might be thought that alloy 2 would also exist as the $\alpha$ solid solution, since this free energy is lower than that of the $\beta$ solid solution. Fortunately, there is a more attractive alternative. If the alloy exists as a mixture of a solid solution of composition $X_1$ and of $\beta$ solid solution of composition $X_2$, it can easily be shown (see Problem 5) that the free energy of the mixture is given by the line tangent to the free-energy curves of the $\alpha$ and $\beta$ solid solutions. A two-phase mixture continues to be the stable structure up to the composition $X_2$, but beyond this point the $\beta$ solid solution has the lowest free energy.

From the viewpoint of free-energy curves, phase changes such as the solidification of a liquid alloy are explained as a relative shifting of the free-energy curves for the various phases as the temperature is changed.
Fig. 6-11. Explanation of phase changes in a eutectic system in terms of the free-energy curves for the liquid, \( \alpha \), and \( \beta \)-phases. The temperatures decrease from \( T_4 \), which is the highest. (After Newkirk.)
This concept is illustrated in Fig. 6-11, which shows the free-energy curves for the liquid \( \alpha \) and \( \beta \)-phases at four different temperatures. At the highest temperature, \( T_4 \), the curve for the liquid phase lies below the other two curves, so that the liquid phase is the stable structure for alloys of all compositions. At a somewhat lower temperature, \( T_3 \), the free-energy curve for the liquid has shifted upward relative to the other two curves and it lies above one of them at each end of the diagram. The argument of Fig. 6-10 then predicts the phase regions shown in the figure.

There is a critical temperature \( T_2 \) in Fig. 6-11 at which all three free-energy curves have a common tangent and the three phases exist in equilibrium with one another. The phenomena that occur at this (eutectic) temperature will be considered in the following section. Below \( T_3 \), for example at \( T_1 \), the free-energy curve for the liquid phase lies above the common tangent of the curves for the two solid phases. Therefore, here the liquid phase is not stable at any composition. The solid phases that exist under these conditions were discussed in connection with Fig. 6-10.

The eutectic equilibrium diagram. This diagram can be developed from time-temperature curves in a manner analogous to that used for the solid-solution diagram, but in this case the experimental curves show a different kind of behavior. Over a wide range of compositions a portion of the solidification of the alloy occurs at a fixed temperature, the eutectic temperature. In one alloy (the eutectic composition) complete solidification occurs at the eutectic temperature. Although the freezing of the eutectic composition thus resembles that of a pure metal, the resulting solid is significantly different, since it is composed of two phases.

Figure 6-12 is a generalized representation of a eutectic equilibrium diagram involving metals \( A \) and \( B \). Like the solid-solution diagram, the eutectic diagram has (1) a liquid-phase field, which lies above the liquidus lines, (2) solid-phase fields (the alpha phase and the beta phase), which lie below the solidus lines, and (3) phase fields containing both liquid and solid, which lie between the liquidus and solidus lines. Because of the presence of the eutectic-reaction horizontal, a phase field containing two solid phases in equilibrium is also introduced. This field is bounded on the sides by solidus lines.

Full information concerning the amounts and compositions of the phases that occur in a given alloy at a certain temperature can be obtained for the eutectic diagram by using the same rules employed for solid-solution alloys. However, it is useful to have a general picture of the nature of the eutectic reaction before beginning detailed calculations.
Fig. 6-12. A generalized eutectic equilibrium diagram involving the hypothetical metals $A$ and $B$. The solidification processes of alloy 1 (eutectic composition) and of alloy 2 are indicated.

The basic equation of this reaction on cooling is

\[ \text{Eutectic liquid} \rightarrow \text{alpha solid solution} + \text{beta solid solution}, \]  

(6-7)

where the compositions of the alpha and beta phases are given by the end points of the eutectic horizontal. This reaction occurs at the temperature of the eutectic horizontal and involves liquid of eutectic composition (the composition of alloy 1 in Fig. 6-12). When eutectic liquid is cooled to the eutectic temperature, the two solid phases (the alpha and beta solid solutions) begin to form in the liquid alloy. But since one of the solid phases is richer (in metal $B$, for example) than the liquid phase, and the other solid phase is poorer than the liquid phase, it is natural for these two solid phases to form side by side in a given portion of liquid. The additional amount of (metal $B$) component needed by one of the solid

* If the liquid alloy is not of eutectic composition initially, it is essential that preliminary solidification of only one of the solid phases occur until the remaining liquid does attain the eutectic composition. This point is considered later.
phases is then obtained from the other solid phase (which needs to lose some of this component). This picture of the solidification process of a eutectic liquid accounts for the fact that the two solid phases generally occur as an intimate mixture. This mixture is called the eutectic structure or the eutectic microconstituent. A schematic representation of a solidified alloy consisting entirely of eutectic structure is given by the sketch of alloy 1 in Fig. 6-12. A photomicrograph of a typical eutectic structure is shown in Fig. 6-13; the 12% silicon alloy is composed entirely of eutectic microconstituent. During equilibrium heating the reverse of Eq. (6-7) occurs, and eutectic liquid forms from the mixture of alpha and beta solid solutions.

Gibbs’ phase rule, Eq. (5-1), can be used to demonstrate that the eutectic reaction must occur at constant temperature. There are two components (metals A and B) in the system, and since three phases exist during the eutectic reaction, the phase rule becomes

\[ P + F = C + 2, \]
\[ 3 + F = 2 + 2, \]
\[ F = 1. \]

But this one degree of freedom has already been used in fixing the pressure at one atmosphere; therefore neither the temperature nor the composition of any of the phases can change during the course of the eutectic reaction under equilibrium conditions.

Most alloys that undergo the eutectic reaction as part of their melting or solidification process are not of eutectic composition (alloy 2 in Fig. 6-12 for example). Since only liquid of eutectic composition can decompose by the eutectic reaction, Eq. (6-7), it is usually necessary that the liquid phase change its composition. This is accomplished through the freezing of primary crystals of one of the solid-solution phases. Consider, for instance, that the liquid alloy initially contains a higher percentage of metal B than that corresponding to the eutectic composition. The primary solid phase that forms first is then the solid phase (beta phase) that is richer in metal B. However, the formation of this solid phase depletes the remaining liquid phase in metal B, and the composition of the liquid shifts toward the eutectic composition during cooling to the eutectic temperature. In general, then, as solidification of the primary crystals proceeds, the liquid phase gradually shifts its composition (and temperature) along the liquidus line towards the eutectic point (the eutectic composition and the eutectic temperature). This process is shown by sketches of the solidification of alloy 2. Here the possibility of dendritic growth is ignored. When the liquid reaches eutectic composition the remaining solidification occurs according to Eq. (6-7), and the primary
crystals are surrounded by a finely divided mixture of the two solid phases in a eutectic structure. It is seen that the final structure of alloy 2 consists of two microconstituents, i.e., primary beta crystals and the eutectic microconstituent.

If an alloy composition is such that the vertical line representing it does not cross the eutectic horizontal, no eutectic reaction occurs during the equilibrium solidification of that alloy. Alloy 3 in Fig. 6-12 is an example of such a composition, and trial will show that its solidification is entirely that characteristic of a solid-solution diagram. Moreover, even a general composition in this diagram, for example alloy 2, experiences solidification of the solid-solution type until the eutectic horizontal is reached. In fact there are helpful similarities of this sort in all the various types of equilibrium diagrams.

Aluminum-silicon: a typical eutectic system. The equilibrium diagram for aluminum-silicon alloys is given in Fig. 6-13, with photomicrographs showing representative structures at room temperature. The photomicrograph of 99.95% aluminum exhibits the typical equiaxed grain structure of a pure metal. The microstructure of the 8% silicon alloy shows long dendrites of primary alpha solid solution surrounded by the eutectic microconstituent. In contrast, when the primary solid phase is the silicon-rich beta phase (in the 20% and 50% silicon alloys), the primary phase crystals have geometric shapes. This dissimilar behavior reflects the pronounced difference between aluminum, a typical metal, and silicon, which has predominantly nonmetallic properties.

It is not quite exact to speak of the two solid phases in the aluminum-silicon system as though they were pure aluminum and pure silicon, respectively. There is some solid solubility in both cases. Solid aluminum can dissolve about 1% silicon. In the alpha solid solution both aluminum and silicon atoms in the ratio of about 99:1 are randomly placed on the crystal lattice of aluminum, the face-centered cubic lattice. Similarly, the beta phase is not pure silicon but consists of silicon plus about 1% aluminum; both kinds of atoms are arranged on the diamond cubic lattice characteristic of silicon.

The following definition of a phase is a useful guide in interpreting photomicrographs. A phase is a homogeneous portion of matter that is physically distinct and mechanically separable. In the photomicrograph of the 20% silicon alloy, for example, the dark primary beta crystals are easily recognized as a phase. The fact that beta is not 100% silicon is immaterial, since the aluminum solute atoms are homogeneously distributed and are dissolved on an atomic scale that does not permit mechanical separation. On the other hand, is the background microconstituent of this photomicrograph a phase? Evidently not, since it is pos-
Possible to imagine a mechanical means of separating the small dark particles from the lighter ones. This microconstituent is the eutectic structure and consists of two phases, the dark beta and the light alpha. The beta in the eutectic structure (called secondary beta) and the large crystals of primary beta are merely different-sized particles of the same beta phase.

**Prediction of phases.** The eutectic diagram is used in exactly the same manner as the solid-solution diagram to obtain information on the chemical compositions and the amounts of the phases present. Therefore, only a single example, the 50% silicon alloy, will be considered, Fig. 6-13. At 2400°F the point determined by this temperature and the 50% silicon composition lies in the liquid-phase field. Only the liquid phase is present at this temperature. Its composition must be the same as that of the alloy, 50% silicon, and its amount is 100% of the weight of the alloy.

When the temperature of the molten alloy is lowered to about 1900°F, solidification begins with the nucleation and growth of primary crystals of beta solid solution. Typical of the phase analyses that can be made in this region of the diagram is the following at 1600°F. The alloy composition-temperature point lies in the liquid-plus-beta phase field; therefore these two phases are present. The ends of the tie line drawn across this two-phase field determine the chemical compositions of the phases: the liquid phase is 34% silicon (66% aluminum); the beta solid-solution phase is 98% silicon. These composition values can be used in applying the lever law to determine the amounts of the two phases. In this instance Eq. (6-5) can be written

$$\% \beta\text{-phase} = \left(\frac{\% \text{Si}_0 - \% \text{Si}_L}{\% \text{Si}_0 - \% \text{Si}_L}\right) \times 100,$$

or, in terms of lengths along the tie line,

$$\% \beta\text{-phase} = \frac{ab}{ac} \times 100.$$

In either case the numbers are

$$\% \beta\text{-phase} = \frac{50 - 34}{98 - 34} \times 100 = \frac{16}{64} \times 100 = 25\%.$$

Since the remaining portion of the alloy is liquid phase, there must be 75% liquid. A convenient form for recording this information is the following:

**Point—50% silicon alloy at 1600°F**

**Phases—liquid and beta**

**Compositions—34% Si and 98% Si**

**Amounts—75%**

$$\frac{50 - 34}{98 - 34} \times 100 = 25\%.$$
Fig. 6-13. The aluminum-silicon alloy system with some room-temperature microstructures. [Photomicrographs, at X100 (reproduced at two-thirds size), courtesy Aluminum Research Laboratories.]
This concise tabular presentation of phase data will be used frequently in the following pages.

As the cooling of this 50% silicon alloy is continued below 1600°F, the amount of primary beta phase increases until the eutectic temperature is reached. At this temperature the liquid phase has reached the eutectic composition, 12% silicon. On cooling through the eutectic temperature, the liquid solidifies at constant temperature to form the eutectic structure consisting of an intimate mixture of small grains of the alpha and beta phases. Since the amounts of the liquid and solid phases change at the eutectic temperature, it is impossible to determine the amounts of the phases present at exactly this temperature. A phase analysis at room temperature is representative of the condition of the alloy in the alpha-plus-beta region:

<table>
<thead>
<tr>
<th>Point</th>
<th>50% silicon alloy at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phases</td>
<td>alpha and beta</td>
</tr>
<tr>
<td>Compositions</td>
<td>1% Si and 99% Si</td>
</tr>
<tr>
<td>Amounts</td>
<td>50% and 50%</td>
</tr>
</tbody>
</table>

The lever law is applied to two solid phases in exactly the same way as to a liquid and a solid phase. The validity of this procedure will be seen when the derivation of the lever law is recalled.

The amount of beta phase (50%) given by the above calculation is the sum of the primary and secondary beta. Frequently it is necessary to calculate not the amounts of the phases but the amounts of the microconstituents. Thus, in the photomicrograph of the 50% silicon alloy at room temperature the microconstituents are (1) the primary beta crystals and (2) the eutectic structure. Consideration of the manner of solidification of this alloy will show that a calculation of the amounts of these microconstituents can be made conveniently just above the eutectic temperature. At this temperature solidification of the primary beta crystals is complete, and all the liquid present must assume eutectic structure on cooling through the eutectic temperature. If the tie line shown in Fig. 6-13 is considered to practically coincide with the eutectic horizontal, the amount of primary beta can be calculated as

\[
\% \text{ primary beta} = \frac{50 - 12}{98 - 12} \times 100 = 44\%
\]

and therefore the amount of eutectic liquid is 56%. However, since all this liquid forms eutectic structure on cooling through the eutectic temperature, there will also be 56% of eutectic structure. Changes occur-
ring between the eutectic temperature and room temperature in the amounts of the microconstituents may usually be neglected if the solvus lines are nearly vertical.

**Property variations in eutectic systems.** In a series of alloys whose compositions extend across a eutectic diagram, as in Fig. 6-13, the physical and mechanical properties might be expected to show a linear variation, Fig. 6-14. This ideal behavior, though it might be expected as the natural consequence of the linear variation in the amounts of the two phases present, is seldom found in practice. Irregularities are caused by the influence of the manner of distribution of the two phases on the properties of the alloy. For example, as the composition changes from hypoeutectic (less than eutectic) to hypereutectic (more than eutectic) in terms of metal B, the primary crystals change from alpha phase to beta phase. Since alpha and beta usually differ sharply in properties, a nonlinear change in properties across the eutectic composition would be expected.

Of still greater significance are changes in conformity with the *principle of the continuous phase*, which states that many important properties of two-phase alloys are primarily determined by the properties of the phase that forms a continuous path through the alloy. This phase need not be present in the larger amount, since less than 1% bismuth in copper can form a continuous grain-boundary network that disastrously embrittles the copper. Related to the principle of the continuous phase is the principle

![Graph](image1)

**Fig. 6-14.** Idealized variation of properties with composition in a simple eutectic alloy system.

![Graph](image2)

**Fig. 6-15.** Variation of typical properties of cast aluminum-silicon alloys across a portion of this eutectic system, Fig. 6-13.
of increasing ductility. If a two-phase alloy can be deformed or worked, there is a tendency for the continuity of the ductile phase to be increased at the expense of breakup of the brittle phase. For example, certain cast alloys can be successfully worked only by slow compression at temperatures near the melting range. After this initial deformation, however, these alloys can be worked by more conventional procedures.

As an example of property variations across an actual eutectic system, some properties of cast aluminum-silicon alloys containing up to 14% silicon are given in Fig. 6-15. Anomalies in the tensile strength and elongation values near the eutectic composition are evident.

Nonequilibrium solidification in eutectic systems. It will be recalled that rapid cooling of a solid-solution alloy from the liquid state produces a cored, inhomogeneous structure. So also may cored grains and even additional phases be produced in rapidly cooled alloys of eutectic systems. The mechanism of such nonequilibrium solidification in an aluminum-4% copper alloy is shown in Fig. 6-16. The equilibrium diagram predicts that this alloy should solidify to form grains of alpha solid solution, Fig. 6-16(b). However, during the rapid cooling that takes place in most
commercial casting operations there is not time for diffusion to occur in the growing crystals of the alpha solid solution. As a result, the composition of a complete crystal varies from about 0.5% copper at the center, which solidifies at about 1200°F, to 5.5% copper at the edge, which solidifies just above the eutectic temperature. This coring or variation in chemical composition of a solid-solution crystal can sometimes be seen under the microscope, as in the cast copper-nickel alloy, Fig. 6-8(a).

Not only coring, but also the formation of (nonequilibrium) eutectic structure can result from rapid cooling. At any temperature the average chemical composition of the cored alpha phase (Fig. 6-16) lies to the left of the equilibrium solidus line. A possible curve of average alpha-phase composition versus temperature for the 4% copper alloy is shown by a dotted line, and the corresponding extension of the eutectic-reaction horizontal is also indicated. Since this dotted curve is the logical left-hand end of tie lines for the cored 4% copper alloy, it follows that solidification has not been completed when the eutectic temperature is reached during rapid cooling. The 5-10% of eutectic liquid that is still present solidifies to produce the alpha-plus-theta eutectic structure in the spaces between the growing dendritic primary crystals, Fig. 6-16(a). This 4% copper alloy consists of a single phase, alpha, at 1000°F under equilibrium conditions. Therefore, heating the cast alloy at this temperature for sufficient time (to allow diffusion to occur) results in the production of the equilibrium structure, Fig. 6-10(b).

**Peritectic Systems**

Solid-solution formation and eutectic reaction are two important mechanisms of solidification shown by various metal systems. Another experimentally determined type of freezing, perhaps less common, is the peritectic reaction. Although superficially the peritectic diagram with its peritectic-reaction horizontal may appear to resemble a eutectic diagram, their behavior has little in common. There is no peritectic microconstituent corresponding to the eutectic structure and, in fact, the peritectic reaction consumes two phases to produce one different phase, behavior just the opposite of the eutectic reaction.

The peritectic equilibrium diagram. Although peritectic reactions are a part of such commercially significant diagrams as the iron-carbon (steel) and copper-zinc (brass) diagrams, there are only a few minor systems whose solidifications are characterized by a single peritectic reaction. The silver-platinum system, Fig. 6-17, is an example of such behavior. As usual the equilibrium diagram consists of one- and two-phase regions separated by phase-boundary lines. Of special interest is the peritectic horizontal at which the peritectic reaction occurs. It is note-
worthwhile that the peritectic composition (54% platinum) is that of the central solid phase produced by the peritectic reaction. If the solidification of an alloy of peritectic composition is considered (alloy 1 in Fig. 6-17), it is seen that primary beta-phase crystals grow in the liquid solution as the alloy is cooled to the peritectic temperature. Just above this temperature a phase analysis gives the following results:

Point—54% platinum alloy at 2200°F
Phases—liquid \( \text{and } \beta \)
Compositions—31% Pt \( \text{and } 86\% \text{ Pt} \)
Amounts—58% \( \frac{54 - 31}{86 - 31} \times 100 = 42\% \)

Slightly below the peritectic temperature a phase analysis of this alloy of peritectic composition gives this surprising information:

Point—54% platinum alloy at 2100°F
Phase—\( \alpha \)
Composition—54% Pt
Amount—100%
How did the liquid and beta phases disappear and give way to homogeneous alpha grains? The peritectic reaction that accomplishes this change on cooling can be expressed by the equation

\[
\text{Liquid} + \beta \text{ solid solution} \rightarrow \alpha \text{ solid solution}, \quad (6-8)
\]

where the chemical compositions of the liquid and beta phases are given by the end points of the peritectic-reaction horizontal and the alpha solid solution has the peritectic composition (54% platinum). Like the eutectic reaction, the peritectic reaction occurs at constant temperature under ideal equilibrium conditions. The physical picture of this reaction is a peculiar one, since the alpha phase must begin to form at the surface of the primary beta crystals, where the liquid and beta are in contact, Fig. 6-18. However, further growth of the equilibrium alpha phase can occur only as a result of diffusion (through the existing alpha) of platinum atoms from the beta phase and of silver atoms from the liquid. If sufficient time is allowed at the peritectic temperature, the formation of homogeneous alpha grains will be completed.

For a peritectic reaction to occur, it is not necessary that an alloy be exactly of peritectic composition but only that its composition pass through the peritectic horizontal. Alloy 2 in Fig. 6-17 is an example of this more general composition. To show that equilibrium diagrams allow the prediction of phase changes that occur on heating an alloy as well as on cooling, the equilibrium heating of alloy 2 will be considered. At low temperatures this alloy consists only of alpha solid solution. On heating to about 1960°F, the liquid phase begins to form from the alpha, and a typical analysis in this two-phase region is the following:

<table>
<thead>
<tr>
<th>Point</th>
<th>60% platinum alloy at 2100°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phases</td>
<td>liquid and alpha</td>
</tr>
<tr>
<td>Compositions</td>
<td>24% Pt 50% Pt</td>
</tr>
<tr>
<td>Amounts</td>
<td>40 - 24 100 = 61%</td>
</tr>
</tbody>
</table>

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<td>24% Pt 50% Pt</td>
</tr>
<tr>
<td>Amounts</td>
<td>40 - 24 100 = 61%</td>
</tr>
</tbody>
</table>
As heating is continued to just below the peritectic temperature additional liquid phase forms at the expense of the alpha, and the compositions of both liquid and alpha change to those characteristic of the peritectic reaction. On heating through the peritectic temperature, the reverse reaction of Eq. (6-8) occurs, and the remaining alpha phase decomposes into beta solid solution and additional liquid. A phase analysis typical of the liquid and beta regions gives the amounts of these two phases just above the peritectic reaction horizontal:

Point—40% platinum alloy at 2200°F
Phases—liquid and beta
Compositions—31% Pt 86% Pt
Amounts—84% \[
\frac{40 - 31}{86 - 31} \times 100 = 16\%
\]

As heating is continued, the liquid phase increases in amount until the alloy is entirely liquid above about 2480°F

**Nonequilibrium solidification in peritectic systems.** The use of peritectic equilibrium diagrams for the prediction of microstructures or of mechanical and physical properties is severely limited by the almost universal occurrence of nonequilibrium structures. For example, the 40% platinum alloy should consist of alpha-phase grains at room temperature, according to the equilibrium diagram of Fig. 6-17, but the actual structure of the cast alloy is quite different, Fig. 6-19. The reason for the persistence of the dendritic beta phase is evident from the course of the peritectic reaction shown in Fig. 6-18. The alpha phase, in forming from the liquid and beta phases, surrounds or encases the beta-phase particles. This sur-

![Fig. 6-19. The microstructure of cast silver-40% platinum alloy showing the dendritic beta phase (light) encased by the alpha phase (light gray, gray, and black). (Courtesy F. N. Rhines and McGraw-Hill Book Company.)](image-url)
rounding or encasement shields the beta phase from further reaction with
the liquid, and diffusion in the solid phases is usually insufficient to allow
equilibrium to be established during cooling.

If the solidified alloy is subjected to a combination of plastic deforma-
tion and high temperature, as in the process of hot-working, the diffusion
process is accelerated and equilibrium may be established. The physical
and mechanical properties of the alloy can then be predicted roughly by
means of the general rules given for solid-solution and for two-phase
alloys.

Non-equilibrium Solidification

In ideal solidification of alloys it is assumed that complete equilibrium
is maintained between the solid and liquid phases. Extremely slow rates
of cooling are required if this condition is to be approached; hence most
alloys actually experience nonequilibrium solidification. Several unde-
sirable results of nonequilibrium freezing have already been discussed for
solid-solution, eutectic, and peritectic alloys. This phenomenon can also
be used to purify metals, to even out nonuniformities in concentration,
and to study properties such as diffusion in the liquid phase. As a back-
ground for understanding these useful aspects of nonequilibrium solidi-
fication, it is helpful to begin with a quantitative study of practical freezing
conditions.

Segregation during normal freezing. Consider the freezing of a liquid
alloy containing a concentration, $C_s'$, of solute. If the corresponding
portion of the equilibrium diagram has the form shown in Fig. 6-20, the
first solid to form (at temperature $T_1$) has the concentration $C_L$, and the
ratio $k_0 = C_L'/C_L'$ is called the equilibrium distribution coefficient. Be-
cause the liquidus and solidus curves are straight lines in the diagram of
Fig. 6-20, at a later stage of equi-
librium freezing at temperature $T_2$
this ratio would still have the same value, although the compositions of
the phases would now be $C_L$ and
$C_L$, that is,

$$k_0 = \frac{C_L}{C_L} \quad \text{(6-9)}$$

During an actual solidification
process the layer of solid being
formed at any instant has the
SEGREGATION DURING NORMAL FREEZING

composition $C_s$ given by this equation, since equilibrium is closely approached at the liquid-solid interface. Usually it is assumed that the liquid phase has a uniform composition and that no diffusion occurs within the solidified alloy. Under these conditions the concentration of solute in the solid increases along the length of a solidifying bar in the manner shown in Fig. 6-21 for various $k$ values less than one. In Problem 9 it is shown that $k$ can also be larger than one, corresponding to the case in which the initial solid is richer in solute than the liquid from which it is forming. The concentration of solute then decreases along the length of the bar. The curves of Fig. 6-21 are based on the equation shown, in which $C_s$ is the concentration of solute in the layer of solid that solidified at the fractional length $g$, and $C_0$ is the mean solute concentration in the entire specimen. The effective distribution coefficient $k$ is used rather than $k_0$ to take account of the enriched (or impoverished) layer of liquid that tends to build up at the solid-liquid interface. In the definition analogous to Eq. (6-9), $k = C_s/C_L$, $C_s$ is the concentration of solute in the layer of solid being formed and $C_L$ is the mean concentration of all the remaining liquid.

Fig. 6-21. Segregation produced along a solidified bar during normal freezing for various values of $k$. (After Pfann.)
Zone melting. Figure 6-22 shows a convenient method for taking advantage of the difference in solute content of a liquid and the solid forming from it. A heater is used to form a molten zone of length $l$ in a bar of length $L$ and initial, uniform concentration $C_0$. The molten zone is initially at the left end of the bar. As the zone slowly progresses to the right the first solid that forms has the concentration $C_S = kC_L = kC_0$. Since this solid contains less solute than the solid that is melted by the advancing molten zone, the solute concentration of the molten zone increases, and therefore the concentration of the solidifying solid also increases. If the molten zone reaches the concentration $C_S/k$, then the solid that forms is $C_S = kC_L = k(C_0/k) = C_0$. That is, the concentration of solute is the same in the solid being formed as in the solid being melted. Use is made of this behavior in the zone-leveling technique to produce a more uniform solute concentration in a bar that initially has nonuniformities in concentration. This and other topics are fully discussed in the reference by Pfann given at the end of the chapter. Figure 6-22 shows that in the last zone length the solute concentration of the solid rises as the enriched liquid freezes. The equation shown does not hold for this final portion of the curve.
Purification of a metal by the zone-melting technique is called zone refining. Usually the molten zone is passed through the bar a number of times to produce successive improvements in the purity of the solid, as shown in Fig. 6-23. After a large number of passes, an ultimate distribution is approached as the theoretical limit. Zone refining is widely used for producing the exacting solute concentrations required in semiconductors.

**Intermediate Phases**

Most phase diagrams do not consist merely of one eutectic reaction or one peritectic reaction, but rather of a combination of the various fundamental reactions. For example, the iron-carbon diagram contains reactions of the solid-solution, peritectic, and eutectic types. In most cases the appearance of several reactions in a single binary diagram is the result of the presence of intermediate phases. These are phases whose chemical compositions are intermediate between the two pure metals, and whose crystal structures are different from those of the pure metals. This difference in crystal structure distinguishes intermediate phases from primary solid solutions, which are based on the pure metals. Some intermediate-
Fig. 6-24. The lead-magnesium diagram illustrating the division of an equilibrium diagram into independent sections by a congruently melting intermediate compound (Mg₃Pb). The cast structures of several alloys are shown by photomicrographs (X100: reproduced at two-thirds size). (Courtesy American Magnesium Corporation and Dow Chemical Company.)
phases can accurately be called intermetallic compounds when, like Mg$_2$Pb, they have a fixed simple ratio of the two kinds of atoms. However, as pointed out in Chapter 5, many intermediate phases exist over a range of compositions and are considered intermediate or secondary solid solutions.

Intermediate phases are divided on the basis of their melting behavior into congruently melting and incongruently melting phases. An incongruently melting phase decomposes into two different phases, usually one solid and one liquid phase, instead of melting in the usual manner. A peritectic reaction is produced by this kind of decomposition (see Problem 8). The peritectic composition is represented by the composition of the intermediate phase at the peritectic temperature. A congruently melting phase melts in the same manner as a pure metal. In this case the equilibrium diagram is divided into essentially independent sections. In Fig. 6-24 the congruently melting beta phase divides the lead-magnesium diagram into two eutectic reactions, each of which can be analyzed separately.

To illustrate the solidification of a typical alloy in a many-reaction diagram, the lead-10% magnesium alloy will be considered. At high temperatures the alloy is liquid, for example,

Point—10% magnesium alloy at 1000°F
Phase—liquid
Composition—10% Mg
Amount—100% liquid

Solidification begins at 900°F with the nucleation and growth of beta-phase grains. A tie line is drawn only within the two-phase region and therefore terminates at the line that represents the composition of the beta phase. An analysis just above the eutectic temperature is typical of analyses in this two-phase region. The eutectic composition is 2.5% magnesium.

Point—10% magnesium alloy at 900°F
Phases—liquid and beta
Compositions—2.5% Mg and 19% Mg
Amounts—55% and 45%

The liquid phase is of eutectic composition, and it forms eutectic structure as it cools through the eutectic temperature. The amount of eutectic structure is therefore equal to the amount of this liquid phase, namely 55%. Note that a phase calculation for the solidified alloy gives the amounts of the alpha and beta phases.
Point—10% magnesium alloy at 450°F

Phases—alpha and beta

Compositions—15% Mg

Amounts—50%

\[
\frac{10 - 1}{19 - 1} \times 100 = 50\%
\]

From the results of these phase analyses at 500 and 450°F it can be concluded that (1) the microstructure of the cast 10% magnesium alloy consists of 45% primary beta crystals and 55% eutectic structure, and (2) the eutectic structure is composed of 50/55 parts alpha phase and 5/55 parts beta phase. Sketches of similar solidification behavior are shown in Fig. 6-12 (alloy 2).

**Solid-State Reactions**

The diagrams in the preceding sections have described the decomposition of a liquid solution into a solid solution, eutectic, and so on. A solid solution can undergo exactly the same kinds of reactions, and such solid-state decompositions are of principal interest in industry. The theory and method of phase analysis are identical for liquid and solid transformations, and it is only necessary to use the slightly different words eutectoid and peritectoid in order to deal adequately with the phase relationships in the decomposition of a solid solution.

Although liquid- and solid-state reactions may be identical in phase theory, we might naturally doubt whether a solid body can decompose into one or more new phases in the same manner that a mobile, liquid solution can. This doubt is justified. Solid-state reactions differ in two important ways from liquid reactions in the manner in which they attain the equilibrium conditions predicted by the phase diagram.

1. Solid-state reactions occur much more slowly, are subject to greater hysteresis (e.g., supercooling), and rarely correspond in practice to true equilibrium conditions.

2. Solid phases consist of atoms arranged in certain crystal structures, and new solid phases forming from an existing solid phase tend to take definite positions with respect to the existing crystal structure. That is, the crystal structure of the new phase has a definite orientation relationship to the crystal structure of the phase from which it formed.

A typical orientation relationship has been described, and the geometric (Widmanstätten) pattern formed by the new phase in such cases is shown in Fig. 6-26(b). However, while slow reaction rates and orientation relationships are of great practical importance, these factors need not be considered now in connection with the study of equilibrium solid-state reactions.
Eutectoid reactions. The fact that steel can be hardened is a direct result of a eutectoid reaction, as given in the iron-carbon equilibrium diagram. (The actual heat treatment of steel is studied in detail in Chapter 14; only equilibrium changes in steel structures are considered here.) Just as a eutectic reaction involves the decomposition of a liquid solution, so does a eutectoid reaction involve the decomposition of a solid solution into two other solid phases. In Fig. 6-25 this solid solution is called austenite or the gamma solid solution. (Austenite forms from the liquid state by solid-solution freezing, which we have already studied.) The equilibrium decomposition of austenite will now be considered.

Austenite of eutectoid composition (which forms 100% austenoid struc-

![Diagram of iron-carbon equilibrium diagram showing eutectoid reaction]

**Fig. 6-25.** A portion of a simplified iron-carbon equilibrium diagram showing a eutectoid reaction with the gamma solid solution acting as the liquid solution in a eutectic reaction. (a) Ferrite (light) and pearlite (dark). (b) Austenite. (c) Pearlite (ferrite (light) and Fe₃C (dark)). (Photomicrographs X500; reproduced at two-thirds size. Courtesy J. R. Vilella, United States Steel Company.)
ture when it is slowly cooled through the eutectoid-reaction horizontal) has the simplest decomposition behavior. Alloy 1 in Fig. 6-25 has this composition, and in the austenite region of the diagram a typical phase analysis of this alloy is

Point—0.8% carbon alloy at 1400°F
Phase—gamma solid solution (austenite)
Composition—0.8% C
Amount—100%

As alloy 1 is cooled through the eutectoid-reaction horizontal the austenite phase decomposes into the alpha solid solution (ferrite) and the iron-carbide phase (Fe₃C or cementite). The nature of this eutectoid decomposition is strictly analogous to that of eutectic decomposition. The two new solid phases form side by side in a given region of the austenite to produce a nodule of pearlite, the eutectoid microconstituent. As the austenite phase is consumed by the growth of many pearlite nodules, at room temperature the nodules meet one another to form the array that is seen in a photomicrograph, such as Fig. 6-25(c). Note that a region in which a group of ferrite and cementite plates have an almost constant orientation is not called a grain of pearlite, but a nodule of pearlite. A grain, by definition, has a single orientation of space lattice. Since pearlite is composed of two phases, it evidently cannot satisfy this definition.

A phase analysis just below the eutectoid-reaction horizontal gives the results

Point—0.8% carbon at 1300°F
Phases—alpha and Fe₃C
Compositions—0.03% C (almost) 0.8% C
Amounts—88% 0.80 — 0.03 0.03 0.80 — 0.03

Since the corresponding microstructure, Fig. 6-25(c), is 100% pearlite, it follows that pearlite consists of 88% ferrite and 12% cementite.

Alloy 2 in Fig. 6-25 is a more general composition in this eutectoid system. As this alloy is cooled from the austenite region, primary ferrite crystals begin to form in the austenite grains starting at about 1500°F. As cooling continues, more ferrite forms and the composition of the austenite approaches the eutectoid composition. Just above the eutectoid temperature the phase analysis is

Point—0.4% carbon alloy at 1335°F
Phases—alpha and gamma
Compositions—0.03% C (almost) 0.8% C
Amounts—52% 0.40 — 0.03 0.80 — 0.03


In cooling through the eutectoid temperature, the austenite (which is then of eutectoid composition) changes to pearlite, the eutectoid structure. Thus the microstructure of the alloy shows about 48% pearlite and 52% ferrite. Of course the percentage of phases is quite different, as shown by the following analysis:

\[
\begin{align*}
\text{Point} & : 0.4\% \text{ carbon at } 1300^\circ F \\
\text{Phases} & : \text{alpha} \quad \text{and} \quad \text{Fe}_3\text{C} \\
\text{Compositions} & : 0.03\% \text{ C} \quad 6.7\% \text{ C} \\
\text{Amounts} & : 94\% \quad \frac{0.40 - 0.03}{6.7 - 0.03} \times 100 = 6\% \\
\text{Phases} & : \text{alpha} \quad \text{and} \quad \text{Fe}_3\text{C} \\
\text{Compositions} & : 0.03\% \text{ C} \quad 6.7\% \text{ C} \\
\text{Amounts} & : 94\% \quad \frac{0.40 - 0.03}{6.7 - 0.03} \times 100 = 6\% \\
\end{align*}
\]

In the photomicrograph of the 0.4% carbon alloy in Fig. 6-25 it is evident that the microconstituents, pearlite and (primary) ferrite, are often convenient quantities of reference. However, for other purposes, such as rating the machinability of a steel, the amount of the hard Fe\(_3\)C phase may be more useful.

**Precipitation from solid solution.** A common type of solid-state reaction is the formation of a second phase within the grains of a solid-solution phase. The reason for such precipitation of the second phase is a decrease in solubility of the solute metal in the base metal. Figure 6-26 shows a portion of the aluminum-silver diagram in which the solubility of silver in aluminum varies from almost 50% at 1000°F to only 2% near room temperature. Alloy 1, containing 20% silver, solidifies from the liquid state to form the alpha solid solution in the manner already discussed for solid-solution equilibrium diagrams. In the alpha-phase region the following analysis can be made, Fig. 6-26(a):

\[
\begin{align*}
\text{Point} & : 20\% \text{ silver alloy at } 1000^\circ F \\
\text{Phase} & : \text{alpha solid solution} \\
\text{Composition} & : 20\% \text{ Ag} \\
\text{Amount} & : 100\% \\
\end{align*}
\]

As the solid alloy is further cooled, the solubility of the silver in aluminum drops to 20% at 830°F and precipitation of the silver-rich beta solid solution begins. As cooling continues, the amount of beta phase increases, until near room temperature a phase analysis gives the following results, Fig. 6-26(b):

\[
\begin{align*}
\text{Point} & : 20\% \text{ silver alloy at } 100^\circ F \\
\text{Phases} & : \text{alpha} \quad \text{and} \quad \text{beta} \\
\text{Compositions} & : 85\% \text{ Ag} \\
\text{Amounts} & : \frac{20 - 2}{85 - 2} \times 100 = 22\% \\
\end{align*}
\]
Fig. 6–26. Simplified aluminum-silver equilibrium diagram showing precipitation from a solid solution. (a) Alpha solid solution. (b) Beta precipitate in alpha grains. (Courtesy A. H. Geisler.)

The alpha and beta phases are not in the form of a eutectic structure, since the eutectic microconstituent can be produced only by the solidification of eutectic liquid. Rather, the beta crystals precipitate as plates on the [111] planes of alpha grains. The resulting geometric pattern on the surface of a polished specimen is called a Widmanstätten structure. Since the orientations of the various alpha grains differ, the character of the Widmanstätten pattern also varies from grain to grain.

Order-disorder reactions. A solid-state transformation that has no parallel in liquid-solid reactions is the ordering of a solid solution. It will be recalled that a solid solution consists of solvent and solute atoms distributed at random on the points of the solvent metal lattice. Figure 6–27(a) is a two-dimensional representation of a body-centered solid solution of equal numbers of atoms of metal A and metal B. The disordered distribution of atoms in this solid solution is quite different from the regular arrangement in the ordered structure, Fig. 6–27(b). It is evident that
ORDER-DISORDER REACTIONS

(a) An ordinary solid solution. The atoms are in a disordered position. (b) An ordered structure.

Fig. 6-27. The arrangements of equal numbers of atoms of metal A and metal B on the points of a two-dimensional "body-centered" space lattice. (a) An ordinary solid solution. The atoms are in a disordered position. (b) An ordered structure.

Fig. 6-28. Equilibrium diagram showing the formation of an ordered structure, α', from the disordered solid solution, α.

perfect ordering of a solid solution can occur only if the two kinds of atoms are present in certain ratios, such as the 1:1 ratio shown in Fig. 6-27. Also, increased thermal vibration of the atoms at high temperatures tends to decrease the perfection of ordering. However, as shown in Fig. 6-28, the more or less perfectly ordered alpha prime (α') phase exists over a range of composition and temperature and can be distinguished from the disordered alpha phase.

The analysis of the solidification and cooling of an alloy in a diagram such as Fig. 6-28 offers no new problems. For example, the general composition, alloy 2, solidifies according to the solid-solution reaction, and at 600°F the phase analysis is
PHASE DIAGRAMS

Point—25% B alloy at 600°F
Phase—alpha
Composition—25% B
Amount—100%

As the temperature is lowered to about 420°F, the ordered structure begins to form, and at 400°F the following analysis can be made:

Point—25% B alloy at 400°F
Phases—α and α'
Compositions—24% B

\[
\text{Amounts—} \frac{25 - 24}{27 - 24} \times 100 = 33\%
\]

On further cooling, the α' structure continues to form and completely replaces α at about 330°F. At room temperature the situation is simply

Point—25% B alloy at room temperature
Phase—α'
Composition—25% B
Amount—100%

The unusual properties associated with the formation of an ordered structure are considered in a later chapter.

Ternary Systems

Since the properties of a pure metal may be improved by addition of one alloying element, why not add several and obtain a greater improvement? This is exactly what is done in practice, so that most commercial alloys are more complex than binary alloys. Metals for high-temperature service, for example, may contain ten important elements. At present there is no satisfactory method of representing phase relations in such multicomponent systems, and three-component diagrams are the most complex that are commonly encountered.

Representation of ternary systems. To plot adequately the variations of pressure, temperature, and the two concentration variables in a three-component system would require the use of four dimensions. By fixing the pressure at one atmosphere, three dimensions are sufficient. Since even this kind of plotting is inconvenient, the temperature also can be fixed to reduce the necessary diagram to two dimensions. Figure 6-29 shows the usual triangular method for plotting the two composition variables in a ternary system when the pressure and temperature are fixed.
A vertex of the diagram represents 100% of one component, such as metal A. The base of the diagram opposite the metal A vertex represents 0% of metal A, and lines parallel to this base indicate varying percentages of metal A. Thus, the point representing alloy 1 lies 20% of the distance between the base and vertex A; therefore alloy 1 contains 20% A. Similar reasoning shows that alloy 1 contains 60% B and 20% C.

This simple composition plot at constant temperature (and pressure) is valuable in determining the phase constitution of alloys. Use of the three-dimensional ternary equilibrium diagram of Fig. 6-30(a) should clarify this fact. Temperature is plotted perpendicular to the composition triangles. As usual, points in the diagram are determined by composition and temperature. Phase regions are volumes rather than areas, but the phases present in a given instance are still determined by the phase region in which the point falls. Thus, during the solidification of alloy 1 the composition-temperature point passes through the following regions: (1) liquid, (2) liquid and beta, (3) liquid, beta, and alpha, and (4) beta and alpha.

Phase analyses in ternary systems. The space diagram is not convenient for making detailed phase analyses. However, a given analysis is made at a single temperature and therefore a constant temperature section through the space diagram is adequate for the analysis. Consider the analysis of alloy 1 in the liquid region, for example at temperature \( T_1 \). The section through the space diagram at this temperature is shown in Fig. 6-30(b), and it is evident that the point lies in the liquid-phase field.
Fig. 6-30. Ternary equilibrium diagram and sections through it. The lines in the two-phase regions represent experimentally determined tie lines. (a) Space diagram. (b) Section at $T_1$. (c) Section at $T_2$. (d) Section at $T_3$. (e) Section at $T_4$. (f) Vertical section at $B'B$. 
The phase analysis is simply

Point—alloy 20% A, 60% B, (20% C) at temperature $T_1$
Phase—liquid
Composition—20% A, 60% B
Amount—100%

The other phase fields that exist at temperature $T_1$ are not involved in this analysis.

When alloy 1 cools to the temperature of the liquidus surface for this composition, solid-solution solidification begins. This solidification reaction is identical with that already studied in two-component systems, except that the beta solid solution formed in this case has both metal A and metal C atoms in solid solution on the space lattice of metal B. A typical phase analysis of alloy 1 in the liquid-plus-beta region can be made at temperature $T_2$ using the isothermal section of Fig. 6-30(c):

Point—alloy 20% A, 60% B at temperature $T_2$
Phases—liquid and beta
Compositions—21% A, 58% B
10% A, 83% B
Amounts—92%

For convenience, the lengths needed in the lever law calculation were measured on the % B composition scale. The tie lines in these isothermal sections are determined experimentally.

When a certain amount of the primary beta phase has formed, the liquid reaches a pseudoeutectic composition and a mixture of secondary beta and alpha phases begins to form in a structure similar to the eutectic microconstituent in a binary system. Temperature $T_3$ is within the range of temperatures over which the alpha and beta phases crystallize simultaneously from the liquid in alloy 1. The isothermal section at $T_3$ is shown in Fig. 6-30(d), and the following phase analysis applies. (It should be noted that the compositions of the three phases are read at the vertices of the triangular three-phase region.)

Point—alloy 20% A, 60% B at temperature $T_3$
Phases—liquid and alpha and beta
Compositions—17% A, 55% B
30% A, 38% B
18% A, 70% B

Amount—25%

$\frac{m_1}{mn} \times 100 = 19\%$
$\frac{m_2}{mn} \times 100 = 56\%$
The construction used to determine the amount of beta phase is shown in Fig. 6-30(d), and is seen to be analogous to the usual lever law relation.* Similar levers can be set up to determine the amounts of the other phases. The total amount of beta phase includes both primary crystals and the secondary beta.

When the last liquid has disappeared, only the alpha and beta phases are present. A phase analysis at a temperature $T_4$ in the solid region of the diagram can easily be made with the aid of the isothermal section given in Fig. 6-30(e):

Point—alloy 20% A, 60% B at temperature $T_4$
Phases—alpha and beta
Compositions—41% A, 33% B
11% A, 72% B
Amounts—31% $\frac{3}{5} \times 100 = 69%$

Although vertical sections through the space diagram, such as Fig. 6-30(f), bear a certain resemblance to binary diagrams, they lack an important characteristic. *Tie lines do not usually lie in the plane of a vertical section.* This can be seen by comparing the direction of the tie line through alloy 1 in Fig. 6-30(c) with the direction of the trace of section $B'B$ in this figure. This restriction on vertical sections of ternary diagrams must be borne in mind when these sections are used. Nevertheless, the vertical sections are quite valuable in showing the phases that are present in an alloy during equilibrium cooling and heating. The vertical sections also reveal the temperatures at which the various phase changes occur.

The ternary diagram of Fig. 6-30 is a relatively simple example of possible ternary systems. The construction and visualization of most technically important ternary diagrams is extremely difficult. However, once the necessary isothermal diagram sections are available, the principles illustrated in Fig. 6-30(a) are sufficient for the solution of most problems involving three-component systems.

**Gas-Metal Equilibrium**

Since the production, melting, and heat treatment of metals are carried out in the presence of gases (oxygen, nitrogen, and hydrogen, for example),

* When three phases are in equilibrium, as in this instance, their relative amounts are such that the three-phase triangle would balance in a horizontal plane if it were supported at the point representing the system composition (20% A and 60% B) and if the weights of the corresponding phases were applied at the vertices of the triangle. This visualization is the analog of Fig. 6-6 for two-phase equilibrium. Construction of the line $mn$ (through the beta-phase and system composition points) reduces the problem of determining the beta phase to that of applying the ordinary lever law.
it is evident that gas-metal reactions are possible. Many aspects of these reactions can be understood most easily by means of the appropriate gas-metal equilibrium diagram. Basically such a diagram is the same as that for an ordinary binary metal system, but it is to be expected that the gas phase and therefore the pressure variable are of greater importance.

As an example of a gas-metal diagram, the equilibrium relations between silver and oxygen are shown in Fig. 6-31 for a pressure of one atmosphere. This system is a good illustration of the importance of a gas phase, since "spitting" can occur during the freezing of silver. The diagram shows that pure silver will melt if it is heated above 1761°F, and that the liquid phase will continue at this temperature even if it dissolves oxygen gas from the surrounding atmosphere. Given sufficient time at the melting point, the composition of the liquid will change from 0% oxygen to about 0.3% oxygen. If the liquid is then cooled, the liquid phase reaches eutectic composition during solidification and then decomposes into the alpha solid solution (almost pure silver) and the gas phase. The gas bubbles rise to the surface of the solidifying mass and produce the spitting of liquid as they escape. Since this gas evolution results in a casting of poor quality, the melting of silver is preferably carried out in an atmosphere from which oxygen is excluded.

While pressure has relatively little effect on solid and liquid equilibria, it is an important factor in reactions involving gases. For example, the maximum solubility of oxygen in the alpha silver phase at a given temperature is greatly increased at higher pressures. In fact the whole appearance of Fig. 6-31 is quite different at much higher or much lower pressures; the Ag2O phase, for instance, is absent at low pressures. Although data
Fig. 6–32. The influence of pressure on the maximum solubility of hydrogen in solid metals. (Smithells.)

Fig. 6–33. The influence of temperature on the maximum solubility of hydrogen in solid and liquid nickel and iron.

are usually not available for the complete effect of pressure on gas-metal systems, the variation of maximum gas solubility $S$ with the pressure $p$ is given by Sievert's law for diatomic gases:

$$S = K\sqrt{p},$$

where $K$ is a constant that depends on temperature. Similarly, the effect
of temperature on solubility at constant pressure is given by

\[ S = A e^{-Q/RT}, \]

(6-11)

where \( A \) and \( Q \) are constants, \( R \) is the universal gas constant (which is given by 2 cal/mole·deg), and \( T \) is absolute temperature in degrees Kelvin.

Data for applying these two equations to many gas-metal problems are available in the literature. Figures 6-32 and 6-33 show some results on hydrogen solubility.

Figure 6-33 indicates that the solubility of iron for hydrogen increases suddenly at 910°C, when the iron changes from body-centered cubic to face-centered cubic. A corresponding decrease occurs at 1400°C, when the iron again reverts to the body-centered cubic structure. The large difference between the solubility of liquid and solid metals is the basis of a method for decreasing the gas content of molten metals prior to casting. The temperature of the molten alloy is allowed to fall to just below the freezing range, and as a result much of the dissolved gas is "precipitated out." If the alloy is then quickly heated to the casting temperature and cast, there is insufficient time for the gas content to increase again to the maximum value. As a result, the gas content of the final casting is significantly reduced.

Typical Industrially Important Equilibrium Diagrams

The diagrams used to illustrate the types of equilibrium usually found in metal systems were chosen for their simplicity. The average equilibrium diagram, however, is made up of a number of these simple reactions (solid-solution, peritectic, eutectic, and so on) and frequently looks complicated. Actually, such a diagram is no more difficult to analyze than one of the reactions of which it is composed, since any composition-temperature point lies only in a single reaction region. Figure 6-34 illustrates this simplifying principle for the iron-carbon system, in which solid-solution formation and peritectic, eutectic, and eutectoid reactions occur. The analysis of alloy 1, for example, involves only a peritectic reaction during solidification; there is an independent eutectoid decomposition of the gamma solid solution at lower temperatures.

A more serious problem in the commercial application of equilibrium diagrams is the fact that equilibrium is often not attained. Although each alloy system requires separate study in this connection, a common governing principle gives assurance that every alloy tends to move toward the equilibrium condition. Thus, even in the absence of ideal reactions the equilibrium diagram is an indispensable part of alloy calculations. Examples based on commercial alloys will illustrate the practical use of equilibrium diagrams.
Fig. 6-34. Iron-carbon equilibrium diagram broken down into its simple component reactions.

Fig. 6-35. The iron-carbon equilibrium diagram.
The iron-carbon system. The useful portion of the iron-carbon equilibrium diagram is shown in Fig. 6-35. Iron-carbon alloys are usually divided into three categories on the basis of composition:

1. Irons, in which the carbon content is very low and has negligible effect on properties;
2. Steels, in which the carbon content is important and usually in the range of 0.1 to 1.5% with 2.0% as a maximum value;
3. Cast irons, in which the carbon content is such as to cause some liquid of eutectic composition to solidify. The minimum carbon content is therefore about 2%, while the practical maximum is about 4.5%.

Each of these categories will be considered separately.

Irons. For special purposes, such as research problems, electrolytic iron and carbonyl iron of 99.99% purity are available. However, commercial ingot iron, Fig. 6-36(a), contains about 0.1% of various impurities (about 0.01% carbon). Iron of even this purity is relatively expensive to produce, and its use is restricted to applications where its superior ductility, corrosion resistance, electrical conductivity, or magnetic permeability with respect to the lower-cost steels is needed. Ingot iron in the form of galvanized or enameled sheets is used for such purposes as roofing and siding.

Wrought iron is not strictly an iron but consists of about 3% slag distributed in an iron matrix. During the hot-working operations involved in making the final wrought iron shapes, the slag particles become elongated, as shown in Fig. 6-36(b), and cause pronounced directional properties. These slag fibers account for the good fatigue-resistant properties of this material and perhaps contribute to its corrosion resistance. A principal application of wrought iron is in piping that handles mildly corrosive liquids like salt water.

The phase analysis of a material like ingot iron is especially easy. The metal is essentially a single phase at all temperatures, with the transition from one phase to another occurring at about the equilibrium temperature. At temperatures between 1670 and 2552°F the iron is in the face-centered cubic gamma iron condition. For example, it is hot-rolled as gamma iron. On cooling, it is transformed into body-centered cubic alpha iron; alpha iron grains appear in the photomicrograph of Fig. 6-36(a). The properties of ingot iron are relatively unaffected by the rate of cooling from high temperatures, and a water-quenched specimen is about as soft as one that has been slowly cooled.

Steels. The term plain carbon steel describes steels in which alloying elements play only a small part in determining the properties. These steels can be classified in a number of ways, two of which are shown in Fig. 6-37. It will be recalled that a steel of eutectoid carbon content, 0.8%, forms a completely pearlitic structure on slow cooling. A hypoeutectoid
Fig. 6-36. (a) Ingot iron (courtesy Armco Steel Company). (b) Wrought iron, longitudinal section, and (c) wrought iron, transverse section (both courtesy of A. M. Byers Company). (All \( \times 100 \); reproduced at three-fourths size.)

Fig. 6-37. Important steel classifications based on carbon content.
Fig. 6-38. Microstructures of a 0.3% carbon steel cast in a one inch thick section. (a) As-cast. (b) Normalized. (X100; courtesy M. F. Hawkes, Carnegie Institute of Technology.)

Steel contains proeutectoid ferrite and pearlite, while a hypereutectoid steel contains proeutectoid cementite and pearlite. These divisions are too large for many purposes, and the low, medium, and high carbon classes of steel are of more practical interest. The significance of these groupings will be illustrated in discussing cast steels and wrought steels.

CAST STEELS. The mechanical properties of a casting tend to be poorer than those of the same alloy in the wrought form, but factors such as an intricate shape or a small number of units to be manufactured may favor a steel casting. Typical uses of steel castings are in agricultural and excavating equipment. A high carbon content increases the strength of a casting but decreases its ductility; therefore most steel castings are in the medium carbon range. During slow cooling of the molten steel after it has been cast in the sand mold, the first solid phase that begins to form is delta. During further cooling, however, this is replaced by coarse austenite, which later decomposes into a Widmanstätten ferrite pattern, Fig. 6-38(a). The (white) ferrite appears at the austenite grain boundaries and as Widmanstätten plates with the (dark) pearlite. Relatively poor mechanical properties are associated with this structure. If the cast-

is heated into the austenite region (about 1600°F, in practice), the entire structure changes to relatively fine austenite grains. On air cooling,
this austenite decomposes into a correspondingly fine mixture of ferrite (white) and pearlite (dark), Fig. 6-38(b), with better properties. The heat treatment, consisting of heating a steel into the austenite region of the equilibrium diagram and then air cooling, is called normalizing.

WROUGHT STEELS. Since the mechanical properties of cast alloys are improved by plastic deformation, most steel is used in the form of wrought alloys produced by hot-working the cast ingot. Hot rolling is the lowest-cost and most common hot-working process. The temperature of hot rolling is in the austenite region; therefore a hot-rolled steel is essentially in the normalized condition after it air cools from the temperature of hot-working. Wrought steels are classified as low-, medium-, and high-carbon alloys.

Low-carbon steels are not hardened by heat treatment. A common example, ordinary boiler plate steel, contains about 0.2% carbon and is used as a general purpose, low-cost construction material. A decrease in carbon content improves the ductility. For this reason killed and rimming steels containing about 0.1% carbon are used in large quantities in the automotive industry for press forming into automobile fenders and bodies.

Medium-carbon steels are stronger than low-carbon steels and can be further strengthened by heat treatment. For example, a forging made of 0.45% carbon steel can be given about twice the strength of a low-carbon steel and still retain adequate ductility. The heat treatment frequently produces a fine pearlite harder than the coarse pearlite that results from equilibrium cooling.

The carbon content of high-carbon steels seriously reduces the ductility, and this type of steel is used only when strength or hardness is more important than ductility. Consequently, high-carbon steels are always given a hardening heat treatment. In a metal cutting tool, such as a drill, high hardness is needed to keep the cutting edge sharp. The 1.0% carbon steel that can be used for making a drill is too difficult to machine in the normalized condition. Even in the annealed (furnace-cooled) condition, high-speed machining is not commercially feasible. Therefore the iron carbide plates in the pearlite are caused to "ball up" by prolonged heating just below the eutectoid temperature. The spheroidized structure, Fig. 6-39(a), produced by this spheroidizing heat treatment is easily machined. After the drill has been made by a machining operation it is heated to 1500°F to change the steel to the austenite phase. Water quenching from this temperature does not prevent the decomposition of the austenite but causes it to occur at a low temperature, about 500°F, and results in the formation of hard martensite, Fig. 6-38(b), rather than soft pearlite. The nature of martensite is discussed in Chapter 14; essentially it is body-centered cubic iron that has formed almost instantaneously from the austenite. The carbon atoms, which were dissolved in the austenite, are
trapped in the body-centered cubic structure and harden it by distorting the lattice. To relieve the stresses produced by the quenching operation, the drill is tempered at 400°F for an hour. The tempering heat treatment also allows the carbon atoms to begin the process of forming Fe₃C, but the tempered martensite now present in the drill is still hard and has little ductility.

Wrought carbon steel is also used in the cold-worked condition. Of the many purposes for which cold-working may be used some of the more important are (1) to improve the machinability of low-carbon steel by decreasing its ductility, (2) to produce steel with a good surface finish and close dimensional tolerances, and (3) to increase the strength of steel in such forms as cold-drawn wire for suspension bridge cables.

**ALLOY STEELS.** When alloying elements are added to steel, both solid-solution and compound formation usually occur, as in most metal systems. However, the presence of both iron and carbon in the steel leads to the peculiar circumstance that the solid solution is formed with the iron, while the compound is usually a carbide. If only a single alloying element is being considered, information on the phases present in a given alloy can be obtained from the corresponding ternary equilibrium diagram. Figure 6-40 shows a phase analysis of a 2% manganese, 1% carbon steel, using an isothermal section of the iron-manganese-carbon diagram.
If similar phase analyses are made of steels of various manganese contents (see Problem 19), it is found that the manganese content of the alloy influences not only the manganese content of the solid solution but also that of the carbide.

Most commercial alloy steels must be treated as at least four-component systems, and few of the corresponding equilibrium diagrams are available. However, qualitative information on the tendency of the individual alloying elements in such steels to form a solid solution or a carbide phase can be given in a table like Table 6-1. A given alloying element (manganese, for example) will typically form both a solid solution and a carbide. The position of the $X$ in Table 6-1 with respect to the lines representing (complete) solid-solution or carbide formation roughly denotes the proportion of the alloying element that enters each of these phases. The $X$ for manganese, for example, indicates that about three-quarters of the manganese in a typical steel is in solid solution in the iron, while the remaining one-quarter is in the carbide phase. A number of elements, such as silicon, dissolve entirely in the solid solution. Others, like titanium, are almost completely combined in carbide phases.

Each alloying element in steel produces specific effects. However, there are a number of general property changes associated with the formation of any carbide phase or of any solid solution. Since the carbide particles are hard, they increase wear resistance, decrease machinability, and slightly increase the hardness of the alloy. These particles may also...
### Table 6-1
**Distribution of Alloying Elements in Steels**

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Tends to form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>X</td>
</tr>
<tr>
<td>Silicon</td>
<td>X</td>
</tr>
<tr>
<td>Aluminum</td>
<td>X</td>
</tr>
<tr>
<td>Nickel</td>
<td>X</td>
</tr>
<tr>
<td>Cobalt</td>
<td>X</td>
</tr>
<tr>
<td>Manganese</td>
<td>X</td>
</tr>
<tr>
<td>Chromium</td>
<td>X</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>X</td>
</tr>
<tr>
<td>Tungsten</td>
<td>X</td>
</tr>
<tr>
<td>Vanadium</td>
<td>X</td>
</tr>
<tr>
<td>Columbium</td>
<td>X</td>
</tr>
<tr>
<td>Titanium</td>
<td>X</td>
</tr>
</tbody>
</table>

### Table 6-2
**Effect of Alloying Elements in Strengthening Ferrite**

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Approximate increase in yield strength of ferrite per 1% alloying element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>100,000</td>
</tr>
<tr>
<td>Beryllium</td>
<td>90,000</td>
</tr>
<tr>
<td>Silicon</td>
<td>15,000</td>
</tr>
<tr>
<td>Manganese</td>
<td>14,000</td>
</tr>
<tr>
<td>Nickel</td>
<td>12,000</td>
</tr>
<tr>
<td>Titanium</td>
<td>10,000</td>
</tr>
<tr>
<td>Aluminum</td>
<td>6,000</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>4,000</td>
</tr>
<tr>
<td>Tungsten</td>
<td>3,000</td>
</tr>
<tr>
<td>Vanadium</td>
<td>3,000</td>
</tr>
<tr>
<td>Cobalt</td>
<td>2,000</td>
</tr>
<tr>
<td>Chromium</td>
<td>1,000</td>
</tr>
</tbody>
</table>
prevent grain coarsening when the steels are heated into the austenite region. A few carbides are capable of markedly hardening the steel by a precipitation-type reaction (see Chapter 13), but usually these particles act like inert granules in the steel. On the other hand, when an alloying element is present in solid solution, it very actively influences most of the properties of the steel. Not only does it appreciably increase hardness and strength, as shown in Table 6-2, but it also affects corrosion resistance, electrical properties, and that most important quality, hardenability, which is considered in detail in Chapter 14.

Cast irons. Perhaps even more strikingly than the steels, the cast irons show the influence of factors other than those shown in the equilibrium diagram in determining the final structure and properties of an alloy. Fundamental to this fact is the instability of iron carbide. At all temperatures the following reaction tends to occur:

\[ \text{Fe}_3\text{C} \rightarrow 3 \text{Fe} + \text{C} \text{ (graphite)}. \]  

(6-12)

At low temperatures, however, the reaction occurs so slowly that iron carbide can exist for thousands of years and so is said to be metastable. At higher temperatures, especially if silicon is present as an alloying element in the iron, rapid graphitization of the iron carbide can take place. If graphitization is complete, the iron-graphite equilibrium diagram (Fig. 6-42) adequately represents the actual structure. For many commercial alloys in which only partial decomposition of the iron carbide occurs, both the iron-carbon diagram, Fig. 6-35, and the iron-graphite diagram must be used.

**White cast iron.** If a cast iron containing 3.0% carbon is rapidly cooled from the molten condition, no graphitization occurs, and the alloy is called white cast iron, Fig. 5-36(a). The manner of solidification of a white cast iron can be determined approximately from the iron-carbon diagram, Fig. 6-35. In cooling to 2066°F the austenite forms from the molten alloy as dendrites; about 50% of the alloy solidifies in this manner. At 2066°F the liquid reaches the eutectic composition, 4.3% carbon, and solidifies as a eutectic of austenite and cementite, called ledeburite. In the photomicrograph of Fig. 6-41(a), this eutectic appears mostly as white cementite and surrounds the fernlike dendrite arms. As the cast iron cools from 2066 to 1333°F, the austenite changes in carbon content from 2.0 to 0.8% by precipitating iron carbide. This additional iron carbide builds up largely on cementite particles already present. At 1333°F the austenite changes to the eutectoid of ferrite and cementite, pearlite. In Fig. 6-41(a) the dark areas are pearlite (too fine to be resolved at the magnification employed) and the white areas are cementite. The analysis used here is only approximate because (1) the alloy is cooled too rapidly for equilibrium to be established, and (2) the ternary Fe-C-Si diagram should have been
used,* since white cast irons contain about 1% silicon. In spite of these approximations the analysis is adequate for many purposes.

Rapid cooling prevents graphitization of the cementite in white cast iron, but if the casting is reheated to about 1600°F graphite is slowly produced in a distinctive form known as temper carbon. The resulting alloy, Fig. 6-41(b), is called malleable cast iron. The matrix† of the alloy may be ferrite, or it may be pearlite if the alloy is more rapidly cooled from a temperature above 1333°F at the end of the malleableizing treatment. The hard, brittle cementite makes white cast iron undesirable except at the surface of some gray iron castings, where it is useful for wear resistance. Nevertheless, large tonnages of white iron castings are made for conversion into malleable iron castings, which are widely employed in industrial and farm machinery.

GRAY CAST IRON. The most common type of cast iron is gray cast iron, in which flakes of graphite form during the solidification of the casting.

* Silicon plays such a significant part in determining the structure of cast irons (see Fig. 6-44, for example) that it is more exact to consider that cast irons are iron-carbon-silicon alloys, not simply iron-carbon alloys. The binary iron-carbon diagram is used in this introductory treatment as a convenient simplification.

† The matrix of a structure is the major portion in which a minor part is embedded. In Fig. 6-41(b) the matrix (or background material) is ferrite, in which the graphite is embedded.
Fig. 6-42. The iron-graphite equilibrium diagram.

An approximate analysis of the solidification of a 3.0% carbon alloy can be made with the aid of the iron-graphite equilibrium diagram, Fig. 6-42. As the molten alloy cools to 2075°F, dendrites of the austenite phase form within the liquid. At 2075°F the liquid reaches eutectic composition and solidifies as a eutectic of austenite and graphite. A phase analysis just below 2075°F yields

Point—3.0% carbon alloy at 2070°F
Phases—austenite and graphite
Compositions—2.9% C and 100% C
Amounts—99% 3 - 2
\[
\frac{100 - 2}{100} \times 100 = 1.0\%
\]

As the solidified alloy continues to cool, additional graphite forms from the austenite, while the austenite approaches the eutectoid composition, 0.7% carbon. Just above the eutectoid temperature the phase analysis is

Point—3.0% carbon alloy at 1365°F
Phases—austenite and graphite
Compositions—0.7% C and 100% C
Amounts—99.7% 3 - 0.7
\[
\frac{100 - 0.7}{100} \times 100 = 2.3\%
\]

An approximate analysis of the solidification of a 3.0% carbon alloy can be made with the aid of the iron-graphite equilibrium diagram, Fig. 6-42. As the molten alloy cools to 2075°F, dendrites of the austenite phase form within the liquid. At 2075°F the liquid reaches eutectic composition and solidifies as a eutectic of austenite and graphite. A phase analysis just below 2075°F yields

Point—3.0% carbon alloy at 2070°F
Phases—austenite and graphite
Compositions—2.9% C and 100% C
Amounts—99% 3 - 2
\[
\frac{100 - 2}{100} \times 100 = 1.0\%
\]

As the solidified alloy continues to cool, additional graphite forms from the austenite, while the austenite approaches the eutectoid composition, 0.7% carbon. Just above the eutectoid temperature the phase analysis is

Point—3.0% carbon alloy at 1365°F
Phases—austenite and graphite
Compositions—0.7% C and 100% C
Amounts—99.7% 3 - 0.7
\[
\frac{100 - 0.7}{100} \times 100 = 2.3\%
\]
The eutectoid austenite may decompose into a mixture of ferrite and graphite, but this additional graphite merely adds to existing graphite flakes, rather than appearing as a separate eutectoid microconstituent. Figure 6-43(a) shows the microstructure of such a ferritic gray cast iron. It is noteworthy that etching is not necessary to reveal the graphite in a cast iron. The microstructure of Fig. 6-43(a) is not greatly changed by etching. It is possible to cause the eutectoid austenite to decompose into pearlite (or into a mixture of ferrite and pearlite) and thus produce a pearlitic gray cast iron like that shown in Fig. 6-43(b).
Two factors determine what structure (white, ferritic gray, pearlitic gray, etc.) a cast iron will have on solidification. These factors are composition and cooling rate. Figure 6-44 is a schematic structural diagram of the effects of carbon and silicon contents and of cooling rate on the microstructure of cast irons. It shows that an increase in cooling rate decreases the tendency to form graphite. An increase in carbon or silicon content, on the other hand, promotes graphitization. Some alloying elements, nickel for example, have essentially the same effect as silicon; that is, they increase the graphitization tendency. Other alloying elements (chromium and molybdenum) stabilize the iron carbide and thus decrease the graphitization tendency. Additional benefits of alloy additions to cast iron are (1) refining the graphite flake size, (2) strengthening the matrix, and (3) improving machinability by preventing the formation of white or mottled iron at edges or thin sections of the casting.

Since a cast iron containing coarse graphite flakes has low strength, various means are used to modify the graphite distribution. Finer graphite flakes tend to form when the alloy is superheated just before casting. A finer flake size can also be produced by inoculating the molten alloy. Typical inoculants are ferrosilicon and calcium-silicon, very small amounts of which are effective in reducing flake size, presumably by causing rapid nucleation. Graphite nodules rather than graphite flakes will form if the molten alloy is treated with magnesium or cerium. The resulting nodular cast iron, Fig. 6-43(c), has superior strength and ductility.

The mechanical properties of cast irons are determined by the standard
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tensile strength, lb/in²</th>
<th>Yield strength, lb/in²</th>
<th>Elongation in 2 inches, %</th>
<th>Modulus of rupture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferritic gray cast iron</td>
<td>25,000</td>
<td>---</td>
<td>0.5</td>
<td>50,000</td>
</tr>
<tr>
<td>Pearlitic gray cast iron</td>
<td>45,000</td>
<td>---</td>
<td>0.5</td>
<td>65,000</td>
</tr>
<tr>
<td>Nodular cast iron</td>
<td>80,000</td>
<td>50,000</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Malleable cast iron</td>
<td>55,000</td>
<td>35,000</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>Cast steel (as cast)</td>
<td>74,000</td>
<td>34,000</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>Cast steel (normalized)</td>
<td>76,000</td>
<td>38,000</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td>Machine steel, 0.2% C</td>
<td>50,000</td>
<td>27,000</td>
<td>35.0</td>
<td></td>
</tr>
<tr>
<td>Hardened and tempered 0.45% C steel</td>
<td>100,000</td>
<td>65,000</td>
<td>28.0</td>
<td></td>
</tr>
<tr>
<td>Wrought iron</td>
<td>50,000</td>
<td>30,000</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>Ingot iron</td>
<td>45,000</td>
<td>30,000</td>
<td>40.0</td>
<td></td>
</tr>
<tr>
<td>Cold drawn 0.80% C steel</td>
<td>200,000</td>
<td>150,000</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Spheroidised 1.0% C steel</td>
<td>80,000</td>
<td>45,000</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>Hardened and tempered 1.0% C steel</td>
<td>250,000</td>
<td>200,000</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
tests, which are discussed in Chapter 9, but in addition the transverse bend test is often employed. In a typical test of this type a bar 1.2 inches in diameter is supported on two knife edges 18 inches apart and is broken by a load applied midway between the two supports. Significant data obtained from this test are the maximum deflection at the center of the bar before fracture and the load necessary to cause fracture. The breaking load is often reported directly, but it may be converted to a modulus of rupture, which is closely related to the breaking stress in the outer fiber:

$$\text{Modulus of rupture} = \frac{M}{cI},$$

where $M$ is the maximum bending moment, $c$ is the distance from the center of the bar to the outer fiber, and $I$ is the section moment of inertia. The modulus of rupture is useful in designs involving lengths of cast iron unsupported in the center, such as lengths of pipe subjected to heavy loading.

**Properties of iron-carbon alloys.** Since iron-carbon alloys are in a price range significantly below that of other structural materials (brass, aluminum alloys, etc.), naturally their use is widespread. However, within this iron-carbon group there are also cost differences which, together with properties, determine the choice of material for a given application. The final cost of a completed metal part is determined by so many factors that the classification here can only be considered suggestive. In Table 6-3 various iron-carbon alloys are listed in approximate order of cost together with typical mechanical properties. The significance of these properties in design is considered in greater detail in subsequent chapters. Alloy steels are discussed in Chapter 14.

**Copper alloys.** The low strength of copper restricts its use as an engineering material. Fortunately, there are a number of ways in which copper can be strengthened. These include cold-working, order hardening, precipitation hardening, and solid-solution formation. Solid-solution formation is the most versatile, the cheapest, and the most widely used of these hardening methods.

**Brasses.** The equilibrium diagram of Fig. 6-45 shows that almost 40% zinc can dissolve in solid copper to form the alpha solid solution. The corresponding changes in tensile strength and percent elongation are plotted in Fig. 6-46. Since zinc is less expensive than copper, the alloys are actually cheaper than pure copper, but the corrosion resistance of the bronzes is generally inferior to that of copper. Desiccation, the loss of zinc at high temperatures or in certain corrosive media, and season cracking, grain-boundary corrosion in cold-worked alloys, are two special corrosion phenomena present in bronzes that contain more than 15% zinc. (See Chapter 10.)
COPPER ALLOYS

When maximum corrosion resistance is not essential, cartridge brass (70% Cu, 30% Zn) gives a good combination of strength and ductility. For example, its good cold-working characteristics are used in the deep drawing of a flashlight case. The machinability of such alpha brasses can be improved by the addition of lead, but only with some sacrifice of cold-working properties. Admiralty metal is essentially cartridge brass with 1% tin replacing part of the zinc. Its improved corrosion resistance makes it suitable for use in condenser tubes. Red brass (85% Cu, 15% Zn) is used for applications such as plumbing pipe, where its good corrosion resistance is needed. Still better corrosion resistance is given by commercially pure tough pitch copper in such applications as chemical process equipment. Large quantities of copper are used also by the electrical industries.

With increases in zinc content above the alpha solid-solution range,
### Table 7-4

**Properties of Several Brasses**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition, %</th>
<th>Tensile strength, lb/in²</th>
<th>Yield strength, lb/in²</th>
<th>Elongation in 2 inches, %</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Zn</td>
<td>Sn</td>
<td>Pb</td>
<td>Mn</td>
</tr>
<tr>
<td>Wrought Alloys (annealed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gilding metal</td>
<td>95</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commercial bronze</td>
<td>90</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red brass</td>
<td>85</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low brass</td>
<td>80</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cartridge brass</td>
<td>70</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow brass</td>
<td>65</td>
<td>35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muntz metal</td>
<td>60</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low-lead brass</td>
<td>64.5</td>
<td>35</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium-lead brass</td>
<td>64</td>
<td>35</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Free-cutting brass</td>
<td>62</td>
<td>35</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Admiralty metal</td>
<td>71</td>
<td>28</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naval brass</td>
<td>60</td>
<td>39</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganese bronze</td>
<td>58.5</td>
<td>39.2</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast Alloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast red brass</td>
<td>85</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Cast yellow brass</td>
<td>60</td>
<td>38</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cast manganese bronze</td>
<td>58</td>
<td>39.7</td>
<td>1</td>
<td>Al</td>
<td>1  Fe</td>
</tr>
</tbody>
</table>
the structure of bronzes changes to a mixture of the alpha and beta phases. This two-phase structure has relatively poor ductility, but high strength. The Muntz metal composition (60% Cu, 40% Zn) combines the strength of the alpha and beta mixture at room temperature with the increased ductility of a one-phase structure at high temperatures. Figure 6-45 shows that Muntz metal consists of only the beta phase at temperatures above 1400°F. The beta phase is soft and plastic in this range of temperatures, and therefore Muntz metal can be hot rolled, extruded, or forged. During cooling to room temperature the strong two-phase structure is produced by precipitation of alpha. Figure 6-47 shows the microstructures of Muntz metal after various treatments. It is seen that precipitation of the alpha phase can be partially prevented by rapidly cooling the beta phase, Fig. 6-47(b). Such control of phase changes is typical of solid-state reactions, and in this case it can be used to obtain smaller alpha particles by using a later precipitation heat treatment, Fig. 6-47(c). Naval brass, an alloy with improved corrosion resistance for such uses as marine hardware, is obtained by replacing about one percent of the zinc in Muntz metal by tin.

The bronzes considered so far have been wrought bronzes, that is, bronzes that are used after being rolled or forged, etc. Bronzes that are to be used in the cast condition must have, in addition to adequate strength and ductility, good machinability and good casting qualities. These properties are improved by the addition of elements such as lead and tin; therefore simple binary copper-zinc alloys are seldom used for castings. Cast red brass (85% Cu, 5% Zn, 5% Sn, 5% Pb) is an example of an alloy that has good corrosion resistance. Cast yellow brass (60% Cu, 38% Zn, 1% Sn, 1% Pb) is a lower-cost material for general use, for example, in plumbing supplies. The properties of these and other bronzes are given in Table 6-4.

Bronzes. The word bronze has come to mean so many different things (witness commercial bronze and manganese bronze in the table of bronzes) that it is useless to hold to its original definition as an alloy of copper and tin. In addition to tin-bronzes, there are aluminum-bronzes, silicon-bronzes, beryllium-bronzes, and many more. A few complications exist even in this system of naming, since the terms usually employed are beryllium-copper and nickel-silver rather than beryllium-bronze and nickel-bronze.

The bronzes cost more than brass, but such superior properties as corrosion resistance and strength justify their use in many applications. Almost all the improvement in corrosion resistance and much of the increase in strength is the result of solid-solution formation, the extent of which is shown in Table 6-5. Some of the bronzes can be further strengthened by heat treatments involving precipitation hardening or eutectoid decomposition, which are discussed in later chapters. Information on several bronzes
Fig. 6-47. Photomicrographs of Muntz metal (60% Cu, 40% Zn). (a) Extruded alloy slowly cooled. Alpha phase is light, beta is dark. (b) Extruded alloy reheated to the beta region and quenched. Alpha phase is dark, beta is light. (c) Extruded and quenched alloy reheated to precipitate additional alpha phase. (X75; reproduced at three-fourths size.) (Courtesy American Brass Company.)

<table>
<thead>
<tr>
<th>System</th>
<th>Maximum solid solubility</th>
<th>Maximum tensile strength of solid solution, lb/in²</th>
<th>Elongation in 2 inches, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper-tin</td>
<td>15% Sn</td>
<td>70,000</td>
<td>70</td>
</tr>
<tr>
<td>Copper-aluminum</td>
<td>9% Al</td>
<td>75,000</td>
<td>65</td>
</tr>
<tr>
<td>Copper-copper</td>
<td>8% Si</td>
<td>70,000</td>
<td>25</td>
</tr>
<tr>
<td>Copper-nickel</td>
<td>100%</td>
<td>75,000</td>
<td>45</td>
</tr>
<tr>
<td>Copper-beryllium</td>
<td>2% Be</td>
<td>72,000</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 6-5

Solid Solution Formation in Bronzes
### Properties of Several Brasses

<table>
<thead>
<tr>
<th>Table 6-6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Copper Alloys</strong></td>
</tr>
<tr>
<td><strong>Condition</strong></td>
</tr>
<tr>
<td><strong>Co</strong></td>
</tr>
<tr>
<td><strong>As-cast</strong></td>
</tr>
<tr>
<td><strong>N</strong></td>
</tr>
<tr>
<td><strong>C</strong></td>
</tr>
<tr>
<td><strong>Si</strong></td>
</tr>
<tr>
<td><strong>Mn</strong></td>
</tr>
<tr>
<td><strong>Sn</strong></td>
</tr>
<tr>
<td><strong>Cr</strong></td>
</tr>
<tr>
<td><strong>P</strong></td>
</tr>
<tr>
<td><strong>S</strong></td>
</tr>
<tr>
<td><strong>Hg</strong></td>
</tr>
<tr>
<td><strong>As-cast</strong></td>
</tr>
<tr>
<td><strong>N</strong></td>
</tr>
<tr>
<td><strong>C</strong></td>
</tr>
<tr>
<td><strong>Si</strong></td>
</tr>
<tr>
<td><strong>Mn</strong></td>
</tr>
<tr>
<td><strong>Sn</strong></td>
</tr>
<tr>
<td><strong>Cr</strong></td>
</tr>
<tr>
<td><strong>P</strong></td>
</tr>
<tr>
<td><strong>S</strong></td>
</tr>
<tr>
<td><strong>Hg</strong></td>
</tr>
<tr>
<td><strong>As-cast</strong></td>
</tr>
<tr>
<td><strong>N</strong></td>
</tr>
<tr>
<td><strong>C</strong></td>
</tr>
<tr>
<td><strong>Si</strong></td>
</tr>
<tr>
<td><strong>Mn</strong></td>
</tr>
<tr>
<td><strong>Sn</strong></td>
</tr>
<tr>
<td><strong>Cr</strong></td>
</tr>
<tr>
<td><strong>P</strong></td>
</tr>
<tr>
<td><strong>S</strong></td>
</tr>
<tr>
<td><strong>Hg</strong></td>
</tr>
</tbody>
</table>

**Note:** The table provides a summary of properties for various copper alloys, including Co, Zn, Pb, N, C, Si, Mn, Sn, Cr, P, S, and Hg concentrations, along with typical applications. The table is designed to help users understand the characteristics and uses of these materials.
is given in Table 6-6. An important property of nickel-silvers is their silvery color, which promotes their use as tableware and in restaurant and dairy equipment. The high-strength alloys, aluminum-bronze and beryllium-copper, cost appreciably more than the standard tin-bronzes.

**Magnesium alloys.** Commercial magnesium alloys illustrate many aspects of practical alloying. Magnesium metal produced by the electrolysis of molten salts has a tensile strength of only 10,000 lb/in² in the cast condition. The strength can be increased severalfold by the use of various alloying elements, but the ductility and corrosion resistance tend to be lowered by some of these added elements. Although very many specific magnesium alloys are used for a variety of applications, most of them contain aluminum as the principal strengthening alloying element, with zinc and manganese added for improved corrosion resistance. Since the zinc and manganese usually dissolve in the alpha and beta solid solutions, it is possible to interpret many magnesium alloy structures satisfactorily on the basis of the magnesium-aluminum equilibrium diagram, Fig. 6-48.

**Cast magnesium alloys.** A typical alloy for sand or permanent mold casting is AZ92, whose composition* and properties are given in Table 6-7. Although no eutectic structure should form during the equilibrium cooling of a 9% aluminum composition, according to the diagram of Fig. 6-48,

---

* Note that the principal alloying elements and their approximate amounts are indicated by the ASTM designation. Thus AZ92 contains 9% aluminum and 2% zinc.
<table>
<thead>
<tr>
<th>Use</th>
<th>Am. Soc. of Testing Mat's designation</th>
<th>Composition, %</th>
<th>Condition</th>
<th>Tensile strength, lb/in²</th>
<th>Yield strength, lb/in²</th>
<th>Elongation in 2 inches, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand and permanent mold</td>
<td>A292</td>
<td>9.0</td>
<td>2.0</td>
<td>0.1</td>
<td>0.2</td>
<td>As-cast 24,000 14,000 2</td>
</tr>
<tr>
<td>Die casting</td>
<td>A291</td>
<td>9.0</td>
<td>0.7</td>
<td>0.2</td>
<td>0.2</td>
<td>As-cast 33,000 21,000 3</td>
</tr>
<tr>
<td>Sheet</td>
<td>A231X</td>
<td>3.0</td>
<td>1.0</td>
<td>0.2</td>
<td>0.2</td>
<td>As-cast 35,000 20,000 15</td>
</tr>
<tr>
<td>Structural shapes</td>
<td>A250X</td>
<td>8.5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.2</td>
<td>Extruded 48,000 32,000 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Extruded and aged 52,000 37,000 8</td>
</tr>
<tr>
<td></td>
<td>ZK60A</td>
<td>6.0</td>
<td>0.6</td>
<td>Zr</td>
<td></td>
<td>Extruded 49,000 38,000 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Extruded and aged 51,000 42,000 10</td>
</tr>
</tbody>
</table>
the structure of the cast alloy, Fig. 6-49(a), shows clear evidence of the solidification of eutectic liquid around the alpha solid solution. Massive particles of the beta solid solution form during solidification of the eutectic liquid. This type of eutectic structure (in which the two solid phases tend to form large, separate pieces) is called a *divorced eutectic*. During further cooling of the solidified casting, a lamellar precipitate forms at the grain boundaries and around the beta-phase particles. It will be recalled (Fig 6-16) that nonequilibrium cooling is responsible for the presence of liquid of eutectic composition during the solidification of this alloy.
MAGNESIUM ALLOYS

Since beta is a brittle intermediate phase, the ductility and strength of the alloy can be improved by dissolving this phase by means of a solution heat treatment. The alloy is well within the alpha-phase region of the diagram at 770°F, and after 20 hours at this temperature the alloy remains almost completely single phase on air cooling to room temperature. Fig. 6-49(b). The strength of the casting can be further improved, but with a loss in ductility, by causing the beta phase to precipitate in a finely divided form in the alpha grains. The equilibri um diagram shows that a mixture of alpha and beta phases is stable at room temperature; therefore it is only necessary to heat the supersaturated alpha solid solution to a temperature at which the atoms have sufficient mobility to cause some precipitation of beta phase to take place. This precipitation or aging heat treatment is carried out by heating the solution-treated alloy to 425°F for 5 hours. Figure 6-49(c) shows the microstructure that results from this treatment.

A preferred magnesium alloy for die casting is AZ91 (Table 6-7). Its microstructure, Fig. 6-50, shows eutectic structure surrounding the alpha solid-solution dendrites. The finer structure, compared with the sand-cast magnesium alloy, is a result of the faster cooling rate of a die casting.

Wrought magnesium alloys. A typical magnesium alloy available in sheet form is AZ31X (Table 6-7). When the sheet is to be formed, by deep drawing for example, it is supplied in the annealed temper. The corresponding microstructure is shown in Fig. 6-51(a). The strength of the alloy is increased if it is subjected to cold rolling, and the hard temper material produced in this manner is superior for applications not involving a forming operation or shock loading. The microstructure of the cold-rolled alloy, Fig. 6-51(b), shows the distorted grains produced by the severe plastic deformation. The small amount of beta phase present in this alloy is usually found at the grain boundaries.

Structural shapes of magnesium alloys are usually formed by extrusion or forging rather than by hot rolling. A typical alloy for these applications is AZ31X (Table 6-7). Since the extruded alloy is air cooled from the extruding temperature, 720°F, its structure at room temperature consists

![Fig. 6-50. Microstructure of die-cast magnesium alloy AZ91. (X500; reproduced at three-fourths size.) (Courtesy P. F. George, Dow Chemical Company.)](image-url)
FIG. 6-51. Microstructures of wrought magnesium alloy AZ31X. (a) AZ31X-O in annealed temper. (b) AZ31X-H24 in hard temper. (X250.)

FIG. 6-62. Microstructure of wrought magnesium alloy AZ80X. (a) as-extruded and aged. (X250.) (Courtesy P. F. George, Dow Chemical Company.)
TITANIUM ALLOYS

of alpha solid solution in which beta phase has precipitated at the grain boundaries, Fig. 6-52(a). Heat treatment of this alloy consists simply in aging the extruded alloy for about 20 hours at 350°F. Figure 6-52 presents the microstructure of the aged alloy showing a fine precipitate of the beta phase. A high-strength extrusion alloy, ZK60A, contains about 6% zinc and 0.6% zirconium. The fine grain size produced and maintained by the zirconium is responsible for the excellent mechanical properties of this alloy, Table 6-7. Recently developed magnesium alloys for use at elevated temperatures exploit rare-earth metals or thorium as alloying elements. One of these alloys, HK31A, is listed in Table 9-6 in a later section on high-temperature properties.

Magnesium alloys are used principally where light weight is important, and so find extensive application in aircraft. Many uses of sheet magnesium alloys depend on their good resistance to atmospheric corrosion. The higher initial cost in comparison with steel has been the principal factor limiting the extensive use of magnesium alloys.

Titanium alloys. The attractive properties of titanium alloys are their high strength-to-weight ratio (density is 4.5 gm/cm³) and their excellent corrosion resistance in many media. These useful properties have aroused much interest in titanium alloys during recent years, with the result that several grades of commercially pure titanium and numerous alloys have been developed. The alloying and heat-treatment of titanium are dominated by the allotropic transformation at 1625°F from the hexagonal alpha phase to the body-centered cubic beta phase. Some alloying elements (Al, Sn, C, O, N) stabilize the alpha phase and can be used to make alloys based on this phase. The most important commercial alloy of the alpha type is Ti-5Al-2.5Sn. Oxygen, carbon, and nitrogen are usually considered as impurities in titanium, but small quantities of oxygen or nitrogen are useful in improving the response to heat treatment. Most alloying elements stabilize the beta phase and cause it to exist as the stable phase at temperatures considerably below 1625°F. This behavior is the basis of the commercial alpha-beta alloys whose heat treatment will now be considered.

The most important beta-stabilizing elements are iron, manganese, chromium, molybdenum, and vanadium. Since each of these elements has a similar effect on the solid-phase reactions in titanium, it is convenient to discuss the behavior of titanium alloys using the generalized phase diagram shown in Fig. 6-53. Strictly speaking, this diagram is correct only for Ti-Mo and Ti-V alloys, since a eutectoid reaction exists for the other three metals at the position shown. However, the eutectoid reaction is sluggish, and usually its effects can be neglected. The shaded zone in the diagram marks the dividing line between "lean" alloys, in which the
Treatment: quenched from alpha-beta field. Lean beta.
Structure: primary alpha, alpha prime, some retained beta.

Treatment: quenched from beta field. Structure: alpha prime (titanium martensite).

Beta phase of greater alloy content is retained on quenching (about 3.5% Fe, 8.5% Mn or Cr, 10% Mo, 19% V).

Eutectoid reaction in sluggish in Ti-Cr, Ti-Mo, and Ti-Mn systems. Initial stages of aging see similar to beta-case of beta-cosmetic systems Ti-Mo, Ti-Mn, and Ti-V.

Treatm ent: quenched from beta field, aged at temperature shown.
Structure: alpha in beta matrix.

Fig. 6-31. Generalized phase diagram for alpha-beta titanium alloys and examples of structures produced by various heat treatmetts (reproduced at two-thirds size). (Courtesy P. D. Frost, Battelle Memorial Institute.)
beta phase is not retained on quenching, and alloys "rich" in solute, which do retain the beta phase on quenching. The importance of this distinction will become evident in the following consideration of possible structures in titanium alloys.

Point A in Fig. 6-53 represents a rich alloy that has been heated into the beta-phase field. The coarse beta grains are retained on quenching, as shown in the corresponding photomicrograph. A fine grain size, which gives better properties, can be obtained if a rich alloy is heated within the alpha-plus-beta region and then quenched, structure B. If lean alloys are slowly cooled from the beta-phase field, primary alpha phase forms in the usual manner. However, if lean beta phase is quenched, it forms a structure somewhat distorted from the equilibrium alpha phase and called alpha prime (α') or titanium martensite, structure C. Unlike martensite in steel, titanium martensite is not brittle and it is a useful structure in certain heat-treated alloys such as Ti-6Al-4V, Table 6-8. The beta phase in lean alloys quenched from the alpha-plus-beta region transforms partially to the alpha prime phase, structure D. This treatment has the advantage of ensuring a fine grain size.

The best combination of strength and ductility is obtained by aging the quenched alloys at about 1000°F to produce a fine dispersion of the alpha and beta phases. The structure produced by this treatment in a lean alloy is shown by E, while F and G show the structures in rich alloys. The coarse beta grain size in G is a consequence of prior quenching from the beta-phase field.

![Diagram](image-url)

**Fig. 6-54.** Correlation of hardness and phase composition for an alpha-beta titanium alloy quenched from the alpha-beta region and aged at 800°F. (After Frost.)
### Table 6-8

**Mechanical Properties of Titanium Alloys**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat treatment</th>
<th>Yield strength, lb/in²</th>
<th>Tensile strength, lb/in²</th>
<th>Elongation in 2 inches, %</th>
<th>Reduction of area, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial titanium</td>
<td>Annealed at 1100 to 1350°F</td>
<td>80,000</td>
<td>95,000</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Water quenched from 1750°F; aged at 1000°F for 2 hr</td>
<td>150,000</td>
<td>170,000</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>Ti-4Al-4Mn</td>
<td>Water quenched from 1450°F; aged at 900°F for 8 hr</td>
<td>170,000</td>
<td>185,000</td>
<td>13</td>
<td>37</td>
</tr>
<tr>
<td>Ti-6Al-2.76Cr-1.25Fe</td>
<td>Water quenched from 1450°F; aged at 900°F for 6 hr</td>
<td>175,000</td>
<td>185,000</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Ti-6Al-1.5Fe-1.4Cr-1.2Mo</td>
<td>Water quenched from 1625°F; aged at 1000°F for 6 hr</td>
<td>170,000</td>
<td>185,000</td>
<td>15</td>
<td>25</td>
</tr>
</tbody>
</table>
An important aspect of the aging of rich alloys is the occurrence of the omega (ω) phase as a transition structure in the transformation of beta to alpha at aging temperatures below about 900°F. Alloys that contain omega are likely to be brittle, and therefore it is important that the aging treatment be adequate for the elimination of this phase. As the time of aging is increased, the omega phase forms and then gradually disappears and is replaced by the alpha phase, Fig 6-54. It is necessary to age beyond the maximum hardness in commercial practice. Aging temperatures of not less than 800°F are employed, and at this temperature the aging time is at least 24 hours. The mechanical properties of commercial titanium and several alloys are listed in Table 6-8. A serious disadvantage of titanium is its high price relative to other structural metals.

**Impurities in Metals**

In most day-to-day applications of metals and alloys, only the base metal and the principal alloying elements are of direct interest. However, when a production-line casting begins to develop serious gas pockets, the gaseous impurities hydrogen, nitrogen, and oxygen suddenly become very important. Solid impurities are even more common, and even a fraction of one percent of an unwanted element can destroy the useful properties of commercial alloys. For example, 0.01% arsenic causes difficulties in the production of lead-antimony alloy cable sheath. Sulfur is a nonmetallic impurity that causes steels to develop cracks when rolled at high temperatures. The cause of this *hot shortness* is the melting of an iron sulfide compound in the steel.

All commercial alloys contain impurities. However, it is only when the amounts of certain critical impurity elements exceed a specific value that objectionable effects are produced. Although each base metal represents a separate, specialised problem, the impurities usually get into the final metal article in the following ways: (1) in the original smelting operation from impurities in the ore, flux, and fuel; (2) during the later melting operations by contamination from the furnace or fuel, or from scrap-metal additions; (3) in the course of heating for hot-working, solution treatment, etc., from furnace or fuel contaminants.

Successful commercial practice consists not in the expensive task of completely eliminating undesirable elements, but in adequately controlling them. Usually this is done by maintaining the impurity elements below a safe minimum, but frequently it is more economical to add a second element to convert the impurity to a relatively harmless form. For example, sulfur in steel can be caused to form harmless manganese sulfide (which actually improves machinability), if a little manganese is added to the steel during manufacture.
METHODS FOR STUDYING METAL STRUCTURES

The subject matter of this chapter has afforded many examples of the use of the light microscope in studying the microstructure of alloys. In addition to this powerful tool a number of other methods are frequently used to study structures ranging in size from those too fine to be resolved by the light microscope to those that can easily be seen by the unaided eye. Some methods have characteristic advantages in their principle of operation. Several of the more important techniques will be considered.

Electron microscope. The resolving power of a microscope (its ability to form distinguishable images of small objects) is roughly equal to the wavelength of the light that it uses. An ultraviolet microscope using 3000 A radiation is better in this respect than the ordinary one using green light of 5000 A. Although the potentially great resolving power of 1 A x-rays has not yet been successfully used in a microscope, the electron beam, of even shorter wavelength, has been adequately focused to produce remarkable magnifications. Figure 6-55 shows the analogy between the focusing of light rays by lenses and the focusing of the electrically charged electron beam by magnetic coils. Electrons produced by the hot-wire cathode are accelerated through the anode by a potential of about 50,000 volts. After the electron beam has been collimated, it passes through the

![Diagram illustrating the analogy between the light microscope and the electron microscope.](image-url)
FIG. 6-56. Comparison of (a) an electron micrograph (×6000) and (b) a photomicrograph (×1800) of high-purity nickel. (Both reproduced at three-fourths size.) (Courtesy R. D. Heidenreich, Bell Telephone Laboratories, Inc.)

specimen and is selectively absorbed by different parts of the specimen. The beam is then magnified by the objective and ocular magnetic coils before it is viewed on a fluorescent screen or is photographed. Because of the high absorption of electrons by metals, it has been impractical so far to use the actual metal specimen in the electron microscope, and thin films on which the metal surface has been imprinted are used instead. Figure 6-56(a) is an electron micrograph of high-purity nickel obtained by this
replica technique. The light micrograph is given for comparison in Fig. 6-56(b). Although the present electron microscope has a resolving power of roughly 20 Å, experimental difficulties limit the resolution in metallurgical applications to about ten times this value.

Radiography. One of the outstanding characteristics of x-rays is their ability to pass through objects opaque to ordinary light. Fortunately this ability is limited and varies in degree from one substance to another; therefore it is possible to obtain x-ray photographs showing the degree of uniformity of such articles as metal castings and welded assemblies. Figure 6-57(a) illustrates one method of obtaining such a radiograph. In the example shown, certain areas of the metallic specimen transmit the x-rays more readily than others, resulting in nonuniform darkening of the photographic film. It can be inferred that the more "transparent" areas of the metal contain hidden nonuniformities, such as holes produced in the casting process. An actual radiograph of a brass casting is shown in Fig. 6-57(b).

Several factors determine whether a given defect in a metal specimen will be indicated on a radiograph. One of these is the intensity of the x-ray beam. This intensity must be sufficiently great so that appreciable darkening of the photographic film occurs during a reasonable time of exposure. The source of x-rays is usually an x-ray tube with a tungsten target, and the intensity of the beam is approximately proportional to the square of the voltage. Higher voltages are therefore convenient for radiographing thick parts or highly absorbent metals. The effective wavelength \( \lambda_{\text{eff}} \) of the white radiation decreases with an increase in voltage \( V \), as shown by the approximate equation

\[
\lambda_{\text{eff}} = \frac{20,000}{V} \text{ Å.} \quad (6-14)
\]

This decrease in wavelength is a second factor that increases the penetrating power of a high-voltage x-ray beam, in this case because of the change in absorption coefficient discussed below. For radiography of steel more than a few inches thick it is often more convenient to use the very short wavelength x-rays (called \( \gamma \)-rays) produced by radium.

The following equation governs the absorption of x-rays by metals and other substances:

\[
I = I_0 e^{-\mu x/p}, \quad (6-15)
\]

where \( I_0 \) is the intensity of the initial x-ray beam, \( I \) is the intensity of the beam after traversing the distance \( x \) centimeters, \( \mu/p \) is the mass absorp-
Fig. 6-57. Radiographic technique. (a) Arrangement for obtaining radiograph of metallic specimen. (b) Radiograph showing shrinkage in brass casting (courtesy General Electric X-ray Corporation). Irregular dark areas in both (a) and (b) are voids in metal.

Fig. 6-58. The variation of the mass absorption coefficients, \( \mu/\rho \), of copper, iron, and aluminum with the wavelength of the x-ray being absorbed.

The absorption coefficient, *e* is the base of the natural logarithms, \( \rho \) is the density of the material being traversed by the x-rays, in gm/cm\(^3\), and \( x \) is the thickness of the material in centimeters.

*It is frequently inconvenient to consider absorption in terms of path length in the absorbing material, since the corresponding linear absorption coefficient \( \mu \) is a function of density. The mass absorption coefficient, on the other hand, is independent of the state of the material.*
The most important term in this equation is the mass absorption coefficient $\mu/\rho$, the value of which not only varies from metal to metal but also depends on the wavelength of the x-rays. Figure 6-58 illustrates these variations and shows the discontinuity that occurs at the K absorption edge. At the wavelength of this absorption edge the incident x-rays have just sufficient energy to eject the K-type electrons from the core of the metal atom, with the result that absorption strongly increases. Values of mass absorption coefficient for several metals are given in Table 4-2 at four wavelengths, and their relation to the K and L absorption edges can be seen.

It can be shown that the larger the mass absorption coefficient, the more easily a given defect is detected in a radiograph. For example, consider a piece of aluminum one inch thick containing an internal void 0.05 inch thick. The ease with which this defect can be observed in a radiograph can be assumed to depend on the ratio

$$\frac{I_v}{I_a} = \frac{\text{intensity of beam passing through void}}{\text{intensity of beam not passing through void}}$$  \hspace{1cm} (6-16)

First, assuming that $\mu/\rho = 0.7$, Eq. (6-15) can be used to obtain the ratio

$$\left(\frac{I_v}{I_a}\right)_{0.7} = \frac{I_{0e^{-0.7(2.7)(2.41)}}}{I_{0e^{-0.7(2.7)(2.54)}}} = e^{-0.7(2.7)(2.41)-2.54} = e^{0.25} = 1.28,$$  \hspace{1cm} (6-17)

A special convention is used in the study of x-rays to designate the principal quantum numbers. The first quantum number is replaced by K, the second by L, the third by M, and so on. Thus K-type x-rays, such as $K_a$, are those produced when an outer electron falls into a vacant position in the first principal quantum-number orbit, 1s (also called the K-shell). Similarly, the energy required to eject a 1s electron can also be described as the energy needed to eject a K-type electron.

† There are some cases in which this rule cannot be followed in practice. If the specimen to be radiographed has a wide range of section thicknesses, it may be necessary to decrease the mass absorption coefficient in order to obtain a usable range of x-ray intensities striking the photographic film. Also, it is sometimes necessary to increase the voltage (and decrease the mass absorption coefficient) to obtain a radiograph with sharp (rather than fuzzy) details.

† This value can be shown to correspond to about 67,000 volts on the x-ray tube. From Fig. 6-58 the wavelength that gives $\mu/\rho = 0.7$ for aluminum is $\lambda = 0.3$. Substituting this value for $\lambda_{eff}$ in Eq. (6-14) gives $V = 20,000/0.3 = 67,000$ volts. Similarly, it can be shown that about 50,000 volts on the x-ray tube leads to $\mu/\rho = 1.4$ for aluminum.
where \( 2.7 \) is \( \rho \), the density of aluminum; \( 2.54 \) is the normal thickness of the aluminum (in centimeters); \( 2.41 \) is the thickness of the section containing the void (in centimeters). On the other hand, if \( \mu/\rho \) is assumed to be twice as large (1.4), then the ratio becomes

\[
\left( \frac{I_1}{I_0} \right)_{1.4} = e^{-(1.4)(2.7)(2.41-2.114)} = e^{0.49} = 1.63. \tag{6-18}
\]

Considering that the ratio \( I_1/I_0 = 1.00 \) would not permit the void to be observed in the radiograph, it is evident that there is more than a twofold advantage in using a \( \mu/\rho \) value of 1.4 rather than 0.7.

There are limitations on the magnitude of the mass absorption coefficient that can be utilized in practice. As shown by Fig. 6–58, to increase the value of \( \mu/\rho \) for a metal such as aluminum, it is necessary to increase the wavelength of the x-ray beam. However, according to Eq. (6–14), this requires that the voltage be decreased, and this in turn greatly increases the necessary exposure time. Therefore, the maximum value of \( \mu/\rho \) is obtained in practice by following the rule that the voltage should be kept as low as is permitted by other factors such as specimen thickness and practical exposure time.

Radiography permits the examination of large metal specimens for gross defects that make up more than about 2 percent of the thickness, but this method fails to reveal the finer details of metal structure. For this purpose a refined version of the same technique, called microradiography,

![Fig. 6-59. Comparison of (a) a microradiograph and (b) a photomicrograph of an unetched gray cast iron. (Both X40; reproduced at three-fourths size.) (Courtesy Naval Research Laboratory.)](image-url)
has been used successfully. Only a small area of a specimen that has been reduced to a thickness of about 1/1000 of an inch is examined, usually with x-rays of long wavelength. When the resulting microradiograph is magnified about one hundred diameters, the distribution of the different constituents of the alloy can be seen, as shown in Fig. 6-59.

Although a microradiograph gives a picture similar to a photomicrograph, it differs from the latter in depending on the whole volume of the specimen rather than merely on the surface. Also, contrast between the constituents of an alloy is produced, not as a result of etching, but because of differences in absorption coefficients. In Fig. 6-59(a) the graphite flakes appear dark because graphite absorbs x-rays comparatively weakly. Even if two constituents have generally similar absorption coefficients, good contrast can be obtained if the x-ray wavelength is chosen to lie between their absorption edges. Consideration of Fig. 6-58 shows that copper $K_{\alpha}$ radiation ($\lambda = 1.54$ Å) would be suitable in this respect for a microradiograph of an iron-copper alloy.

**Macrostructure.** Since the use of a high-power microscope is almost always necessary to see the individual phases or microconstituents in alloys, the naked eye sees only other more obvious structural features. Such macrostructural details include cracks, gas pockets, segregation of alloying elements, fracture characteristics, and forging flow lines. Three different kinds of procedures are used to observe the various types of macrostructure: examination of (1) the specimen surface, (2) a macroetched section, or (3) a fractured section.

**Examination of the specimen surface.** Many defects (large cracks and surface irregularities in castings, for example) are immediately evident on looking at metal parts. However, in critical machine components, such as an aircraft engine crankshaft, even very small cracks may be dangerous. The location of small surface flaws is made easy by the use of magnetic particles for ferromagnetic alloys, and by the use of fluorescent dyes in penetrating oils for both magnetic and nonmagnetic alloys. Figure 6-60(a) shows a metal surface on which no cracks are visible. The Magnaflux process reveals many networks of cracks, Fig. 6-60(b), as the small magnetic particles collect preferentially at these discontinuities in the surface. In the Magnaglo process, Fig. 6-60(c), a dye-containing oil is allowed to penetrate into the cracks, and they are then seen clearly when the dye is caused to fluoresce in ultraviolet light.

**Examination of a macroetched section.** Much information on the quality of hot-rolled steel bars and similar metal products can be obtained by deeply etching (usually in hot hydrochloric acid) a specimen representing a cross section of the part. This technique discloses the following types of macrostructure:
FIG. 6-60. The use of the Magnaflux and Magnaglo processes to locate cracks in a king pin for a truck. (a) Appearance of king pin under visual inspection. (b) Previously unnoticed cracks made visible by the Magnaflux process. (c) The same cracks made visible by the Magnaglo process. (Courtesy Magnaflux Corp.)

1. coarse grain structural features such as columnar and dendritic patterns not completely removed by the hot-working process;
2. internal cracks produced in the working process or during heating or cooling;
3. center porosity, "pipe," or segregation derived from initial ingot defects;
4. surface defects such as laps, seams, or decarburization produced by improper hot-working practice;
5. flow lines in a forging; Fig. 9-28 shows both a desirable and an undesirable pattern of flow lines.

The segregation of certain elements such as sulfur and phosphorus can also be determined on a cross-sectioned specimen. Photographic paper soaked in suitable reagents is placed on the specimen, and chemical reaction of the reagents with the segregated element produces a permanent record on the paper.
Examination of a fractured section. When a metal part fails in service, observation of the broken surfaces frequently reveals the nature of the failure. If a service failure is a result of the presence of internal cracks or gas pockets, these imperfections are easily detected in the fractured section. Fatigue failures, which frequently cause the breaking of metal pieces subject to repeated loading, have a characteristic appearance. A typical fatigue fracture is shown in Fig. 9-21, and its interpretation is discussed in the accompanying text.

Metal bars are fractured in the plant or laboratory and their surfaces examined to determine the following properties: (1) the grain size; (2) the ductility; a cup-and-cone fracture in a tension test indicates good ductility; (3) the soundness or structure of castings; (4) the depth of hardened surface layer in steel; (5) the chemical analysis in certain instances, such as carbon content in low-carbon steels; (6) the presence of segregation, such as carbide streaks in tool steels. The examination of fractured surfaces is of especial importance in judging tool steel quality.

Nondestructive testing. There are a number of techniques in addition to radiography for determining whether a metal part contains internal flaws (techniques that do not require internal access). Magnetic and electrical methods have been developed for a number of applications, but the use of high-frequency sound waves has proved most generally useful. Figure 6-61 illustrates the principle of this ultrasonic inspection. A combination generator and receiver of ultrasonic waves obtains a wave pattern...
from the metal specimen being tested. This pattern is caused to appear on
the screen of a cathode-ray tube, and the presence of a flaw is indicated by
the appearance of extra reflections on the screen.

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PROBLEMS

1. (a) Sketch a $P-X$ diagram for a temperature above the triple points of both metals in Fig. 6-1. (b) Sketch a $P-X$ diagram for a temperature between the two triple points. Use the phase rule to show that there are no additional degrees of freedom (once the temperature has been fixed) for a binary system containing three phases, and therefore the three phases exist in equilibrium only at a given pressure.

2. Sketch a two-dimensional picture of the relative positions of (about twelve) atoms of a 50% copper-50% nickel alloy (a) at 2000°F, (b) at 2200°F, and (c) at 70°F. (See Figs. 5-1 and 6-7.)

3. Derive Eq. (6-5). (Note that the principle of the derivation is sketched in the text.)

4. Consider an alloy consisting of 30% gold and 70% silver, Fig. 6-62. (a) At 1850°F: (1) What phase(s) are present? (2) What is the chemical composition of each phase? (3) What percentage of each phase is present? (b) Make a similar phase analysis at 1825°F. (c) Make a similar phase analysis at 1815°F. (d) Make a similar phase analysis at room temperature. (f) Sketch a possible microstructure for each of these five temperatures.

5. Prove that the tangent line in Fig. 6-10 gives the free energy of mixtures of the $\alpha$- and $\beta$-phases for alloys in the composition range between $X_a$ and $X_\beta$. Use the lever law to determine the amounts of the two phases that exist at a given composition $X$, and then write the expression for the free energy as the sum of contributions from the two phases, using $F_a$ and $F_\beta$ to represent the free energy per unit amount of each phase. Show that the resulting expression is the equation of the tangent line in question.

6. Consider the equilibrium diagram of Fig. 6-12. (a) Using alloy 1, determine the percentage of alpha solid solution in the eutectic microconstituent. (b) Make phase analyses of alloy 2, (1) at a temperature just above the liquidus curve, (2) at temperature $T_1$, (3) at temperature $T_2$, (4) at a temperature just below the eutectic reaction horizontal. (c) Make phase analyses of alloy 3, (1) at temperature $T_1$, (2) at a temperature slightly below the liquidus curve, (3) at a temperature slightly above the solidus curve, (4) at temperature...
(d) How does the solidification of alloy 3 compare with the solidification of an alloy in a complete solid solubility diagram, such as Fig. 6-5?

7. Using the equilibrium diagram of Fig. 6-17: (a) make phase analyses of alloy 1 at (1) 3000°F, (2) 2200°F, and (3) 2100°F, and sketch a possible microstructure for each of these three temperatures. (b) Make phase analyses of alloy 2 at (1) 2200°F, (2) 2100°F, and (3) 1800°F, and sketch a possible microstructure for each of these three temperatures. (c) Make phase analyses of the 20% platinum alloy at (1) 2200°F, (2) 2000°F, and (3) 1800°F, and sketch a possible microstructure for each of these three temperatures.

8. An incongruently melting intermetallic compound often produces a peritectic reaction in its equilibrium diagram. With the aid of Fig. 6-63, sketch a possible equilibrium diagram in this case. [Note: A eutectic reaction would almost always occur on the left-hand side of such an equilibrium diagram.]

9. (a) Sketch a diagram similar to Fig. 6-20, except with the liquidus and solidus lines sloping upward, and show that \( k_0 \) is then greater than one. (b) Explain why the curve for \( k = 5 \) decreases with increase in \( g \) in Fig. 6-21.

10. For slow rates of solidification the effective distribution coefficient \( k \) is essentially equal to \( k_0 \). Use a sketch of the variation of solute concentration in the liquid to explain why the value of \( k \) is between \( k_0 \) and unity for faster rates of solidification.

11. Using the equilibrium diagram of Fig. 6-24, make phase analyses of a 25% magnesium alloy at (a) 900°F, (b) 800°F, and (c) 400°F, and sketch a possible microstructure for each of these three temperatures.

12. Using the equilibrium diagram of Fig. 6-25, make phase analyses of a 0.2% C alloy at (a) 1650°F, (b) 1550°F, (c) 1335°F, and (d) 1330°F. (e) What percent of the alloy is pearlite at 1330°F? Sketch a possible microstructure for each of these three temperatures.

13. (a) Is it possible to cause the eutectic microconstituent to form in alloy 1, Fig. 6-26? (b) What is the minimum silver content of an alloy in which the eutectic structure appears on equilibrium cooling?

14. In a face-centered cubic space lattice there are three times as many face-centered positions as there are cube-corner positions. From this fact you would conclude that ordering of a face-centered cubic solid solution of metal B in metal A would be more likely at the composition \( A_2B \) or at \( A_3B \)? Why?

15. On Fig. 6-29 find these alloys:
   (a) 100% A, 0% B, 0% C
   (b) 20% A, 80% B, 0% C
   (c) 33% A, 33% B, 34% C
16. Using Fig. 6-30, make phase analyses of the alloy 25% A, 25% C, 50% B at (a) T1, (b) T2, (c) T3, and (d) T4. (e) Estimate the amount of pseudoeutectic structure at T4.

17. Make a phase analysis of ingot iron at (a) 3000°F, (b) 2700°F, (c) 1800°F, and (d) 1300°F, using the equilibrium diagram of Fig. 6-35.

18. If a hypereutectoid steel is slowly cooled from the austenite region, the primary cementite crystals form a continuous layer in the austenite grain boundaries. This brittle network seriously reduces the ductility of the steel at room temperature. What heat treatment would be most effective in removing this cementite network?

19. Use Fig. 6-40 to make a phase analysis of (a) a 1% C, 6% Mn alloy, and (b) a 2% C, 2% Mn alloy. Draw tie lines according to the pattern illustrated in Fig. 6-30. Compare these results with the result of the analysis of the 1% C, 2% Mn alloy given in the text. What conclusions can you draw concerning (c) the effect of carbon content and (d) the effect of manganese content on the carbide-forming tendency of manganese?

20. Assume that the yield strength of commercially pure iron is 30,000 lb/in². What would be the yield strength of a normalized high-strength low-alloy steel containing 0.10% C, 0.90% Mn, 0.3% Si, 0.10% P, and 0.02% S? The strengthening effect of carbon in normalized steels is about the same as that of phosphorus.

21. Show by means of a sketch based on the equilibrium diagram of Fig. 6-48 why a eutectic structure appears in the photomicrograph of the magnesium-9% aluminum alloy, Fig. 6-49(a). (See Fig. 6-16.)

22. If an exposure time of one minute is satisfactory for radiographing an aluminum spot weld 0.1 inch thick, what time would be necessary for a thickness of 0.25 inch if the voltage were held fixed at 40,000 volts? (Assume that the darkening of a photographic film by x-rays is proportional to the product of the x-ray intensity and the time of exposure.)
CHAPTER 7

PHYSICAL PROPERTIES

"... a natural body is an aggregate of imperceptible particles which is subject to the operation of forces proceeding from the magnet, fire, and sometimes light, also..."

STENO (1666)

INTRODUCTION

The structure of metals, the subject matter of the previous chapters, is closely related to the properties of metals and hence to the solution of engineering problems. From a knowledge of atomic, crystal, or phase structure it is often possible to estimate property values of industrial interest. Such a structural approach to engineering properties may appear to be indirect, and therefore perhaps inefficient. However, there are only a few aspects of structure that must be determined for each alloy, while the number of properties is almost unlimited. It is thus extremely practical to use information on structure as a preliminary guide to engineering properties in order to reduce the amount of laboratory development and service testing required.

The metal properties that are of interest vary with each alloy application. Since there are many different applications, an extremely large number of properties have been investigated. These are frequently divided into the following categories: (1) physical properties, (2) mechanical properties, (3) chemical properties. Additional metallurgical properties, such as reactions to cold-working and to various heat treatments, are usually considered separately. Study of the properties of metals is conveniently begun with a consideration of physical properties.

ELECTRICAL PROPERTIES

Typical of physical properties are those involving electrical phenomena. Although conductivity is the most important electrical property, it is not the only one that needs to be considered. There are also thermoelectric effects in thermocouples, electrochemical phenomena in storage batteries, electrophysical effects in contact potentials, and even electromechanical effects in radar. Only a brief introduction to some of these subjects can be given here.
Resistance. Metals with high electrical resistance are needed for some applications, as in a toaster heating element, while low electrical resistance is essential for such uses as long-distance transmission lines. In any event, it is necessary to have a quantitative measure of this property for design purposes. The actual resistance depends on the shape of the metal as well as on the resistivity. Values of the latter property are given in Table 7-1. For a conductor of constant cross section the following equation is valid:

\[ R = \rho \frac{l}{A} \]  

(7-1)

where \( R \) is the resistance in ohms, \( l \) is the length in centimeters, \( A \) is the area in square centimeters, and \( \rho \) is the resistivity in ohm-centimeters. Since the actual resistivity value for a given metal is strongly influenced by many factors, it is necessary to consider the nature of these influences.

Table 7-1

**ELECTRICAL PROPERTIES OF SOLIDS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity at 20°C, ohm-cm</th>
<th>Temperature coefficient ( a ), per °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals and Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper, annealed</td>
<td>( 1.67 \times 10^{-6} )</td>
<td>( 4.29 \times 10^{-3} ) (0-100°C)</td>
</tr>
<tr>
<td>Copper, reduced 75%</td>
<td>( 1.71 \times 10^{-6} )</td>
<td></td>
</tr>
<tr>
<td>by cold drawing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cartridge brass, annealed</td>
<td>( 6.2 \times 10^{-6} )</td>
<td>( 1.48 \times 10^{-3} ) (20°C)</td>
</tr>
<tr>
<td>70% Cu, 30% Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum, annealed</td>
<td>( 2.65 \times 10^{-6} )</td>
<td>( 4.29 \times 10^{-3} ) (20°C)</td>
</tr>
<tr>
<td>Iron, annealed</td>
<td>( 9.71 \times 10^{-6} )</td>
<td>( 6.57 \times 10^{-3} ) (0-100°C)</td>
</tr>
<tr>
<td>Constantan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55% Cu, 45% Ni</td>
<td>( 49 \times 10^{-6} )</td>
<td>( 0.02 \times 10^{-3} ) (25°C)</td>
</tr>
<tr>
<td>Manganin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>84% Cu, 12% Mn, 4% Ni</td>
<td>( 44 \times 10^{-6} )</td>
<td>( 0.000 \times 10^{-3} ) (25°C)</td>
</tr>
<tr>
<td>Nichrome</td>
<td></td>
<td>( -0.042 \times 10^{-3} ) (100°C)</td>
</tr>
<tr>
<td>80% Ni, 20% Cr</td>
<td>( 108 \times 10^{-6} )</td>
<td>( 0.14 \times 10^{-3} ) (0-500°C)</td>
</tr>
<tr>
<td><strong>Semiconductors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Germanium</td>
<td>( 10^{-2} ) to 60</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>( 10^{-4} ) to ( 2.3 \times 10^{5} )</td>
<td></td>
</tr>
<tr>
<td><strong>Insulators</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td>( 10^{12} )</td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td>( 10^{14} )</td>
<td></td>
</tr>
</tbody>
</table>
Since electricity is carried in a metal by electrons, problems in electrical conductivity involve the motion of these electrons. Thus, if there are \(N\) free electrons per \(\text{cm}^3\) and if their average net (drift) velocity under the action of an electric field is \(v_D\), then the electric current per \(\text{cm}^2\) is

\[
j = Ne v_D,
\]

(7-2)

where \(e\) is the charge on the electron. It is characteristic of an electric current that the electric field does not continuously accelerate the electrons as it would in the absence of friction, but rather, the current quickly reaches a constant value. This behavior is explained by the phenomena of random collisions of the electrons with their surroundings, where the average distance \(l\) between collisions is called the mean free path. Alternatively, the corresponding time \(\tau\) between collisions can be used,

\[
l = \tau v,
\]

(7-3)

where \(v\), the velocity of an electron, is much greater than \(v_D\), the drift velocity. The relaxation time \(\tau\) is the more generally useful concept, and it can be shown (see Problem 2) that \(v_D\) depends on the value of \(\tau\) according to the equation

\[
v_D = \frac{E e}{m} \tau,
\]

(7-4)

where \(E\) is the electric field and \(m\) is the mass of an electron. The conductivity \(\sigma\) is defined as \(j = \sigma E\), and therefore when Eq. (7-4) is substituted in Eq. (7-2) it follows that

\[
\sigma = \frac{N e^2}{m \tau}.
\]

(7-5)

By using the effective mass \(m^*\) in this final equation, the equation correctly describes the results given by wave mechanics as well as those obtained by the following treatment in which only free electrons are considered. (See the discussion of this point in Chapter 3.)

Semiconductors. The characteristics of the principal types of electrical behavior are conveniently explained in terms of \(N\), the number of current carriers. Figure 3-10 of Chapter 3 shows why there are no electrons available to conduct electricity in insulators. The second type of electrical behavior, semiconductivity, is also explained in terms of filled Brillouin zones. Figure 7-1 shows the types of energy bands that characterize intrinsic semiconductors and impurity semiconductors. Intrinsic semiconductors such as pure silicon and germanium have a narrow energy gap \(E_0\) between the lower, valence band and the higher, conduction band,
Fig. 7-1. The mechanisms of conduction in (a) intrinsic semiconductor at room temperature, and (b) impurity semiconductor at room temperature.

Fig. 7-1(a). At temperatures near 0°K an intrinsic semiconductor will have a completely filled valence band and a completely empty conduction band, and therefore it will behave like an insulator. However, at room temperature some of the more energetic valence electrons are raised into the conduction band and are available to help conduct electricity. Since there are then unoccupied energy states in the valence band, this band also contributes to the electrical conductivity. This portion of the conductivity is conveniently described in terms of the unoccupied states or holes in the valence band. For each electron that is raised to the conduction band, a hole is left that behaves as though it were a unit positive charge. The number of current carriers, conduction electrons plus holes, increases with temperature. Consequently, the conductivity of intrinsic semiconductors increases with an increase in temperature, while metals characteristically exhibit the opposite behavior.

A more versatile material for use in transistors and similar devices is the impurity semiconductor, Fig. 7-1(b). If a small quantity of an impurity of valence \( n + 1 \) is added to a crystal of an element whose valence is \( n \), there will be an extra electron per impurity atom beyond the number required to fill the valence band. At low temperatures each of these extra electrons will move about one of the donor impurity ions in response to the additional positive charge on these ions. It is possible to approximate the weak binding energy in this interaction using a procedure analogous to the Bohr theory for hydrogen. These localized donor energy states \( E_D \) lie close to the bottom of the conduction band, as shown in Fig. 7-1(b). Therefore thermal energy at room temperature is sufficient to raise some of the extra electrons to the conduction band and so produce semi-conductivity. An \( n \)-type semiconductor, the type described in this example...
based on Fig. 7-1(b), involves conduction by negative carriers, that is, electrons. If the impurity element has a valence of \( n - 1 \), rather than \( n + 1 \), an argument similar to that given above leads to the prediction of acceptor energy states \( E_A \), lying slightly higher than the top of the valence band \( E_V \). These states are vacant at absolute zero, but at room temperature some of the valence electrons are raised to \( E_A \) by thermal energy. These electrons are localized and cannot conduct electricity, but the holes they create in the valence band act as positive carriers. The name “p-type semiconductor” is used in this case.

**Metallic conduction.** In contrast to conduction in insulators and semiconductors, which involves filled energy bands, metallic conduction involves bands that are only partially occupied. This theory was discussed in Chapter 3, and it will be applied here to several aspects of metallic conduction. Figure 3-11 can be used in explaining why monovalent metals usually have better conductivity than divalent metals. Because the one valence electron in a monovalent metal fills only half the first energy band, two conditions favorable for conduction are created:

1. When a band is half filled, the density of electron-energy states \( N(E) \) is high. Consequently, when an electric field is applied, a large number of electrons are raised above the existing level.

2. These most energetic electrons have an effective mass approximately equal to \( m \), the mass of a free electron.

The corresponding conditions in a divalent metal are the following:

1. The two valence electrons nearly fill the first band and only slightly fill the second, overlapping band. The \( N(E) \) value is low at these positions in both bands.

2. In the upper portion of the first band \( m^* \) is considerably larger than \( m \).

Thus both these factors tend to produce lower conductivity in divalent metals.

The anomalous increase in conductivity of bismuth upon melting is another phenomenon attributable to Brillouin zones. Most metals experience a decrease in conductivity upon melting because of the resulting disruption of the orderly atomic arrangement. This disruption also occurs in bismuth, but the predominant factor determining the change in conductivity is the breaking-down of the Brillouin zones that accompanies the disintegration of the crystalline structure of solid bismuth. Conductance is so severely restricted in solid bismuth by the zone structure that a net increase in conductivity occurs when this restriction is substantially removed during melting.

Engineering problems concerning electrical conductivity often involve only a given base metal, perhaps with small amounts of alloying elements.
Figure 7-2 is a schematic representation of the character of the terms in Eq. (7-6). We see that $\rho_R$ is assumed to be independent of temperature, while $\rho_T$ decreases with decreasing temperature. At 0°K, $\rho_T$ becomes negligibly small and the only remaining (residual) resistance is $\rho_R$. This term arises because of disturbances in the crystal lattice, as described below.

The variation of $\rho_T$ with temperature reveals several significant features of electronic conduction in metals. In suitable pure crystals for which $\rho_R$ is zero, the resistivity approaches zero at temperatures near 0°K. This means that the electrons move freely through the lattice without experiencing collisions with the ion cores that constitute the crystal lattice. Although this behavior cannot be explained from the classical viewpoint, it is entirely consistent with wave mechanics, since the periodic electron waves have a perfectly periodic lattice in which to move. Under these conditions, when collisions of electrons with the ion cores are virtually eliminated, the shape of the specimen affects the observed resistivity value. The electrons are reflected more often from the walls of a thin specimen, and therefore the observed resistivity is higher than in a thicker specimen. At higher temperatures the thermal disturbance of the lattice can be described in terms of quantized elastic waves or phonons, and the increase in $\rho_T$ can be visualized as resulting from collisions between the electrons and phonons. For most metals $\rho_T$ increases linearly with temperature near room temperature and above, although the behavior at very low temperatures is more complex.

The residual resistivity $\rho_R$ results from disturbances in the lattice other than those caused by thermal vibration. By far the most drastic increases in $\rho_R$ are caused by foreign atoms in solid solution in the matrix metal. Table 7-1 shows, for example, that the resistivity of copper is increased almost fourfold by the addition of 30% zinc to make cartridge brass. Cold-working, on the contrary, increases this resistivity term only slightly. For this reason cold-working is a suitable means of strengthening alloys to be used as electrical conductors.
The effect of temperature on resistivity is usually determined with sufficient accuracy by means of the equation

\[ \rho_t = \rho_{20}[1 + \alpha(t - 20)], \]  

(7-7)

where \( \rho_t \) is the resistivity at \( t \)°C, \( \rho_{20} \) is the resistivity at 20°C, and \( \alpha \) is the temperature coefficient of resistivity per °C. Values of \( \alpha \) are given in Table 7-1. In conductors that operate at high temperatures, such as heating elements, the temperature correction term has a large value and is an important design factor. In critical electrical devices the variation of resistance with temperature can be made negligibly small by the use of manganin (84% Cu, 12% Mn, 4% Ni) or similar alloys that have low-temperature coefficients.

Several other factors influence resistivity. In a few metals, of which lead is an example, resistivity drops to essentially zero at a temperature near absolute zero, 7.2°K for lead. This phenomenon, called superconductivity, is not completely understood. Commercial applications include the superconducting electronic devices now being developed to operate on extremely low power. Another interesting aspect of resistivity is its dependence on the direction of the electrical current in single crystals of noncubic metals. The resistivities parallel to the c-axis and perpendicular to this axis for several metals are tabulated here:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electrical resistivity at 20°C, ohm-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parallel</td>
</tr>
<tr>
<td>Magnesium</td>
<td>( 3.78 \times 10^{-6} )</td>
</tr>
<tr>
<td>Zinc</td>
<td>( 6.13 \times 10^{-6} )</td>
</tr>
<tr>
<td>Cadmium</td>
<td>( 8.30 \times 10^{-6} )</td>
</tr>
<tr>
<td>Tin</td>
<td>( 14.3 \times 10^{-6} )</td>
</tr>
<tr>
<td>Tellurium</td>
<td>( 56,000 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

This anisotropy of resistivity has potential uses in special electrical devices. Of considerable industrial interest is the variation of resistivity produced by alloying. Solid-solution formation causes a pronounced increase; this behavior was shown in Fig. 6-7 for the copper-nickel system. In two-phase alloys the resistivity tends to change proportionally with composition between the resistivities of the two phases.

An isotropic substance has the same value of a given property in every direction of testing. For example, the resistivity of an aluminum single crystal, which is face-centered cubic, is \( 2.65 \times 10^{-6} \) ohm-cm in any arbitrary direction.
of testing. An anisotropic substance, such as a magnesium single crystal, shows a variation in the value of a given property as the direction of testing is varied. The values given above are only the maximum and minimum values. The value of resistivity \( \rho_0 \) in a direction that makes an angle \( \alpha \) with the \( c \)-axis in hexagonal or tetragonal crystals is

\[
\rho_0 = (\rho_{\parallel \parallel}) \cos^2 \alpha + (\rho_{\perp \perp}) \sin^2 \alpha.
\]

It should be noted that a given crystal may be isotropic with respect to one property and anisotropic with respect to a different property. For example, an aluminum single crystal exhibits anisotropy with respect to Young's modulus (see Chap. 8), and isotropy with respect to resistivity.

The concepts of anisotropy and inhomogeneity are sometimes confused. A homogeneous substance is defined as one that has the same properties at every point. At every point in a homogeneous magnesium single crystal, electrical resistivity has the same dependence on direction, that is, the same anisotropy. Thus, a homogeneous substance can be anisotropic. Inhomogeneous substances are often complex, but such substances could conceivably exhibit either isotropic or anisotropic properties.

Thermoelectric effects. The term thermoelectric refers to the interdependence of certain thermal and electrical effects in metals. Two thermoelectric phenomena, the Peltier and Thomson effects, are of special interest because they are basic to the operation of thermocouples. Two additional quantities, Joule heat and contact potentials, are often confused with these more significant thermoelectric effects, and therefore all four of these phenomena are shown in Fig. 7-3.

The temperature of any conductor tends to rise as a result of Joule or resistance heating when there is a current in the conductor, Fig. 7-3(a). Since this factor is easily taken into account, it will not be discussed further here. The Peltier effect is also a heat effect associated with current. It differs from Joule heating in that heat may be absorbed or evolved depending on the direction of the current, Fig. 7-3(b). The Peltier effect occurs at the junction between two different metals, and its magnitude depends on the nature of the metals, the temperature, and the first power of the current. The Thomson effect, Fig. 7-3(c), is the production of a current in a homogeneous metal (e.g., copper) when a temperature gradient exists along its length.

An important practical application of the Peltier and Thomson effects is in thermocouples, which are widely used for temperature measurement and control. Figure 7-4 shows the essential features of a thermocouple and its use. The junction of two dissimilar metals is placed in the region whose temperature is to be measured. The voltage at the ends of the two wires indicates this temperature with respect to the temperature of the
THERMOELECTRIC EFFECTS

Heat generated per second = \( I R \)

Battery

Electric current \( I \)

Metal wire of resistance \( R \)

(a)

Electric current \( I \)

Wire of metal \( A \)

Wire of metal \( B \)

(heat given off)

(b)

The current \( I \) is used to flow if \( T_1 \) and \( T_2 \) are different temperatures.

(c)

\[ T_2 - I - T_1 \]

Metal wire

Wire of metal \( A \)

Wire of metal \( B \)

(d)

FIG. 7-3. Thermoelectric and related effects in metals. (a) Joule heat. (b) Peltier effect. (c) Thompson effect. (d) Contact potential.

FIG. 7-4. One method of using a thermocouple of metals \( A \) and \( B \).

cold junction. The voltage is developed as the result of (1) heat flow at the junctions of the thermocouple (Peltier effect), and (2) temperature gradients along each of the two wires (Thomson effect). Since the thermocouple voltage is the sum* of these component voltages, it is not necessary to evaluate the Peltier and Thomson coefficients separately. When the cold junction of a thermocouple is fixed at a standard temperature like 32°F, its voltage is determined completely by the temperature of the hot junction. Figure 7-5 shows the magnitudes of the voltages developed by several of the commonly used pairs of metals. When precision greater than 0.1°F is required, a resistance thermometer is preferable to a thermometer.

* The term Seebeck effect is sometimes used in this connection.
couple, while radiation and optical pyrometers permit the measurement of higher temperatures and do not depend on actual contact with the hot body.

It is to be noted that contact potentials are not the cause of thermoelectric effects. These potentials, $V_n$, are developed at the junction of two dissimilar metals, Fig. 7-3(d), but they cancel in a completely metallic circuit like the one shown in this figure. Contact potentials are commonly a few tenths of a volt and are essentially independent of temperature.

**Magnetic Properties**

The engineer has a dual interest in magnetic phenomena: first, because the commercial magnetic materials, such as transformer iron, are widely used in modern industry, and second, because the science of magnetism explains many aspects of the structure and behavior of matter and is the source of many engineering developments. Since these two aspects of magnetic phenomena have much in common, it is desirable to begin with a general treatment of magnetism and then to consider the special alloys of commercial interest.

Atomic magnetism. Every electron in both inner and outer orbits of the various elements has a quantity of magnetism or magnetic moment (defined as one Bohr magneton) as a result of "spin" of the electron. The sign of this magnetism may be positive or negative, depending on the direction of spin of the electron, (+) or (−). It will be recalled from the discussion of quantum numbers in Chapter 3 that a given energy level can
accommodate an equal number of electrons with (+) and (−) spins. Thus all filled energy levels have essentially no resultant magnetic moment because of cancellation. When an energy level is only partly filled with electrons, two opposing factors determine the spin of these electrons. The dominant factor in most cases is the lower energy that results when the available quantum states are occupied in regular succession starting with the state of lowest energy. The outer, valence electrons normally behave in this manner for the reason shown schematically for the 4s electrons of nickel in Fig. 7-6. The 4s band in Fig. 7-6(a) covers a broad range of energies, and consequently there are relatively few electron states for each increment of energy \(dE\). Figure 7-6(c) is a schematic representation of the electron states near the energy level \(E_{max}\) to which the 4s band is filled. States that differ only in spin are shown as having the same energy, but the electron energy increases toward the right as shown. Therefore, the energy is a minimum when states of both (+) and (−) spin are occupied up to \(E_{max}\).

The 3d band can accommodate a maximum of ten electrons, compared with a maximum of two for the 4s band. Also, the 3d band shown in Fig. 7-6(a) is typical in being narrower than the 4s band. As a result, the number of electron states at a given energy value is relatively large in the 3d band, as shown in Fig. 7-6(b). There is less advantage in having states of both (+) and (−) spin occupied in this case, and a second factor determining spin comes into play. This is an electrostatic energy that favors the existence of electrons having the same spin. It is not shown in Fig. 7-6(b), but as a result of its action the electrons preferentially occupy the states of negative spin. Consequently, there is an excess of electrons with negative spin and the atoms can be considered to have a net magnetic moment.

Although many of the elements satisfy the above condition, only a few metals and alloys exhibit ferromagnetism, the pronounced magnetism that is of primary interest in engineering. The explanation of this anomaly involves an electrostatic interaction between adjacent atoms that affects the alignment of the resultant electron spins of the atoms. If the interaction is positive, the spins are aligned parallel to one another, their magnetic moments are additive, and ferromagnetism results. If the interaction is negative, the net spins of neighboring atoms are aligned in opposite directions (antiparallel), producing the phenomenon of antiferromagnetism. In the latter case it might be expected that the over-all magnetic moment would be essentially zero, and Fig. 7-7(a) shows an arrangement for which this is true. However, if the material is composed of two atoms having different degrees of magnetism, then in an ordered crystal structure there can be over-all magnetism, Fig. 7-7(b). Although the actual behavior is more complex than suggested by the figure, the distribution of Mn\(^{++}\) ions in solid MnO is similar to Fig. 7-7(a), so that
MnO is nonmagnetic. On the other hand, the Fe^{++} and Fe^{+++} ions in magnetite, FeO·Fe_{2}O_{3}, occupy two types of sites as in Fig. 7-7(b). This configuration causes the pronounced magnetic properties suggested by the name of this substance, "magnetic iron oxide." The term ferrimagnetism is used to describe this type of magnetization, which approaches ferromagnetism in intensity, and the corresponding substances are called ferrites.
The interaction between atoms having net spins can also be zero, and in this case the spins of the various atoms in a substance are randomly oriented. The magnetism is then only about one-millionth that of ferromagnetic substances. This kind of magnetic behavior is called paramagnetism and is characteristic of such nonmagnetic metals as tungsten.

The positive interaction that characterizes ferromagnetic materials is gradually decreased by thermal energy as the temperature is increased, and as the Curie temperature is approached the interaction quickly falls to zero. The corresponding decrease in the intensity of magnetization of iron is shown in Fig. 7-8, and it can be seen that above 1430°F iron is paramagnetic, that is, essentially nonmagnetic. Nickel and cobalt, the other two important ferromagnetic metals, show a similar behavior.
Magnetic domains. In view of the alignment of spins that is characteristic of ferromagnetism, it is puzzling that a ferromagnetic body, such as the steel shaft of a screwdriver, is not actively magnetic under all circumstances. A screwdriver that initially does not attract small iron screws frequently takes on magnetism after it has been used near electrical equipment or stored in contact with a horseshoe magnet. That is, a magnetic material may or may not exhibit over-all magnetization. Also, while all ferromagnetic substances become magnetized in a magnetic field, such as that generated by an electric current in a coil, there are important differences in the degree to which magnetization is retained. Many materials are easily demagnetized after the magnetizing field is removed; these are called magnetically soft. Materials that strongly retain appreciable magnetization when the field is removed are called magnetically hard, and are used for permanent magnets. Figure 7–9 shows how these phenomena are explained by the domain structure of ferromagnetic materials.

A domain is a region in which the magnetic moments of the atoms are aligned and point in the same direction. The interaction energy discussed above would tend to make an entire metal crystal one large domain, but this would create magnetic poles on the surface of the metal and the associated magnetostatic energy would be very high. A compromise between these two energies is reached when the metal assumes a domain structure, Fig. 7–10. Here, regions with various directions of magnetization form closed loops, so that there are few magnetic poles at the surface or in the interior of the metal.

It will be noticed in Fig. 7–10 that the directions of magnetization in all the domains are either vertical or horizontal; these are [100]-type

![Diagram showing magnetic domains](image)

**Fig. 7–9.** The difference between a magnetically hard and a magnetically soft material. The small magnets represent domains in the bars.
Fig. 7-10. Domain structure in a single crystal of iron revealed by a colloidal suspension of fine magnetic particles. Arrows show the direction of magnetization within each domain. Photograph by H. J. Williams. (By permission from Ferromagnetism by R. M. Bozorth. Copyright Van Nostrand, 1951.)

Fig. 7-11. Effect of applying a magnetizing field in each of three different crystallographic directions in a single crystal of iron. Full magnetization is easily obtained in the [100] direction.
directions in the crystal. This behavior is favored because the ease of magnetization varies with crystallographic direction within a single crystal, and the [100] direction in an iron single crystal is the direction of easiest magnetization, Fig. 7-11. In nickel this direction is the [111] direction, and in cobalt it is the hexagonal axis, [001]. If magnetization is to be maintained in a direction other than the direction of easiest magnetization, an additional energy, the anisotropy energy, is required.

An especially important feature of domain structure is the boundary between domains, called the Bloch wall. Consideration of two adjacent vertical domains in Fig. 7-10 shows that the direction of magnetization must turn out of the direction of easiest magnetization in making the transition from one domain to another. The anisotropy energy increases the energy of such domain boundaries, but the increase is a minimum if the transition between domains is gradual and occurs over a region about 1000 atoms wide. This region is the Bloch wall. Because of the relatively large extent and high energy of domain boundaries, if the dimensions of a ferromagnetic substance are sufficiently small, each particle will exist as a single domain and will have exceptional magnetic properties. These fine-particle magnets are discussed below.

**Magnetically soft materials.** In electrical devices such as motors, transformers, and relays it is desirable that the magnetization of the alloy follow very closely any change in the magnetizing field. This magnetic behavior is conveniently described using a general $B-H$ diagram, Fig. 7-12(a). If a specimen is initially unmagnetized, then its magnetization $B$ will increase along the dashed curve as the magnetizing force $H$ increases in magnitude. The degree of magnetization eventually reaches an essentially constant value $B_{\text{sat}}$, the saturation magnetization. When the magnetizing force is reduced toward zero, $B$ decreases along the solid curve and reaches the value $B_r$, the residual magnetization, when $H = 0$. As the magnetizing force is increased in the opposite direction, $B$ continues to decrease and becomes zero when the reverse magnetizing force is equal to $H_c$, the coercive force. As the reverse magnetizing force becomes even greater, the magnetization becomes reversed also and eventually reaches $(-)B_{\text{max}}$. The remaining half of the solid curve is obtained when the magnetizing force is again reversed and increases in the positive sense.

Figure 7-13 shows schematically how the domain structure changes during initial magnetization, the dashed curve in Fig. 7-12(a). In the unmagnetized specimen the magnetic effects of the domains cancel out. When a small magnetic field, $H > 0$, is applied in the direction indicated by the arrow, domains with orientations close to this direction have lower energies and are more stable. There is then a tendency for a more stable domain to increase in size by motion of the Bloch wall separating it from
MAGNETICALLY SOFT MATERIALS

Hysteresis loss is proportional to area inside hysteresis loop

Fig. 7-12. B-H curves illustrating some of the important properties of magnetic materials. (a) Generalized B-H diagram. (b) Ideal B-H diagram for magnetically soft material.

Unmagnetized condition
Process of boundary displacement
Process of rotation of direction of magnetization

Fig. 7-13. The process of magnetization in a ferromagnetic material.
<table>
<thead>
<tr>
<th>Material</th>
<th>(B - H)max. saturation induction, gauss</th>
<th>μ, permeability</th>
<th>$B_r$, residual magnetization, gauss*</th>
<th>$H_{ec}$ coercive force, kOe*</th>
<th>$H_{uni}$ uniaxial anisotropy, erg/cm²</th>
<th>Total core loss, watts/ft, 10,000 gauss, 0.014 inch sheet</th>
<th>Resistivity, ohm-cm</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure iron (99.9% Fe)</td>
<td>13,000</td>
<td>2</td>
<td>11,000</td>
<td>1.0</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>6.0</td>
<td>Small ac motors</td>
</tr>
<tr>
<td>Ingot iron (99.9% Fe)</td>
<td>13,000</td>
<td>2</td>
<td>11,000</td>
<td>1.0</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>6.0</td>
<td>Induction motors</td>
</tr>
<tr>
<td>1% silicon steel</td>
<td>21,000</td>
<td>3</td>
<td>10,000</td>
<td>1.0</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>6.0</td>
<td>Power transformers</td>
</tr>
<tr>
<td>2.5% silicon steel</td>
<td>21,000</td>
<td>4</td>
<td>6,000</td>
<td>0.8</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>6.0</td>
<td>Power transformers</td>
</tr>
<tr>
<td>4.25% silicon steel</td>
<td>21,000</td>
<td>5</td>
<td>6,000</td>
<td>0.8</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>6.0</td>
<td>Telephone transmitters</td>
</tr>
<tr>
<td>3% silicon steel &quot;grain oriented&quot;</td>
<td>21,000</td>
<td>6</td>
<td>6,000</td>
<td>0.8</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>6.0</td>
<td>Radio transformers</td>
</tr>
<tr>
<td>Supermalloy 75% Ni, 15% Fe, 10% Mo</td>
<td>7,900</td>
<td>7</td>
<td>100,000</td>
<td>0.3</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>6.0</td>
<td>(Constant permeability at low fields)</td>
</tr>
<tr>
<td>Hypermalloy 50% Ni, 40% Fe</td>
<td>10,000</td>
<td>8</td>
<td>100,000</td>
<td>0.3</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>8.0</td>
<td>(Constant permeability at low fields)</td>
</tr>
<tr>
<td>Permalloy 65% Ni, 25% Co, 10% Fe</td>
<td>15,000</td>
<td>9</td>
<td>20,000</td>
<td>0.3</td>
<td>200</td>
<td>10 × 10⁻⁸</td>
<td>8.0</td>
<td>(Constant permeability at low fields)</td>
</tr>
</tbody>
</table>

* Determined for saturation induction, (B - H)max.  
† Determined for $B = 100$ rather than for $B = 0$.  

**TABLE 7-2**

**PROPERTIES OF SEVERAL MAGNETICALLY SOFT METALS AND ALLOYS**
a less stable domain. The final stage of the magnetization process involves the rotation of the direction of magnetization of the stable domains from the original easy direction toward the direction of the applied field. This process requires a relatively large magnetic field, $H \gg 0$.

The ideal behavior of a magnetically soft material is shown in Fig. 7-12(b) in comparison with the general $B$-$H$ diagram. In particular, the following property values may be of special interest, depending on the exact application.

1. **Saturation magnetisation, $B_{\text{max}}$.** This quantity* determines the degree of magnetization that can be developed in a magnetic material. A high value of $B_{\text{max}}$ is almost always desirable.

2. **Permeability, $\mu$.** The permeability is defined as $\mu = B/H$. The larger the value of $\mu$, the smaller is the magnetizing force $H$ necessary to produce a given magnetization $B$. A large initial permeability is especially significant for applications in which only a weak magnetizing force is available.

3. **Coercive force, $H_c$.** This quantity is the reverse magnetizing force necessary to eliminate the residual magnetization $B_r$. The coercive force should be small in magnetically soft materials.

4. **Total core loss.** This quantity is the total power loss (watts per pound of alloy) under given conditions. It is the sum of hysteresis loss (which depends mainly on $H_c$) and eddy current loss.

Table 7-2 lists these data and typical applications for several magnetically soft alloys. It is seen that chemical composition has an important influence on magnetic properties. For example, the total core loss of silicon steel is reduced 50 percent by increasing the silicon content from 1.0 to 4.25 percent. Suitable heat treatments and the prevention of mechanical strains also contribute to desirable properties in magnetically soft alloys. Iron-silicon alloys are far easier to magnetize if the grains composing a sheet of alloy are oriented so that a [100] direction is in the direction of the field, Fig. 7-11. Table 7-2 shows the improved permeability of such "grain-oriented" steels compared with regular silicon steels. This is an example of the general phenomenon of preferred orientation shown in Fig. 8-5 in connection with its effect on elastic properties.

**Permanent (hard) magnets.** Although the most powerful magnetic fields are obtained by means of electromagnets, in which magnetically soft materials are used, it is frequently desirable to have a constant magnetic field that does not depend on an electric current. Permanent magnets made of magnetically hard materials satisfy this need. Some of the basic uses of permanent magnets are: (1) to convert electrical energy to me-

* Usually the saturation magnetic induction, $(B - H)_{\text{max}}$, is reported in the literature; see Table 7-2. Since $H$ is generally small at $B_{\text{max}}$, $(B - H)_{\text{max}}$ is approximately equal to $B_{\text{max}}$. 

---

**Table 7-2**

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>Saturation Magnetisation ($B_{\text{max}}$)</th>
<th>Permeability ($\mu$)</th>
<th>Coercive Force ($H_c$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular Silicon</td>
<td>1.0</td>
<td>50%</td>
<td>100%</td>
</tr>
<tr>
<td>Grain-Oriented</td>
<td>4.25</td>
<td>75%</td>
<td>25%</td>
</tr>
<tr>
<td>Silicon Steel</td>
<td>1.0</td>
<td>75%</td>
<td>25%</td>
</tr>
</tbody>
</table>

---

**Note:** The values in Table 7-2 are approximate and may vary depending on specific application and conditions.
<table>
<thead>
<tr>
<th>Material (Balance of composition, if any, is iron)</th>
<th>$B_n$, residual magnetization, gauss</th>
<th>$H_n$, coercive force, oersteds</th>
<th>$(BH)_{max}$, maximum magnetic energy</th>
<th>$B_k$, magnetization at $(BH)_{max}$</th>
<th>Mechanical properties</th>
<th>Commercial methods of fabrication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel (0.9% C, 1% Mn)</td>
<td>10,000</td>
<td>50</td>
<td>$0.20 \times 10^6$</td>
<td>5,200</td>
<td>These magnetic steels are similar to tool steels and are usually formed by hot rolling or forging. They are quenched in oil or water to harden them and therefore have high hardness and low ductility.</td>
<td></td>
</tr>
<tr>
<td>Tungsten steel (8% W, 0.7% C, 0.3% Mn)</td>
<td>10,300</td>
<td>70</td>
<td>$0.32 \times 10^6$</td>
<td>6,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt steel (88% Co, 4% Cr, 8% W, 0.7% C)</td>
<td>10,000</td>
<td>240</td>
<td>$1.0 \times 10^6$</td>
<td>6,800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alnico V (8% Al, 14% Ni, 24% Co, 3% Cu)</td>
<td>12,700</td>
<td>600</td>
<td>$4.8 \times 10^6$</td>
<td>10,000</td>
<td>Hard, brittle</td>
<td>Casting</td>
</tr>
<tr>
<td>Conife (60% Cu, 20% Ni)</td>
<td>5,400</td>
<td>500</td>
<td>$1.3 \times 10^6$</td>
<td>4,000</td>
<td>Ductile, relatively soft</td>
<td>Cold rolling, punching, machining</td>
</tr>
<tr>
<td>Ferroxdur (BaFe$<em>{12}$O$</em>{19}$)</td>
<td>3,400</td>
<td>1,800</td>
<td>$2.5 \times 10^6$</td>
<td>2,000</td>
<td>Hard, brittle</td>
<td>Hard, brittle</td>
</tr>
<tr>
<td>Fine powder (30% Co)</td>
<td>9,000</td>
<td>1,000</td>
<td>$5.0 \times 10^6$</td>
<td>2,000</td>
<td>Weak</td>
<td>Powder metallurgy</td>
</tr>
<tr>
<td>Biemanol (MnBi)</td>
<td>4,300</td>
<td>3,400</td>
<td>$4.3 \times 10^6$</td>
<td>2,000</td>
<td>Hard, brittle</td>
<td>Compacted by pressing</td>
</tr>
</tbody>
</table>

TABLE 7-3

PROPERTIES OF TYPICAL PERMANENT (HARD) MAGNETIC ALLOYS
PERMANENT (HARD) MAGNETS

...mechanical motion, as in electric clocks and meters; (2) to convert mechanical motion to electrical energy, as in a magneto or a phonograph pickup; (3) for mechanical holding as in magnetic separation or as a latch for a refrigerator door.

Properties of typical permanent magnet alloys are listed in Table 7-3. Two of these materials, Ferroxdur and Bismanol, are examples of the strong magnetism that can be developed by ferrimagnetic substances, which were discussed above in connection with antiferromagnetism. The remaining alloys in the table are ferromagnetic. The fine powder magnet was developed after it had been shown theoretically that a particle of iron about 300 A in size would be a single domain and would have remarkable magnetic properties, since the direction of magnetization could change only by rotation. It is predicted that a \( (BH)_{\text{max}} \) value of \( 25 \times 10^6 \) should eventually be obtainable with this type of alloy. Single domains also account for the excellent properties of Alnico V. It has been shown that this alloy consists of fine, platelike particles, and that these single-domain particles orient themselves in the direction of a strong magnetic field that is applied during heat treatment.

Permanent-magnet materials have the characteristic of strongly retaining magnetization when the magnetizing field is removed. The residual magnetization \( B_r \) is the degree of magnetization that remains when the (saturation) magnetizing force is reduced to zero. The coercive force \( H_c \) is the reverse magnetizing force required to decrease magnetization to zero; \( H_c \) is thus a measure of the resistance of the permanent magnet to demagnetizing forces, such as stray magnetic fields. A more generally useful design quantity than either \( B_r \) or \( H_c \) alone is the maximum external

![Diagram](image)

**Fig. 7-14.** (a) The demagnetizing curve of Alnico V showing the optimum design values, \( B_d \) and \( H_d \), of magnetization and of the demagnetizing field. (b) The curve of magnetic energy, \( BH \), obtained from (a).
**Magnetostriiction.** When the degree of magnetization of a ferromagnetic material is changed, a small corresponding change in length results. This phenomenon is called *magnetostriiction*. Conversely, an externally produced strain in a magnetized material causes a change in the amount of magnetization. The actual magnitude of magnetostriiction in iron-nickel alloys is shown in Fig. 17-16. In spite of the small changes of length involved, this phenomenon is the operating principle of *Sonar*, a type of underwater radar, and of certain supersonic generators for metal testing and treatment.

**THERMAL PROPERTIES**

A number of properties determine the total effect of adding heat to a metal or alloy. For example, the *specific heat* $c_p$ controls the temperature increase $\Delta T$ produced by the addition of a given quantity of heat $Q$ to one gram of metal:

$$Q = c_p \Delta T.$$

(7-8)
THERMAL PROPERTIES

Fig. 7-16. The longitudinal magnetostriction produced in iron-nickel alloys by a magnetizing field of 250 oersteds. (After Schulze.)

Fig. 7-17. Idealized thermal expansion curve for iron during slow heating. The discontinuous contraction and heat absorption during the allotropic change are indicated.

The rate at which heat can flow through a material under the influence of a given temperature gradient is determined by the thermal conductivity \( k \):

\[
\frac{dQ}{dt} = k(T_2 - T_1) \frac{A}{l} \text{ cal/sec,}
\]

where \( A \) is the area through which flow occurs, and \( l \) is the distance separating the surfaces that are at temperatures \( T_2 \) and \( T_1 \). A third property
Table 7-4 THERMAL PROPERTIES OF SEVERAL METALS AND ALLOYS

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature, °C</th>
<th>Specific heat, $c_p$, cal/gm·°C</th>
<th>Thermal conductivity $k$, cal/sec/cm/cm²/°C</th>
<th>Coefficient of thermal expansion $\alpha$, per °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>0</td>
<td>0.222</td>
<td>0.57</td>
<td>$22 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.250</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.253</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.268</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>0</td>
<td>0.090</td>
<td>0.95</td>
<td>$15 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.094</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.103</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>0.114</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>0</td>
<td>0.104</td>
<td>0.18</td>
<td>$11.5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.114</td>
<td>0.16</td>
<td>$12.6 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.114</td>
<td>0.11</td>
<td>$16.5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.230</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Invar (36% Ni, 64% Fe)</td>
<td>0</td>
<td>0.123</td>
<td>0.026</td>
<td>$1.4 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.123</td>
<td>0.15</td>
<td>$1.5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.136</td>
<td>0.11</td>
<td>$6.3 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.230</td>
<td>0.08</td>
<td>$13.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>Kovar (29% Ni, 17% Co, 54% Fe)</td>
<td>0-450</td>
<td>0.123</td>
<td>0.026</td>
<td>$5.0 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

that is frequently of interest is the coefficient of thermal expansion, $\alpha$, defined so that the length at temperature $T$ is given by

$$l_T = l_{20}[1 + \alpha(T - 20)]$$,

where $l_{20}$ is the length at 20°C. Table 7-4 lists these thermal properties for several metals and alloys.

The magnitudes of thermal properties depend on the nature of the solid phase and on its temperature. Moreover, these properties show abrupt variations when a phase change takes place. Figure 7-17 shows the sharp decrease in length and the absorption of heat that occur when alpha iron changes to gamma iron at 1670°F. Sudden changes of this kind are especially troublesome in commercial heat-treating operations.
### OPTICAL PROPERTIES

#### Table 7-5

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wavelength of the incident light, Å</th>
<th>Refractive index n</th>
<th>Absorption coeff. α</th>
<th>Reflectivity R, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>4000</td>
<td>0.075</td>
<td>1.93</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>0.090</td>
<td>2.75</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>7500</td>
<td>0.080</td>
<td>5.05</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>9500</td>
<td>0.110</td>
<td>6.56</td>
<td>99</td>
</tr>
<tr>
<td>Gold</td>
<td>4500</td>
<td>1.40</td>
<td>1.88</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>0.23</td>
<td>2.97</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>7500</td>
<td>0.16</td>
<td>4.42</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>9500</td>
<td>0.19</td>
<td>6.10</td>
<td>98</td>
</tr>
<tr>
<td>Copper</td>
<td>4500</td>
<td>0.87</td>
<td>2.20</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>0.17</td>
<td>3.07</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>7500</td>
<td>0.12</td>
<td>4.82</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>9500</td>
<td>0.13</td>
<td>6.22</td>
<td>99</td>
</tr>
<tr>
<td>Aluminum</td>
<td>4000</td>
<td>0.40</td>
<td>3.92</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>0.97</td>
<td>6.00</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>7500</td>
<td>1.80</td>
<td>7.12</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>8500</td>
<td>2.08</td>
<td>7.15</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>9500</td>
<td>1.75</td>
<td>8.50</td>
<td>91</td>
</tr>
<tr>
<td>Steel</td>
<td>5893</td>
<td>2.49</td>
<td>3.44</td>
<td>58</td>
</tr>
<tr>
<td>Sodium</td>
<td>5893</td>
<td>0.005</td>
<td>2.61</td>
<td>96.7</td>
</tr>
</tbody>
</table>

#### OPTICAL PROPERTIES

We usually think of transparent substances like glass or quartz when optical properties are mentioned, but the data of Table 7-5 show that such quantities as refractive index $n$ and absorption coefficient $\alpha$ can be measured for metals. The absorption coefficient is nearly zero in transparent substances, so that only the refractive index is required for a description of their optical properties. For metals, on the other hand, both optical constants are significant. For example, the most important optical property, reflectivity, is given by the following equation for normal incidence:

$$\text{Reflectivity} = \frac{(n - 1)^2 + \alpha^2}{(n + 1)^2 + \alpha^2}. \quad (7-11)$$

Reflectivity influences the choice of metals for mirrors and also determines the color exhibited by an alloy in ordinary light. The exact value of
reflectivity depends on such factors as the condition of the metal surface and the angle of incidence, but its dependence on wavelength is of principal interest. Figure 7–18, giving the reflectivity curves for aluminum, copper, and iron, shows that copper reflects the red end of the visible spectrum much more strongly than it does the violet. As a result, copper appears reddish when seen in ordinary white light. Aluminum reflects red light even more strongly than copper does, and it reflects almost equally well light of other wavelengths. Consequently aluminum appears metallic gray in ordinary light. Iron has only moderate reflecting power for all wavelengths and therefore shows a duller metallic gray color.

The actual appearance of a metal is greatly influenced by a relatively thin oxide film that forms on the surface with exposure to air. For example, unoxidized iron is much brighter than the pieces ordinarily seen. This surface film has been put to good use in aluminum by dyeing the artificially thickened film and thus producing a variety of bright surface colors.

All metals absorb light strongly, and ordinary pieces of metal are opaque to visible light. However, if an appreciably transmitted beam is obtained by the use of extremely thin metal foil, the transmitted color is complementary to the color seen by reflected light. This phenomenon is explained by the fact that absorption and reflection vary in a parallel fashion with change in wavelength. A wavelength that is strongly reflected and contributes significantly to a reflected beam is also strongly absorbed and tends to be absent from a transmitted beam.
PROBLEMS

REFERENCES


Problems

1. Assume that a rough calculation has shown that a small electric furnace can be heated to 500°C if 1000 watts are supplied. How many feet of nichrome wire 0.1 cm in diameter are needed to give this wattage at 115 volts, based on the room temperature resistance value? Assuming that the wire will operate at 300°C, show how this will affect the length of wire needed.

2. The drift velocity $v_d$ is the velocity that an average electron has when a conducting substance is acted on by an electric field. Consider how $v_d$ can be expressed as a function of the relaxation time $\tau$ (Eq. 7-4), starting with the defining equation

$$v_d(t) = v_d(0)e^{-t/\tau}.$$  

(7-12)

An example of the application of this equation is the decrease in $v_d$ when the electric field is removed at time $t = 0$; $v_d(0)$ is then the value of $v_d$ in the presence of the field $E$, and $v_d(t)$ is the value at any later time $t$. After a sufficiently long time, $v_d = 0$. (a) Using Newton’s second law and assuming a frictional force proportional to velocity, show that the equation

$$F_e = m\left(\frac{dv}{dt} + \frac{1}{\tau} v_d\right)$$  

(7-13)

describes the motion of an electron of charge $e$ and mass $m$ in an electric field $E$. (b) If $v_d$ is the steady-state value in Eq. (7-13), show that $v_d(t)$ at time $t$ after removal of the electric field is given by Eq. (7-12). This proves that $(1/\tau)v_d$ is a suitable frictional term in Eq. (7-13). (c) At the steady-state condition $v_d$ is constant. Show that Eq. (7-13) then reduces to the desired expression, Eq. (7-4).

3. You are asked for an opinion on the following suggestion. Since silver has excellent conductivity and since several percent of it can be dissolved in solid aluminum, why not strengthen aluminum for use in high-voltage transmission lines by solid-solution hardening using silver? (a) Is this idea basically sound? (b) Can you suggest a better strengthening method for the purpose? (c) Explain the advantages of the method you suggest.
4. A resistor of exactly 5 ohms resistance is needed for a routine laboratory test. Contrast the errors introduced by normal temperature fluctuations if (a) copper or (b) constantan wire is used in winding this resistor.

5. How may (a) Joule heating and (b) contact potential effects be reduced to a negligible value in thermocouple circuits?

6. Explain what commercial thermocouple is most suitable for measurements at 400°F.

7. Contrast the meanings of "magnetic alloy" and "magnetized alloy."

8. Give reasons why pure iron is not used in transformers.

9. Would it be feasible to use the magnetostriction effect in pure nickel to operate a valve requiring a linear displacement of 0.25 inch to operate it?

10. It is impossible to cool a piece of metal instantly from a high temperature. Consider a large plate of iron 10 cm thick initially at 700°C. Make an approximate analysis to estimate the time necessary to cool the center of the plate to 350°C, assuming that the two surfaces of the plate can be cooled instantly to 0°C. The density of iron is about 8 gm per cubic centimeter.

11. In order to make readings of the relative displacement of two arms in a creep-testing device, a dial gage is to be equipped with extension bars that have a total length of 20 inches. Assuming a maximum variation in room temperature of 10°C, (a) what error would be introduced by expansion if the extension bars were made of iron? (b) If they were made of invar? The dial gage can be read to ±0.0005 inch.
CHAPTER 8
ELASTICITY OF METALS

"... all bodies, even those thought hardest, such as steel... are really elastic and bend a little... and at once regain their former shape."

HUYGENS (1650)

INTRODUCTION

All metals in use are subjected to forces that pull, push, and twist. Often it is inconvenient to use these forces directly in determining the effect they produce, and the corresponding tensile, compressive, and torsional stresses are employed instead (see below). To a first approximation no permanent effect is produced by stresses within the elastic range.* In contrast, stresses in the plastic range may cause large deformations of metal parts. Figure 8-1 illustrates this significant difference. Although elastic effects are only about one-hundredth as large as those encountered in the plastic range, these small effects interest engineers greatly for two reasons. (1) For most mechanical devices it is imperative that the stresses be within the elastic range to avoid the larger plastic deformations. In this connection, the importance of the yield strength of an alloy (see Chapter 9) is that it represents the stress below which the deformation is almost entirely elastic. (2) In many devices even small elastic deformations must be adequately controlled to maintain minimum clearances or to satisfy similar design requirements.

Several aspects of elasticity closely related to metallic structure are considered in this chapter. These include stress raisers, residual stresses, and Young's modulus, E. A significant factor in the behavior of metallic single crystals is the anisotropy of their elastic properties, such as Young's modulus. That is, these properties vary with the direction of testing in a crystal. Many other properties show a similar anisotropy, and the procedure developed here for handling elastic properties can be applied more generally, for example to the treatment of electrical resistivity. The concepts of stress and strain, which are essential for understanding the elastic behavior of metals, are treated in the following sections.

* Figure 9-1 is a graphic illustration of the difference between the slight effect of stresses in the elastic range and the significant deformations produced by the larger stresses in the plastic range.
Fig. 8-1. The effects of loads that produce stresses in the elastic range and in the plastic range.

**STRESS**

Consider a typical metal part in service, such as a turbine wheel. Forces are applied at the periphery of the wheel, and these forces are then transmitted through the body of the wheel to the shaft of the turbine. Thus the essential phenomenon occurring within the metal is the exertion of force by one portion of the metal on the neighboring portions. This picture of a metal under load suggests the following definition: a body is in a state of stress when one portion of the body exerts forces on neighboring portions.

In many engineering problems the state of stress is determined primarily by surface forces, such as those acting on the periphery of the turbine wheel, but sometimes other types of forces are important. For example,
two types of body forces must be considered in many turbine designs. One body force is the centrifugal force that acts on each volume element of the wheel. The other body force is created by differences in temperature within the wheel and the accompanying differences in thermal expansion. These thermal stresses are considered in a later section.

In view of the various factors that can contribute to the state of stress of a body, it is surprising that the most general state of stress can be described in a relatively simple manner. The steps in this description can be given with the aid of Fig. 8-2.

1. An appropriate set of coordinate axes (x, y, z) is chosen.
2. An infinitesimal volume element is constructed with its edges parallel to the coordinate axes. This volume element is sufficiently small that there is negligible variation in the stress components across it.
3. Three stress components are considered to act on each of the faces of the volume element, one normal stress (σ) and two shear stresses (τ). Only the positive faces of the volume element can be seen in Fig. 8-2, but the stress components acting on the negative faces must be equal to these, according to (2), although they act in the opposite directions.
4. It can be shown (see Problem 2) that \( \tau_x = \tau_y, \tau_z = \tau_y, \text{ and } \tau_{xz} = \tau_{yz} \). Therefore only six stress components are needed to describe the most general state of stress.

The description of a state of stress by the six components \( \sigma_x, \sigma_y, \sigma_z, \tau_{xx}, \tau_{xy}, \text{ and } \tau_{xz} \) can be used in the most general problems involving static equilibrium. However it is convenient to consider the special relations that exist when: (1) only surface forces are acting on the body, and (2) the stress is homogeneous (the stress components have the same values at each point in the body).

Figure 8-3 shows the simple case in which an axial force \( F \) acts on the ends of a bar of square cross section. Consider the problem of determining the stresses that act across an arbitrary plane, such as the plane inclined at the angle \( \theta \). Now, if the force \( F \) is to be transmitted along the

---

* For convenience, the special case of mutually perpendicular axes is used for the illustrations and problems of this chapter. However, the appropriate axes for treating the elastic behavior of a triclinic crystal (see Chapter 4), for example, would be the crystal axes, which are not mutually perpendicular.
Area of \( \frac{\text{I}}{\text{I}} \)

(a) ELASTICITY OF METALS \([\text{CHAP. 8}]\)

(b)

(c)

Fig. 8-3. The action of an axial force \( P \) on a bar of square cross section. The hypothetical action of the top portion of the bar on the bottom portion across a plane inclined at the angle \( \theta \) is shown in (a). Drawing (b) shows how the force \( P \) can be resolved into components \( F_x \) and \( F_y \), while drawing (c) shows similarly how the stress vector \( F/A \) can be resolved into its components \( \tau_{xx} \), \( \tau_{yy} \), and \( \tau_{yz} \) (which is zero in this instance).

metal bar, the upper portion of the bar (shown in phantom view in Fig. 8-3a) must exert a force equal to \( P \) on the lower portion of the bar across the inclined plane. But according to the definition of stress, this force must determine the state of stress, and the method of Fig. 8-2 can be used to determine the stress components. The inclined plane in Fig. 8-3(a) represents one of the planes in Fig. 8-2. If it is taken to be the plane perpendicular to the \( \mathbf{x} \)-direction, then the appropriate coordinates are shown in Fig. 8-3(b). It should be noted that the axis of the bar, \( \mathbf{a} \rightarrow \mathbf{a} \), is not one of the coordinates for an inclined plane. The force per unit area, \( F/A \), exerted across a given plane is called the stress vector, and the three stress components acting on the plane must combine vectorially to give \( F/A \) as their resultant. Figure 8-3(c) shows how this concept is applied to the inclined plane of Fig. 8-3(a). A similar analysis can be made for the other two planes shown in Fig. 8-2 (see Problem 4). It will be noted in Fig. 8-3(c) that one of the shear-stress components, \( \tau_{yz} \), is zero, since \( F_y \) lies along the \( \mathbf{z} \)-axis and therefore has no component in the \( \mathbf{y} \)-direction.
The magnitudes of the stress components acting on a given plane, such as in Fig. 8-3(c), are given by the equations

\[ \sigma = \frac{F_n}{A} \]  
\[ \tau = \frac{F_p}{A} \]  

where \( F_n \) is the component of \( F \) acting normal to the plane and \( F_p \) is the component acting parallel to the plane, Fig. 8-3(b).\(^*\)

Although a maximum of six stress components are needed to describe the most general state of stress, in most practical problems only one to three stresses are required. This reduction in number may result when some of the stress components are omitted from consideration; for example, the stresses acting on the \( y- \) and \( z- \) planes were not considered in connection with Fig. 8-3. The number of stress components can also be reduced by a suitable choice of the coordinate axes used in determining the stress components. For example, in a tension test the stress state in the elastic range can be described by a single tensile-stress component, \( \sigma \), if the axis of loading is chosen as one of the coordinate axes (see Problem 5). More generally, for any complex condition of loading there is an orientation of coordinate axes (called the principal axes) for which the shear-stress components are zero. Only the three tensile-stress components are then needed to describe the most general state of stress. To avoid possible confusion, these principal stresses are usually designated \( \sigma_1 \), \( \sigma_2 \), and \( \sigma_3 \), rather than \( \sigma_x \), \( \sigma_y \), and \( \sigma_z \). Most treatments of elastic behavior utilize principal stresses, but in such special problems as the elasticity of crystals it is more convenient to use all six stress components in order to have the freedom to choose appropriate coordinate axes (in this case, the crystal axes).

Displacements of the points of a metal may be of three kinds:

1. Relative movement of the points in the body; this displacement is a measure of the strain of the body.

\* Equations (8-1) and (8-2) apply when \( F_p \) lies along one of the coordinate axes. More generally, the two shear stresses acting on the \( z- \) plane are given by

\[ \tau_{xz} = \frac{(F_p)_z}{A}, \quad \tau_{zy} = \frac{(F_p)_y}{A}, \]

where \( (F_p)_z \) is the component of \( F_p \) in the \( z- \) direction and \( (F_p)_y \) is the component in the \( y- \) direction.
2. Ordinary translation of all the points, which occurs when a block of metal is slid along the floor.

3. Rotation of all the points (for example, a piece of metal turning in a lathe).

In practice it is usually not difficult to separate the displacements caused by strain from those produced by translation and rotation. The last two are not of interest in elasticity calculations.

Just as the stresses are obtained by resolving forces into convenient components referred to unit area; so the strains are obtained by resolving displacements into convenient components referred to unit length. An analysis similar to that shown for stresses in Fig. 8-2 can be used to obtain the following strain components (see Problem 7):

- $\varepsilon_x$, $\varepsilon_y$, $\varepsilon_z$ : Normal strain components in the directions of the coordinate axes $x$, $y$, and $z$, respectively.

- $\gamma_{xy}$, $\gamma_{yz}$, $\gamma_{zx}$ : Shear-strain components; the first letter specifies the plane on which shearing occurs; the second letter specifies the direction in which shearing occurs.

The three normal-strain components $\varepsilon_x$, $\varepsilon_y$, and $\varepsilon_z$ correspond to ordinary extensions or contractions in the directions of the respective coordinate axes. A shear-strain component, such as $\gamma_{xy}$, describes a shear about the direction that is not used in the description of the component, for example the $x$-direction in the case of a $\gamma_{xy}$ shear.

The physical meaning of these strain components is given in Fig. 8-4 for simple cases in which only a single strain component need be considered. Figure 8-4(a) shows pictorially the definition of the normal strain $\varepsilon_z$:

$$\varepsilon_z = \frac{e_z}{l_z}$$

Rearrangement of this equation gives

$$e_z = \varepsilon_z l_z$$

That is, when a length $l_z$ experiences a normal strain $\varepsilon_z$, the resulting displacement in the $z$-direction per unit of the length $l_z$ being considered.

* Here use is made of the familiar convention of designating a plane by the coordinate axis that is perpendicular to it.
FIG. 8-4. The physical significance of (a) a normal strain, \( e_x = e_{xx}/l_x \), and of (b) a shear strain, \( \gamma_{xy} = e_{xy}/l_y \). The displacements \( e_x \) and \( e_y \) are shown greatly exaggerated.

Displacement is in the \( x \)-direction and has the magnitude \( e_{xx} \). Similarly, Fig. 8-4(b) illustrates the definition of the shear strain \( \gamma_{xy} \):

\[
\gamma_{xy} = \frac{e_{xy}}{l_y} = \text{displacement in the } x \text{-direction per unit of the length } l_y \text{ being considered.}
\]  

(8-5)

Rearrangement of this equation gives

\[
e_{xy} = \gamma_{xy} l_y.
\]  

(8-6)

That is, when a length \( l_y \) experiences a shear strain \( \gamma_{xy} \), the resulting displacement is in the \( x \)-direction and has the magnitude \( e_{xy} \).

It will be noted that both the separate straining processes shown in Fig. 8-4 result in a displacement in the \( x \)-direction. In fact, the total displacement in the \( x \)-direction, \( e_x \), is the sum of contributions from the normal strain \( e_x \) and from the two shear strains \( \gamma_{xy} \) and \( \gamma_{xz} \). This relation and the corresponding statements for the \( y \)- and \( z \)-directions are conveniently written

\[
e_x = e_x + \gamma_{xy} y + \gamma_{xz} z,
\]

\[
e_y = \gamma_{xy} x + e_y + \gamma_{yz} z,
\]

\[
e_z = \gamma_{xz} x + \gamma_{yz} y + e_z.
\]  

(8-7)

These equations describe the displacements at a point \((x, y, z)\) relative to the origin. It will be seen that under these conditions the lengths \( l_y \) and \( l_y \) in Eqs. (8-4) and (8-6) are given simply by the \( x \)- and \( y \)-coordinates of the point.
As in the case of stress, it is possible to treat the most general state of strain using only the three principal strains $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$, provided the strains are defined in terms of principal axes. The principal axes for stress are usually identical with the principal axes for strain in cases of practical interest. Also, a homogeneous state of stress is usually associated with a homogeneous state of strain.

**STRESS-STRAIN RELATIONS**

Note that the condition of stress in a body is completely described by the stress components and does not necessarily involve a description of the deformation produced by this stress condition. Similarly, the condition of strain in a body is completely described by the strain components; that is, the stress that produced the given strain need not be specified in describing the state of strain. In practice, however, it is of the utmost importance to know how strain is related to stress. The stress-strain relations within the elastic range are quite simple in principle, as the following discussion shows.

It is well known that the relation between a single stress $\sigma_x$ and the corresponding strain $\varepsilon_x$ is given by Hooke's law:

$$
\varepsilon_x = \frac{1}{E} \sigma_x,
$$

(8-8)

where $E$ is Young's modulus, and $\sigma_x$ and $\varepsilon_x$ are the normal stress and strain in the $x$-direction. However, this equation considers the effect of only a single normal stress. An equation that also considers the effect of stresses in the $y$- and $z$-directions is often used:

$$
\varepsilon_x = \frac{1}{E} \sigma_x - \nu \left( \frac{\nu}{E} \sigma_y - \frac{\nu}{E} \sigma_z \right)
$$

$$
= \frac{1}{E} \left( \sigma_x - \nu (\sigma_y + \sigma_z) \right),
$$

(8-9)

where $\nu$, Poisson's ratio, is the ratio of the contractive strain (at right angles to the applied stress) to the strain produced in the direction of a given stress. Thus, Eq. (8-9) allows for the fact that stresses $\sigma_y$ and $\sigma_z$ in the $y$- and $z$-directions contribute to the total strain in the $x$-direction. Even this equation is completely adequate only for isotropic substances, that is, for substances that show the same properties in all directions of testing. In anisotropic substances such as metallic single crystals, $E$ and $\nu$ vary with direction. Also, even shear stresses can produce normal strains in some anisotropic substances.
A logical extension of these simple stress-strain relations is the generalized Hooke's law, which relates all the possible stresses to all the possible strains. Since there are six stress components and six strain components* at a point, the most general relations among them are given by the six equations (usually referred to crystal axes)

\[
\begin{align*}
\gamma_x &= S_{11}\sigma_x + S_{12}\sigma_y + S_{13}\sigma_z + S_{14}\tau_{xy} + S_{15}\tau_{xz} + S_{16}\tau_{yz}, \\
\epsilon_x &= S_{21}\sigma_x + S_{22}\sigma_y + S_{23}\sigma_z + S_{24}\tau_{xy} + S_{25}\tau_{xz} + S_{26}\tau_{yz}, \\
\epsilon_y &= S_{31}\sigma_x + S_{32}\sigma_y + S_{33}\sigma_z + S_{34}\tau_{xy} + S_{35}\tau_{xz} + S_{36}\tau_{yz}, \\
\gamma_{xy} &= S_{41}\sigma_x + S_{42}\sigma_y + S_{43}\sigma_z + S_{44}\tau_{xy} + S_{45}\tau_{xz} + S_{46}\tau_{yz}, \\
\gamma_{xz} &= S_{51}\sigma_x + S_{52}\sigma_y + S_{53}\sigma_z + S_{54}\tau_{xy} + S_{55}\tau_{xz} + S_{56}\tau_{yz}, \\
\gamma_{yz} &= S_{61}\sigma_x + S_{62}\sigma_y + S_{63}\sigma_z + S_{64}\tau_{xy} + S_{65}\tau_{xz} + S_{66}\tau_{yz},
\end{align*}
\]  

(8-10)

where \(S_{11}, S_{12}, \text{etc.}\) are the elastic compliances and are constants for a given material. These equations allow for the fact that a given stress component, say \(\sigma_x\), may contribute to any one of the six strain components. In most practical cases \(\sigma_x\) does not contribute to the shear strains \(\gamma_{xy}, \gamma_{xz},\) and \(\gamma_{yz}\); that is, \(S_{41} = S_{51} = S_{61} = 0\). However \(\sigma_x\) always contributes to the three normal strains. \(S_{11}\) determines the component of the normal strain in the \(x\)-direction produced by \(\sigma_x\), the normal stress in the \(x\)-direction. Comparison of this term with Eq. (8-8) shows that \(S_{11}\) is the reciprocal of Young's modulus \(E\) for this direction of testing. \(S_{21}\) determines the component of the normal strain in the \(y\)-direction produced by \(\sigma_x\). Comparison with Eq. (8-9) shows that \(S_{21}\) is equal to \(-v/E\) for these directions of testing. \(S_{31}\) determines the component of the normal strain in the \(z\)-direction produced by \(\sigma_x\). \(S_{31}\) is also equal to \(\nu/E\) for the directions of testing involved. Similar reasoning can be used in connection with \(\sigma_y\) and \(\sigma_z\), the normal-stress components in the \(y\)- and \(z\)-directions, to see the significance of many of the remaining \(S\)'s.

In considering the compliances \(S_{44}, S_{55}, \text{and } S_{66}\), it is helpful to recall

* The six shear-strain components \(\gamma_{xy}, \gamma_{yz}, \text{etc.}\) used in this chapter are those commonly used in engineering practice. It is not necessary that \(\gamma_{xy}\) be equal to \(\gamma_{yz}\), even though relations of the type \(\tau_{xy} = \tau_{yz}\) are true of the stress components. In fact, usually when an engineering problem involves \(\gamma_{xy}\), the conditions are such that \(\gamma_{xy} = 0\), and it is for this condition that Eqs. (8-10) are valid. However, for cases in which both shear-strain components defined by a given pair of letters (for example, \(\gamma_{xy}\) and \(\gamma_{yz}\)) have finite values, the only change required in Eqs. (8-10) is the use of the sum \(\gamma_{xy} + \gamma_{yz}\) as the left-hand member of the equation in place of the corresponding single term \(\gamma_{xy}\).

† To obtain a value of \(E\) in the usual units, lb/in², the following conversion factor can be used:

\[
1 \text{ lb/in}^2 = 6.88 \times 10^4 \text{ dynes/cm}^2.
\]
### Table 8-1

The Elastic Compliances of Several Metal Crystals

(The units are $10^{-12}$ cm$^2$/dyne)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal structure</th>
<th>$S_{11}$</th>
<th>$S_{22}$</th>
<th>$S_{33}$</th>
<th>$S_{12}$</th>
<th>$S_{13}$</th>
<th>$S_{23}$</th>
<th>$S_{44}$</th>
<th>$S_{55}$</th>
<th>$S_{66}$</th>
<th>$S_{46}$, $S_{13}$, etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Face-centered cubic</td>
<td>1.50</td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
<td>$-0.58$</td>
<td>$S_{12}$</td>
<td>$S_{12}$</td>
<td>3.52</td>
<td>$S_{44}$</td>
<td>$S_{44}$</td>
<td>0</td>
</tr>
<tr>
<td>Copper</td>
<td>Face-centered cubic</td>
<td>1.49</td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
<td>$-0.63$</td>
<td>$S_{12}$</td>
<td>$S_{12}$</td>
<td>1.33</td>
<td>$S_{44}$</td>
<td>$S_{44}$</td>
<td>0</td>
</tr>
<tr>
<td>Iron</td>
<td>Body-centered cubic</td>
<td>0.80</td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
<td>$-0.28$</td>
<td>$S_{12}$</td>
<td>$S_{12}$</td>
<td>0.86</td>
<td>$S_{44}$</td>
<td>$S_{44}$</td>
<td>0</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Body-centered cubic</td>
<td>0.26</td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
<td>$-0.073$</td>
<td>$S_{12}$</td>
<td>$S_{12}$</td>
<td>0.66</td>
<td>$S_{44}$</td>
<td>$S_{44}$</td>
<td>0</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Hexagonal</td>
<td>2.23</td>
<td>$S_{11}$</td>
<td>$1.98$</td>
<td>$-0.77$</td>
<td>$S_{13}$</td>
<td>$S_{13}$</td>
<td>5.95</td>
<td>$S_{44}$</td>
<td>2($S_{11}$-$S_{12}$)</td>
<td>0</td>
</tr>
<tr>
<td>Zinc</td>
<td>Hexagonal</td>
<td>0.84</td>
<td>$S_{11}$</td>
<td>2.87</td>
<td>$+0.11$</td>
<td>$S_{13}$</td>
<td>$S_{13}$</td>
<td>2.64</td>
<td>$S_{44}$</td>
<td>2($S_{11}$-$S_{12}$)</td>
<td>0</td>
</tr>
<tr>
<td>Tin</td>
<td>Body-centered tetragonal</td>
<td>1.85</td>
<td>$S_{11}$</td>
<td>1.18</td>
<td>$-0.99$</td>
<td>$S_{13}$</td>
<td>$S_{13}$</td>
<td>5.70</td>
<td>$S_{44}$</td>
<td>13.5</td>
<td>0</td>
</tr>
<tr>
<td>Iron</td>
<td>Polycrystalline (and therefore isotropic)</td>
<td>0.48</td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
<td>$-0.14$</td>
<td>$S_{12}$</td>
<td>$S_{12}$</td>
<td>2($S_{11}$-$S_{12}$)</td>
<td>$S_{44}$</td>
<td>$S_{44}$</td>
<td>0</td>
</tr>
</tbody>
</table>
the form of Hooke's law that relates a shear stress $\tau$ and a shear strain $\gamma$,

$$\gamma = \frac{1}{G} \tau,$$  \hspace{0.5cm} (8-11)

where $G$ is the shear modulus (also called the torsion modulus or the modulus of rigidity). Now, if only the shear stress $\tau_{xy}$ is applied to a body, Eq. (8-10) can be used to determine the shear strain $\gamma_{xy}$ produced by this stress:

$$\gamma_{xy} = S_{xy} \tau_{xy}.$$  \hspace{0.5cm} (8-12)

Comparison of Eqs. (8-11) and (8-12) shows that $S_{44}$ is the reciprocal of the shear modulus $G$ for this direction of testing. Similar reasoning applies to $S_{55}$ and $S_{66}$.

The remaining compliances are zero in most metallurgical applications. This is true, for example, for all the metal crystals in Table 8-1. The large number of zero compliance values for a typical metal, tin, will be shown by Eq. (8-13) in connection with an illustration of the use of the equations governing elastic behavior.

Equations (8-10) are indispensable in treating the elastic behavior of such anisotropic substances as single crystals of metals. The directions $x$, $y$, and $z$ are then the directions of the crystal axes (not necessarily mutually perpendicular) and the compliances are experimentally determined for use in these directions. In the most general case all the $S$'s exist. However, the number of independent and nonzero terms in Eqs. (8-10) rapidly decreases in going from triclinic crystals to the more common crystal structures that have higher symmetry. Table 8-1 shows the terms that must be considered in dealing with typical metal crystals. (A term such as $S_{21}$ is not shown in the table because it has the same value as $S_{12}$; and in general $S_{ij} = S_{ji}$.) To illustrate the use of the data of Table 8-1, the following set of equations for tin is given in full for $\sigma$ in units of $10^{12}$ dynes/cm$^2$.

$$
\begin{align*}
\varepsilon_x &= 1.85\sigma_x - 0.99\sigma_y - 0.25\sigma_z + 0 + 0 + 0, \\
\varepsilon_y &= -0.99\sigma_x + 1.85\sigma_y - 0.25\sigma_z + 0 + 0 + 0, \\
\varepsilon_z &= -0.25\sigma_x - 0.25\sigma_y + 1.18\sigma_z + 0 + 0 + 0, \\
\gamma_{xy} &= 0 + 0 + 0 + 0 + 5.70\tau_{xy} + 0 + 0, \\
\gamma_{xz} &= 0 + 0 + 0 + 0 + 0 + 5.70\tau_{xz} + 0, \\
\gamma_{yz} &= 0 + 0 + 0 + 0 + 0 + 0 + 13.5\tau_{yz}.
\end{align*}
$$  \hspace{0.5cm} (8-13)

Shear stresses do not produce normal strains in this case. It can be seen that a tin crystal has greater "stiffness" in the $z$-direction than in the $x$-
or $y$-direction. For example, if the only stress acting on the crystal is a stress of $0.001 \times 10^{12}$ dynes/cm$^2$ in the $z$-direction, the normal strain in this direction is

$$
\varepsilon_z = -0 - 0 + 1.18 \times 0.001 + 0 + 0 + 0 = 0.00118.
$$

On the other hand, if a single stress of the same magnitude acts in the $x$-direction, the normal strain in the $x$-direction is

$$
\varepsilon_x = 1.85 \times 0.001 - 0 - 0 + 0 + 0 + 0 = 0.00185.
$$

Thus the effect produced by stress of a given magnitude depends on the direction of testing.

The values of elastic compliances listed in Table 8-1 are determined for directions that coincide with the crystal axes of the metal crystal. For example, the $S_{11}$ given for iron refers only to the normal strain produced by a normal stress applied along one of the cube axes, [100]. If a normal stress were applied in a different direction (for example a [111] direction in an iron crystal), a different compliance value, $S_{11}$, would relate this stress to the resulting strain. It is possible to calculate an $S_{11}$ value for any direction of application of a normal stress, and the results for iron show that the compliance in a [111] direction has the smallest value, $0.35 \times 10^{-12}$ cm$^2$/dyne, while the compliance in a [100] direction has the largest value, $0.80 \times 10^{-12}$ cm$^2$/dyne. Thus the stiffness of an iron crystal changes by more than a factor of two as the direction of testing is varied.

### Elastic Properties of Engineering Alloys

In contrast with the behavior of single crystals, ordinary alloys used in engineering construction usually show no effect of direction on their elastic properties; that is, they are isotropic. These alloys are made up of millions of very small crystals, and if the crystals are randomly oriented, the average elastic properties are the same in all directions. The value of $S_{11}$ for an ordinary (polycrystalline) bar of iron given in Table 8-1 is seen to lie between the maximum and minimum values for an iron single crystal. As a result of casting, rolling, or heat-treating processes, however, it is possible for the grains in a polycrystalline bar to assume very nearly identical orientations, in which case the bar is said to have a preferred orientation of its crystals. Figure 8-5 shows that a suitable preferred orientation can greatly increase the stiffness of an iron bar. In this case the orientation of the small cubes in Fig. 8-5(b) indicates that all the grains in the bar have a [111] direction along the direction of loading. Therefore, the extension in this direction is
The effect of a possible preferred orientation of the crystals in an iron bar in changing the elastic behavior of a polycrystalline alloy. The orientations of the crystal axes of the separate grains in each bar are represented by the small cubes. (a) Random orientation. (b) Preferred orientation \([111]\) direction along axis of bar.

\[
\varepsilon = \frac{S_1 \sigma}{E} = \frac{(0.35 \times 10^{-12} \text{ cm}^2/\text{dyne}) \sigma}{E} \\
= \frac{(0.35 \times 10^{-12} \text{ cm}^2/\text{dyne}) \times (10,000 \text{ lb/in}^2)}{(6.88 \times 10^4 \text{ dynes/cm}^2/\text{lb/in}^2)} \\
= 0.00024 = 0.024\%.
\]

On the other hand, using \(3.0 \times 10^7\) as the value of Young’s modulus \(E\) for ordinary polycrystalline iron gives

\[
\varepsilon = \frac{\sigma}{E} = \frac{10,000}{3.0 \times 10^7} = 0.00033 = 0.033\%
\]

as the extension produced by the same stress in the absence of the preferred orientation, Fig. 8-5(a).

The most important elastic property of commercial alloys is Young’s modulus \(E\). The range of values of Young’s modulus in commercial alloys is shown in Table 8-2 and is seen to be large. Since the deflection of a stressed member is usually inversely proportional to the \(E\) value of the metal used, it is possible to decrease the deflection for a given load by a factor of 7.5 by changing from magnesium to molybdenum.

Except for preferred orientation or substantial changes in composition, there is no known method for significantly increasing the Young’s modulus of a given material. Thus if a steel rod of a given size deflects too much under load, the amount of this deflection cannot be decreased by heat
# Elasticity of Metals

## Table 8-2

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus $E$ at 20°C, lb/in²</th>
<th>Temperature coefficient $dE/dT$ in the range 0–100°C, lb/in²/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>$10 \times 10^6$</td>
<td>$-4.4 \times 10^3$</td>
</tr>
<tr>
<td>Beryllium</td>
<td>$37 \times 10^6$</td>
<td>$-5.8 \times 10^3$</td>
</tr>
<tr>
<td>Cobalt</td>
<td>$30 \times 10^6$</td>
<td>$-7.4 \times 10^3$</td>
</tr>
<tr>
<td>Copper</td>
<td>$18 \times 10^6$</td>
<td>$-5.5 \times 10^3$</td>
</tr>
<tr>
<td>Iron</td>
<td>$30 \times 10^6$</td>
<td>$-8.0 \times 10^3$</td>
</tr>
<tr>
<td>Lead</td>
<td>$2.6 \times 10^6$</td>
<td>$-2.7 \times 10^3$</td>
</tr>
<tr>
<td>Magnesium</td>
<td>$6.3 \times 10^6$</td>
<td>$-2.6 \times 10^3$</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>$47 \times 10^6$</td>
<td>$-6.3 \times 10^3$</td>
</tr>
<tr>
<td>Nickel</td>
<td>$30 \times 10^6$</td>
<td>$-10 \times 10^3$</td>
</tr>
<tr>
<td>Osmium</td>
<td>$80 \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>$15 \times 10^6$</td>
<td>$-10 \times 10^3$</td>
</tr>
<tr>
<td>Tungsten</td>
<td>$60 \times 10^6$</td>
<td>$-6.0 \times 10^3$</td>
</tr>
<tr>
<td>Sintered carbide (94% WC, 6% Co)</td>
<td>$100 \times 10^6$</td>
<td>$-4.7 \times 10^3$</td>
</tr>
<tr>
<td>Elinvar (36% Ni, 12% Cr + W, balance Fe)</td>
<td>$24 \times 10^6$</td>
<td>0</td>
</tr>
<tr>
<td>Invar (36% Ni, balance Fe)</td>
<td>$21 \times 10^6$</td>
<td>$+10 \times 10^3$</td>
</tr>
<tr>
<td>Ni-Span C (42% Ni, 5.5% Cr, 2.5% Ti, balance Fe)</td>
<td>$27 \times 10^6$</td>
<td>0</td>
</tr>
</tbody>
</table>

The magnitude of the change of Young’s modulus with temperature for iron is shown by the following:

- Treatment or ordinary alloying. On the other hand, the value of $E$ may be somewhat decreased by precipitation hardening, eutectoid decomposition, cold-working, or other changes that produce internal stresses in the alloy.
- Increasing the operating temperature also tends to decrease Young’s modulus, as shown in Fig. 8-6. This temperature effect may be significant in devices such as Bourdon tubes and precision springs. In these instances special alloys with low temperature coefficients, $dE/dT$, are used, for example Elinvar and Ni-Span C, Table 8-2.
ELASTIC PROPERTIES OF ENGINEERING ALLOYS

Fig. 8-6. The effect of temperature on the value of Young's modulus for several pure metals. (Köster.)

Fig. 8-7. Examples of the variation of Young's modulus $E$, across binary phase diagrams. (a) Solid-solution system. (b) Eutectic system. (c) Intermetallic compound system. (Köster.)
calculation. Between 0 and 100°C Young's modulus decreases by
\[
100 \times \frac{dE}{dT} = 100(8.0 \times 10^3) = 800,000 \text{ lb/in}^2,
\]
whereas the values for Elinvar and Ni-Span-C are essentially constant over this temperature range.

Large changes in chemical composition produce variations in Young's modulus. In the absence of intermetallic compounds the variation of \( E \) with composition is roughly linear across a phase diagram. This behavior is illustrated for a complete solid-solution system by the molybdenum-tungsten diagram in Fig. 8-7(a), and for a eutectic system by the lead-tin diagram in Fig. 8-7(b). If an intermetallic compound is present in the alloy system, a discontinuity exists in the curve of \( E \) versus composition. This behavior is shown for the magnesium-tin system in Fig. 8-7(c).

Fig. 8-8. The difference between nominal stress and actual stress in a steel part subjected to a load \( L \). (a) Nominal stress at section \( b-b' \) caused by the load \( L \). \( A \) is the area of section \( b-b' \). (b) Actual stress at section \( b-b' \) produced by stress raisers. (c) Possible stress at \( b-b' \) caused by the stress raiser and a hardening heat treatment.
STRESS RAISERS

ELASTIC STRESSES IN DESIGN

The chief design principle concerning elasticity is the following: the working stress must lie within the elastic range. The preceding sections have considered the possible values of Young's modulus in this range, and the following chapter defines a practical maximum stress limit to the elastic range, the yield strength. All this information is of little value, however, if the actual working stress is not known. The stress calculated in the usual manner (total load divided by the total cross-sectional area) is the nominal stress. Its magnitude for the section b-b' is shown in Fig. 8-8(a), but for a number of reasons the actual working stress may differ from this nominal stress.

1. The shape of the part may cause the stress to be higher in certain portions of the cross section. Such a shape effect is called a stress raiser. Figure 8-8(b) shows that the change in cross section near b-b' has a stress-raising effect which causes the actual stress to differ significantly from the nominal stress.

2. Even in the absence of stress raisers the nominal stress may differ from the actual stress as a result of the presence of residual stresses. These are stresses produced by differences in plastic deformation of the metal, as described below. They can arise during casting, welding, heat-treating, or cold-working operations. Figure 8-8(c) shows a possible stress pattern resulting from the combined effects of the stress raiser and a hardening heat treatment.

Stress raisers. It is known both from calculations and from actual measurements that the stress in the region of a discontinuity may be different from the nominal stress. An example of this stress-raising effect is shown in Fig. 8-9, where a high tensile stress exists at the top of the hole and a compressive stress is produced at the side. (Note that the magnitudes of only certain stress components at only a few positions in the plate are

![Fig. 8-9. The stress-raising effect of a small hole through a flat plate subjected to a tensile force.](image)
Fig. 8-10. The stress-raising effect of several machine element shapes. (a) A large hole through a flat plate in tension. (b) Circular notches of various depths in a flat plate in tension. (c) Fillet at a change in section of a flat plate in tension. (d) Protrusion of a flat plate in tension. (e) Hole through a cylindrical shaft in bending. (f) Fillet at a change in section of a cylindrical shaft in torsion. (Courtesy O. H. Neugebauer and Product Engineering.)

indicated in this figure.) The high tensile stresses at the top (and bottom) of the hole can be roughly visualized as being caused by the inability of the stress to pass across the hole. The fibers adjoining the hole must carry this portion of the stress in addition to their normal share. It is frequently convenient to describe such increases in stress in terms of a stress concentration factor $K$, defined as follows:

$$K = \frac{\text{maximum actual stress}}{\text{nominal stress}}.$$  \hspace{1cm} (8-14)
In Fig. 8-9 the stress concentration factor is $K = 3$. The $K$ values for a number of important stress raisers are given in Fig. 8–10.

Because many alloys undergo plastic deformation when acted on by sufficiently high stresses, the stress values corresponding to these stress concentration factors are often not fully developed. Ductile materials can often deform locally in the highly stressed regions and thus partially relieve the stresses. In general stress raisers are not dangerous in ductile materials subjected to static loads. When the stresses rapidly alternate from tension to compression, however, even ductile materials are greatly affected by stress raisers. Most brittle alloys are sensitive to stress concentration effects under all conditions of loading. An interesting exception is gray cast iron, in which the graphite flakes that make it brittle also act like internal stress raisers that are much more severe than small notches cut into the surface.

Residual stresses. Almost every heat-treating shop has its story about a freshly hardened piece of steel that flew apart while merely resting on a bench. A similar phenomenon occasionally occurs on a larger scale, as in the case of a welded steel bridge that broke in two with a loud noise and collapsed at a time when there was no load on it. These examples demonstrate clearly that metal parts often experience stresses in addition to those produced by the external load. Since all stresses influence the behavior of the metal in service, it is important to understand their natures and the circumstances that cause them. For the purpose of this discussion it is convenient to distinguish between body stress, which usually varies on a macroscopic scale, and textural stress that arises because of microscopic inhomogeneities in a metal.

The stress produced by an external load is one kind of body stress, but similar body stresses in the elastic range can also arise under the following circumstances:

1. Uniform thermal expansion in a bar that is fixed at the two ends (see Problem 12) or nonuniform expansion even in an unrestrained part.
2. Imposition of restraints at the surface of a metal as a result of a chemical treatment, such as nitriding or electroplating.

Stresses of this kind are called contingent body stresses, because their existence is dependent (contingent) on the continuing presence of a source of stress, such as external load, nitrided layer, etc. These stresses disappear when the source is removed.

Residual stress is the second type of body stress. As its name suggests, it remains after its source has been removed. Several examples of the generation of residual stress will now be discussed, and in every instance it will be seen that the cause of the retention of the stress is the occurrence of inhomogeneous plastic deformation.
Cold-working always produces residual stresses. However, the resulting stress pattern varies greatly, depending on the type of working that is employed. If the metal is only lightly worked, so that plastic deformation is limited to regions near the surface, the surface layers will be left with compressive stresses, see Problem 13. Figure 8-11(a) gives an example of this pattern of residual stresses, which is produced by processes such as shot-peening, light cold-drawing, and surface rolling. Usually if the working is severe, so that deformation occurs throughout the cross section of the metal, the pattern of residual stresses will be similar to that shown in Fig. 8-11(b) for a cold-drawn rod, and there will be tensile stresses in the surface layers. It is known that tensile residual stresses in the surface layers can seriously reduce the resistance of a metal to cracking, for example, in endurance testing. Therefore it is common practice to use one of the processes of light plastic deformation to convert tensile residual stress in the surface layer to compressive stress. Figure 8-11(c) shows the action of surface rolling in improving the pattern of residual stresses originally present in a cold-drawn steel rod.

Another major source of residual stresses is nonuniform change in volume because of thermal effects. In many cases, such as fusion welding, several thermal factors may act simultaneously to produce the final, complex pattern of residual stress. These factors include (1) thermal expansion on heating or cooling, (2) a change from one solid phase to another with an accompanying change in volume, and (3) a change from the liquid state to the solid state. Each of these three sources of residual stress will be discussed separately.
Consider a hot, solid metal rod that is rapidly cooled, for example, by being plunged into water. The surface cools more rapidly than the center, and therefore it shrinks faster. This nonuniform shrinkage tends to cause plastic compression of the hotter, softer interior of the rod to preserve "matching" of adjoining portions of the rod. After the surface of the rod becomes cool, the interior continues to contract as its temperature continues to fall. When both the interior and the surface of the rod are able to support large stresses, this contraction of the interior produces compressive stresses at the surface of the rod. Thus the final pattern of residual stress is similar to that shown in Fig. 8-11(a). The magnitude of the longitudinal stress at the surface produced by severe quenching is about \(-30,000\) lb/in\(^2\) in iron and about half this value in nonferrous metals, such as aluminum. As would be expected, use of a milder quench reduces these residual stresses. This beneficial effect is especially pronounced in aluminum, where the use of oil quenching almost eliminates residual stresses.

The most important example of a phase change involving expansion is the formation of martensite from austenite. An argument similar to that used above for contraction during cooling can be used to show that the expansion accompanying martensite formation should result in tensile residual stresses at the surface and compressive stresses in the interior. This pattern, similar to Fig. 8-11(b), can be produced experimentally if special care is taken to minimize effects due to thermal contraction. The maximum tensile stress at the surface is then about \(80,000\) lb/in\(^2\). In actual hardening of steel the final pattern of residual stress is determined by a combination of thermal contraction and martensitic expansion. Consequently the patterns vary greatly, depending on the steel and the details of the heat treatment used, and the surface layers can be either in tension or under compression.

Although surface stresses are developed even in such simple shapes as a cylindrical bar, they are intensified by the presence of discontinuities in the steel part being quenched. Typical causes of distortion, cracking, or breakage of steel parts during heat treatment are sharp corners, re-entrant angles, and abrupt changes in section. Figure 8-12 shows the improvement in the design of typical steel parts by the reduction of these discontinuities. When the part to be heat treated is unavoidably complex in shape, the stresses can be greatly reduced by the use of a milder quenching medium (oil instead of water, for example).

The residual stresses in hardened steel parts are largely removed if the steel is given a high-temperature tempering treatment, for example at 1100°F. More generally, residual stresses existing in any alloy for any of the reasons discussed above can be reduced to a safe level by a stress-relief heat treatment in which the alloy is heated to a temperature at which local plastic flow occurs under the action of the residual stresses.
Fig. 8-12. Examples of correct and incorrect design of steel parts that are to be quenched during heat treatment. (a) An undercutting form tool in which differences in section thickness and in the severity of re-entrant angles have been reduced. (b) A doubled-ended side mill in which abrupt section changes and sharp re-entrant angles have been reduced in severity. (c) Keyways improved by balancing their positions to reduce warping and by introducing fillets. (Courtesy Tool Steel Simplified, published by Carpenter Steel Company, Reading, Pennsylvania.)

Typical temperatures for stress relief in one hour are: brass, 500°F; nickel alloys, 900°F; stainless steel, 1600°F.

In designing parts to be cast, an additional stress problem must be considered, that is, the development of stresses caused by shrinkage during solidification of the molten alloy. These stresses may become great enough to cause the formation of cracks while the casting is solidifying, a phenomenon called hot tearing. Although section discontinuities are also important in this case, an additional factor is the solidification behavior of the alloy. In most cases a solidifying alloy becomes a "connected solid" through interlocking of the previously independent dendrites only after solidification is about 80 percent complete. Cracking can occur, therefore, only after this connection has been accomplished. It has been shown experimentally that the tendency toward hot tearing is related to the length of the temperature interval over which the remaining solidification occurs. If approximately the last 20 percent solidification occurs at constant temperature because of the presence of eutectic liquid, then hot tearing is greatly reduced.
In contrast to the body stresses considered above, which tend to vary in a characteristic fashion with macroscopic position in a metal bar (Fig. 8-11), textural stresses are localized about certain microstructural features of the metal. The stress field that exists around a dislocation (see Chapter 4) is a good example of this type of stress. Textural stresses also arise across the boundary between adjacent grains during plastic deformation, because of differences in deformation behavior. Similar grain-boundary stresses can be produced by anisotropic expansion of grains as a result of magnetic effects (magnetostriction) or anisotropic thermal expansion. When a second phase forms within an existing solid phase, large textural stresses are created in both phases. Although many details of textural stresses remain to be studied, it is certain that these stresses are comparable in magnitude to body stresses and that they profoundly influence the behavior of metals.

REFERENCES

1. Give three examples of mechanical designs in which (a) it is important that the stresses remain within the elastic range and (b) it is permissible or necessary to have some plastic deformation.

2. Make a sketch similar to Fig. 8-2, but show on it the stress components acting on the minus $z$- and $y$-faces as well as those shown in the figure acting on the corresponding positive faces. Note that a stress component on a negative face is numerically equal to the corresponding component on the positive face but is pointed in the opposite direction. Since the element of volume being considered is at equilibrium, the algebraic sum of the moments of the forces about an axis, such as the $z$-axis, must be zero. (a) Obtain an expression for this sum and show that it will be zero if $\tau_{zy} - \tau_{yz}$. (b) What conclusion can be drawn about $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$?

3. Consider a square bar 10 inches long and 0.2 square inch in cross-sectional area hanging vertically from a support with a 1000-pound weight attached to its lower end. What are the magnitudes of the shear stress and the tensile stress on the following planes, which are considered to be at about the center of the bar along its length?

(a) A plane perpendicular to the axis of the bar, i.e., a plane whose normal makes an angle of 0° with the axis of the bar. A plane whose normal with the axis of the bar makes an angle of (b) 30°, (c) 40°, (d) 45°, (e) $\theta$. (f) Plot the magnitudes of shear stress and tensile stress as a function of the angle between the plane normal and the axis of the bar. (g) What is the meaning of the statement, "In a tension specimen the maximum shear stress exists on a plane at 45° to the axis of loading"?

4. Obtain expressions involving $F$, $\sigma_0$, and $\theta$ for all the stress components in the bar shown in Fig. 8-3(a) referred to the system of axes shown in Fig. 8-3(c). Note that the $y$-face of the volume element (see Fig. 8-2) is conveniently taken as lying in one of the lateral surfaces of the bar. For the purpose of this analysis the $z$-face is treated analogously to the $x$-face (Fig. 8-3a), except that the angle involved is 90° − $\theta$.

5. Obtain expressions for the stress components in the bar shown in Fig. 8-3(a) referred to the following system of axes: the $x$-axis is the axis of the bar and the $y$- and $z$-axes are perpendicular to the lateral faces of the bar.

6. Explain why you would use the axes of Problem 4 or of Problem 5 in treating each of the following phenomena. (a) A long rod is loaded in tension and the resulting elongation is to be measured. (b) When a long rod is loaded in tension, it is observed that at a critical load faint markings appear on the surface. Their traces make an angle of 45° with the axis of the bar.

7. Consider a rectangular parallelepiped described by the edge lengths $l_x$, $l_y$, and $l_z$ (Fig. 8-13) that experiences elastic (small) deformation into the parallelepiped described by the edge lengths $\Delta l_x$, $\Delta l_y$, and $\Delta l_z$. Note that this arbitrary deformation is completely described by the three displacement vectors $\Delta l_x$, $\Delta l_y$, and $\Delta l_z$. However, it is more convenient to work with the three components of each of these vectors.

(a) Show how a displacement vector
\( e_{e}, \) for example, can be resolved into components \( e_{xx}, e_{yy}, \) and \( e_{zz} \) along the three axes \( l_x, l_y, \) and \( l_z. \)

(b) Explain how the displacement components, such as \( e_{xx}, e_{yy}, \) and \( e_{zz}, \) which have the disadvantage of depending on the value chosen for \( l_x, \) can be converted into the strain components \( e_{s}, \gamma_{s}, \) and \( \gamma_{s}, \) which are conveniently referred to a unit length.

8. If a body, such as a steel sphere one foot in diameter, is placed in a liquid that is under pressure, the body is said to be under hydrostatic pressure. The components of the strain tensor then have the values \( e_{s}, \gamma_{s}, \gamma_{s}, \) and \( \gamma_{s}, \gamma_{s}, \gamma_{s}, \gamma_{s}, = 0, \) when, as in this case, the body is isotropic.

(a) If \( E = 3 \times 10^7 \text{ lb/in}^2 \) and \( v = 0.3, \) use Eq. (8-9) to show that \( k = 10^{-3} = 0.001 \) when the pressure on the liquid is \( 7.5 \times 10^4 \text{ lb/in}^2. \) [Note that the set of coordinate axes can be chosen at random because of symmetry.]

(b) Explain why Eq. (8-9) cannot be used to determine \( k \) in (a).

(c) If the center of the steel sphere is chosen as the origin of coordinates, what is the displacement with respect to this origin of the point having the coordinates \( x = 3.2 \text{ inches}, y = 0, z = 0? \)

(d) As in (c), what is the displacement of the point having the coordinates \( x = 3, y = 3, z = 3? \)

(e) Show that the magnitudes of the displacements in (c) and (d) are equal, and that both are directed toward the center. That is, (c) and (d) represent the solution of the same problem but with two different sets of axes.

9. Use Eqs. (8-9) and (8-10) and the data given in Table 8-1 to determine the value of Poisson's ratio for polycrystalline iron.

10. Consider a metal ladder designed so that it is much like the conventional wood ladder, except that the corresponding structural members of the metal ladder are thinner. Assume that aluminum was used as the material for building such a lightweight ladder and that the ladder was found to deflect excessively under a man's weight, although no permanent bending took place. Consider some of the following possible remedies for this condition:

(a) use of a higher-strength aluminum
alloy, (b) use of steel in place of aluminum, (c) use of magnesium in place of aluminum, (d) redesign of the ladder.

11. A flywheel shaft is designed so that a bearing section one inch in diameter is adjacent to a shaft section two inches in diameter. The radius of the fillet connecting these two sections is \( \frac{1}{4} \) inch.

(a) If the nominal shear stress in the surface fibers of the bearing section is 6000 lb/in², what is the actual maximum stress?

(b) Compare the reduction of the stress concentration factors produced by (1) increasing the fillet radius to \( \frac{3}{4} \) inch, (2) decreasing the shaft diameter from 2.0 to 1.2 inches.

12. Consider a thin steel rod that is rigidly fixed at both ends. Calculate the stress that is produced in the rod by lowering its temperature from 100 to 0°C. It can be assumed that the rod is not able to contract and that the tendency towards contraction (given quantitatively by \( \alpha \) in Table 7-4) is just balanced by a stress tending to cause tension.

13. It will be shown in the following chapter that plastic deformation begins when a certain value of stress is obtained. Looking at this another way, we could say that plastic deformation tends to prevent stress from rising above this value. Now, assume for simplicity that the elongations produced by surface rolling, Fig. 8-11(a), vary linearly from zero at the center of the bar to a maximum in the surface layers. These elongations produce only elastic stresses in the central portion of the bar, but they ordinarily cause plastic deformation of the surface layers. Therefore the stress can be pictured as rising linearly from the center of the bar to a plateau in the surface layers where plastic deformation has occurred.

(a) First consider the simple case of extremely light surface rolling in which even the surface layers of the bar are subjected only to stresses within the elastic region. Sketch the distribution of stress under load and explain what happens to this distribution when the load is removed.

(b) Now apply the same analysis to an example of surface rolling in which the outer 10 percent of the bar undergoes plastic deformation. Sketch the distribution of stress under load. When the load is removed there is a tendency for the stresses to return the bar to its original shape. Show that the unaltered central part of the bar is restrained by the plastically elongated surface layers. Sketch the final distribution of residual stresses that represents a balance between the unrelieved tensile stresses in the central part of the bar and the balancing compressive stresses produced in the surface layers.
CHAPTER 9
PLASTICITY OF METALS

"Notwithstanding the hardness of solid bodies, or the difficulty of moving the particles one amongst another, there are several that admit of such motion without fracture..."

DALTON (1800)

INTRODUCTION

A properly designed machine member operates in the elastic range of stresses, but the plastic behavior of metals is also important. The explanation is simple. The more efficiently a given alloy is used in design, the more closely its operating stress approaches the limit of elastic behavior, and therefore the more necessary is a knowledge of its behavior in the "beyond-elastic" stress range. Although it is not possible to ensure that a machine member will not be subjected to extraordinarily high stresses, even above the safety factor invariably employed, it is possible to make reasonably certain that the result of such misuse is only an inconvenience, not a catastrophe. For example, an automobile rounding a curve at high speed may strike its wheel against the curbing. If the resulting stress is above the elastic range, the wheel may be bent if plastic deformation occurs. The inconvenience of this result is far preferable to the alternative of fracture, which would result in the breaking of the wheel and the possibility of a serious accident. Metallic plasticity is also involved in the forming operations that are carried out on all wrought metals. Hot rolling or forging of steel, even at the extremely high temperatures used in practice, must be done at a rate determined by the deformation characteristics of the individual alloy. Cold forming operations, so important in the mass production of many metal parts, are even more restricted by plastic properties. Although the quantitative application of the theory of plasticity to industrial forming operations is complex, a basis for understanding these applications is furnished by the subject matter of this chapter.

It is convenient to consider that the behavior of an alloy subjected to stresses above the elastic range may be divided as follows:

<table>
<thead>
<tr>
<th>Total behavior</th>
<th>Beyond-elastic deformation</th>
<th>Plastic deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture</td>
<td></td>
<td>elastic deformation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>anelastic deformation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>permanent plastic deformation</td>
</tr>
</tbody>
</table>
Actually, it is difficult to separate sharply the phenomena of plasticity and fracture, since few commercially important alloys fracture without first undergoing some plastic deformation. Typical behavior is shown in Fig. 9-1, a complete stress-strain curve. Such a curve is obtained by making a tension test on the metal with a testing machine of the kind shown in Fig. 9-15. The test bar is elongated (strained) by the downward movement of the moving crosshead, and the load necessary to cause this elongation is indicated on the dial gage. While the test bar is being pulled until it fractures, data on changes in length and diameter are taken with the load data. Stress and strain values calculated from these data are then plotted to give the stress-strain curve. The strain in the elastic range is very small, and the stress-strain curve appears in this figure to rise on the stress axis itself until the range for plastic deformation is reached. The strain then increases rapidly with increasing stress until fracture occurs.

All the strain referred to in Fig. 9-1 is essentially permanent plastic strain. For some purposes, however, it is necessary to distinguish the very small components of elastic strain and of anelastic strain present in the usual experimental measurement of the total strain. This distinction can be made with the aid of Fig. 9-2, which shows the initial portion of a stress-strain curve. When the load is removed from a plastically deformed specimen, the total strain is immediately reduced by the amount $\sigma/E$, the elastic strain, where $E$ is Young's modulus and $\sigma$ is the stress corresponding to the load that acted on the specimen. Even the remaining strain is not
all permanent plastic strain, since a portion of it, the anelastic strain, disappears gradually after the load has been removed. When the total deformation is small, as in Fig. 9-2, the elastic and anelastic portions are significant, but they can be neglected in studying large plastic deformation of the kind shown in Fig. 9-1.

Plasticity of metals is an outstanding example of structure-sensitive phenomena, which were discussed in Chapter 3. It will be recalled that dislocations in the crystal structure of a metal permit deformation to occur by the slip process at very low stresses compared with the theoretical value for a perfect crystal structure. The various factors that influence strength and ductility (alloying, heat treatment, cold-working, service temperature, rate of straining, state of stress) are thought to act by changing the number of dislocations or their behavior. As a background for understanding the nature of these effects, the mechanisms of plastic deformation will now be considered.

Mechanisms of Plastic Deformation

The motion of dislocations plays a fundamental role in the deformation of metals. However, the type of motion that occurs in a given instance depends on such factors as the temperature at which the deformation occurs, the rate of deformation, and the structure of the metal. A consideration of several of the principal modes of motion of dislocations will show why these factors are important.

Deformation at normal temperatures. At ordinary temperatures deformation occurs most easily by the slip mechanism described in Fig. 4-25. The restrictions on this mechanism are: first, that the slip process occurs only on certain planes in the crystal, the slip planes, and in certain directions, the slip directions; and second, that a minimum stress, the critical resolved shear stress, must act to produce slip. An example of a slip system for face-centered cubic metals is given in Fig. 4-30, namely, slip on \{111\} planes in (101) directions.

The concept of a critical resolved shear stress can be understood with the aid of Fig. 9-3. If a cylindrical crystal of cross-sectional area \(A\) is acted on by an axial force \(F\), only the component of this force in the slip direction is effective in moving the dislocation. This force component is \(F \cos \lambda\), and when it is divided by the area of the slip plane, \(A / \cos \phi\), the corresponding shear stress \(\tau\) is obtained (see Eq. 9-2). Thus,

\[
\tau = \frac{F}{A} \cos \lambda \cos \phi. \tag{9-1}
\]

It has been shown experimentally that slip occurs for a given metal when
Fig. 9-3. Description of the angles $\lambda$ and $\phi$ used in determining the critical stress for slip.

Table 9-1

Typical Values of Critical Resolved Shear Stress, $\tau_c$, for Slip in Metal Crystals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temp., °C</th>
<th>$\tau_c$, kg/mm²</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face-centered cubic metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>20</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>20</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>50Ag-50Au</td>
<td>20</td>
<td>0.35</td>
<td>Silver and gold form a complete series of solid solutions. $\tau_c$ has a maximum value at about the 50 atomic percent composition.</td>
</tr>
<tr>
<td>20Ag-80Au</td>
<td>20</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>20</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Close-packed hexagonal metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>20</td>
<td>0.03</td>
<td>These values are for slip on the (0001) plane in the [1120] direction.</td>
</tr>
<tr>
<td>Mg</td>
<td>20</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>330</td>
<td>0.07</td>
<td>This value is for slip on (10T1) type planes in the [1130] direction.</td>
</tr>
<tr>
<td>Mg</td>
<td>330</td>
<td>0.400</td>
<td></td>
</tr>
</tbody>
</table>

† $1$ kg/mm² = 1422 lb/in².
DEFORMATION AT NORMAL TEMPERATURES

Fig. 9-4. Photomicrographs illustrating slip phenomena in aluminum. (a) Single slip and deformation band (vertical) in an aluminum single crystal elongated 20% (×500; reproduced at two-thirds size). (Courtesy R. W. Cahn.) (b) Multiple slip in a coarse-grained aluminum specimen elongated 15% (×50; reproduced at two-thirds size). (Courtesy R. W. Cahn.) (c) The microstructure of aluminum after 90% reduction by cold rolling. This structure is typical of severely deformed metals. (Courtesy Alcoa Research Laboratories.)

\( \tau \) reaches a definite, critical value \( \tau_c \). Representative values of this critical resolved shear stress are given in Table 9-1. The magnitude of \( \tau_c \) for a given base metal is affected by solid-solution alloying, as shown by the data for the silver-gold system, and also by temperature. An increase in temperature causes a moderate decrease in \( \tau_c \) for a given slip system. A more important effect of increased temperature, however, is the activation of an additional slip system in some metals. For example, above about 225°C magnesium crystals can slip on (10\( \overline{1} \)1) type planes as well as on the usual (0001) plane. This phenomenon explains why magnesium alloys can be more severely deformed at slightly elevated temperatures (warm-working) than at room temperature (cold-working).

A metal may exhibit several kinds of behavior during slip. The simplest is single slip on a single, parallel set of slip planes, Fig. 4–1(b). The displacement on each slip plane is hundreds of atomic distances, and the active slip planes tend to be in groups called slip bands. The spacing of slip lines within a band is about 200 Å, while the separation of adjacent bands is 100 times this value. The microscopic appearance of slip bands can be seen in Fig. 9–4(a). This figure also shows the occurrence of deformation bands, a phenomenon that often accompanies single slip. These bands are thin platelike regions in which the lattice has rotated differently than in the surrounding metal. During single slip the crystal lattice is not disturbed, except in the immediate neighborhood of a plane on which slip has occurred, and therefore the critical resolved shear stress remains nearly constant during the entire deformation by this process.
Although considerable deformation can occur by single slip in single crystals of some metals, in ordinary polycrystalline metals the necessity for compatibility at grain boundaries requires that slip occur on several slip systems. An example of multiple slip at an early stage in the deformation process is given by Fig. 9-4(b). In the course of severe deformation the crystal lattice of each grain in a metal becomes quite disorganized, Fig. 9-4(c). This picture of the deformation process explains why the stress rises continuously with increasing strain for ordinary metals (a phenomenon called strain hardening).

When a crystal is prevented from slipping for any reason (for an example see Problem 4), other mechanisms of plastic deformation may operate, even though the stress required is higher than for unrestrained slip. The twinning mechanism shown in Fig. 9-5 is especially important in the deformation of close-packed hexagonal metals such as magnesium and zinc. The characteristic crystal plane involved in twinning is called the
twinning plane, Fig. 9-5(b). Under the action of a critical shear stress the atoms on adjacent lattice planes are sheared relative to one another by the fraction of an atomic distance shown in the figure. These slight atomic displacements are sufficient to cause the final orientation of the twin lattice to be the mirror image of the matrix lattice across the twinning plane. Although the actual deformation that is accomplished by twinning is small, the twinned region is often in an orientation that permits slip to occur, and in this way twinning contributes significantly to the over-all deformation process.

The gradual growth of a twin during progressive deformation of a metal is shown in Figs. 9-5(c) and (d). This behavior is typical of lattice transformations that occur by a shear mechanism, such as the martensite reaction that is discussed in a later chapter. An important characteristic of shear processes is the high rate at which they can occur. In contrast, it is known that in some metals a definite time, the delay time, is required for slipping to begin after a given stress has been applied. For low-carbon steel at room temperature, the delay time is about 0.1 second for a stress 10 percent above the minimum needed for deformation, and it is about $10^{-8}$ second for twice the minimum stress. Because of the delay time...
for slip, when steel is strained very rapidly it forms twins (Neumann bands), although at moderate strain rates it deforms by slip.

Another mode of deformation, kinking, has been observed in crystals of zinc or cadmium that are compressed nearly parallel to the (0001) plane. Figure 9-6(a) is a schematic illustration of the process by which dislocations could move along the (0001) slip planes during deformation of the central portion of the crystal and create boundaries between the kink band and the main body of the crystal. Note that dislocations of opposite sign accumulate at the upper and lower boundaries. The photograph of Fig. 9-6(b) shows a kink band in a cadmium crystal; the dark line indicates the inclination of the (0001) plane to the axis of the specimen.

High-temperature deformation. If a metal is deformed at sufficiently high temperatures, its microstructure may appear to be unaffected by the deformation that the metal has undergone. Specifically, the slip lines that characterize deformation at normal temperatures are absent, and the metal also fails to strain harden. As in the case of deformation at normal temperatures, the basic mechanisms of high-temperature deformation are slip and twinning by the motion of dislocations. However, at high temperatures two processes occur that permit the deformed lattice to rearrange itself and eliminate the disturbances produced during deformation. One of these processes is the movement through the lattice of vacancies and interstitial atoms that are created in the deformation process. This behavior is an example of diffusion in metals, which is considered in Chapter 11. The vacancies and interstitialcies move from disturbed regions, where the energy is high, to adjacent portions of the lattice where they can aid in forming structure of higher perfection and lower energy. The second process is "climb" of dislocations out of their original slip planes. Figure 9-7 is a schematic illustration of the manner in which a vacancy can diffuse to a dislocation and cause it to climb to the next higher slip plane. Similarly, an interstitial can add to the extra plane of atoms and cause the dislocation to climb in the opposite direction.

An important example of high-temperature deformation is the gradual straining or creep that metals experience under relatively low stresses at high temperatures. During the creep process it is necessary that readjustment of lattice dimensions and orientations occur both within each grain and at the boundaries between grains. Examination of the microstructure of a creep specimen, Fig. 9-8, shows that readjustments within each grain occur by cell formation. It has also been demonstrated that grains slide along one another at their boundaries. These two processes result when dislocations produced during creep accumulate at grain boundaries or cell boundaries. In the latter case the dislocations produce a low-angle boundary that separates two cells of slightly different orientation. Each
HIGH-TEMPERATURE DEFORMATION

Fig. 9-7. Climb of a dislocation. (a) An edge dislocation with a vacancy in its vicinity. (b) Two "jumps" of the vacancy removes an atom from the extra plane and causes the dislocation to climb to the next slip plane.

Fig. 9-8. Cell formation during creep of high-purity aluminum. (a) Initial microstructure of the annealed aluminum, and (b) cell formation that occurred during 46% extension by creep during 850 hours at 200°C (both X100, reproduced at two-thirds size). (Courtesy D. McLean, National Physical Laboratory; Crown copyright reserved.)
cell has an undeformed lattice comparable in perfection to that of the original grain. This picture of high-temperature deformation explains why the creep process can take place for prolonged periods at an almost constant rate.

**STRESS-STRAIN RELATIONS IN PLASTIC DEFORMATION**

A metal crystal is anisotropic with respect to plastic and to elastic deformation, but it is convenient to restrict the present treatment of plastic deformation to an isotropic material. It will be recalled that an actual bar of metal made up of millions of small, randomly oriented crystals behaves in an isotropic manner. Therefore the equations given here will apply to ordinary, polycrystalline metals.

Definitions of stress and strain. Plastic deformation may involve large changes in length and cross section of metal specimens. Therefore it is necessary to examine critically the definition of strain that is customarily used in the analysis of small, elastic deformations, before applying it to the study of plastic deformation. Consideration of the meaning of strain leads to the conclusion that any small increase in length $dl$ must be divided by the length $l$ that the specimen has at that time. That is, the small strain $\varepsilon$ corresponding to the small deformation $dl$ is given by the equation

$$\varepsilon = \frac{dl}{l}. \tag{9-2}$$

If the total deformation $\Delta l$ is small, say $\Delta l = 0.001 l_0$, then to a good approximation $l$ can be considered constant at its initial value $l_0$. The total strain $\varepsilon$ in this case is

$$\varepsilon = \int_{l_0}^{l_0 + \Delta l} \frac{dl}{l_0} = \frac{\Delta l}{l_0} = 0.001. \tag{9-3}$$

This method of calculating strain is used in problems involving elastic deformation.

Evidently the approximation $l = l_0$ is not a good one if the total deformation $\Delta l$ is large. Fortunately, it is not difficult to calculate the true (exact) value of the strain, using Eq. (9-2). If a bar has been plastically deformed uniformly to a length $l$ from an initial length $l_0$, the true strain $\delta$ is given by

$$\delta = \int_{l_0}^{l} \frac{dl}{l_0} = [\ln l]_0 = \ln \frac{l}{l_0}. \tag{9-4}$$
It is convenient to use $\delta$ to represent plastic strain, just as $\varepsilon$ represents elastic strain. For a large total deformation such as $\Delta l = l_0$, the true strain calculated by Eq. (9-4), namely,

$$\delta = \ln \frac{l}{l_0} = \ln \frac{2l_0}{l_0} = \ln 2 = 0.693,$$

is significantly different from the strain given by the approximate equation, Eq. (9-3):

$$\delta' = \frac{\Delta l}{l_0} = \frac{l_0}{l_0} = 1.000.$$  

(9-5)  

(9-6)

It is to be noted that $\delta'$ (rather than the more accurate $\delta$) is used in the approximate stress-strain curves widely used in industry (see p. 333).

Equation (9-4) is valid only if the deformation is uniform over the length considered. If the deformation is nonuniform, that is, if necking of the specimen occurs (see Fig. 9-10), it is evident that the plastic strain has different values in various parts of the bar. Since the maximum strain is usually of principal interest, it is sufficient to determine the strain at the necked section. It can be shown (see Problem 6) that the strain at this position is

$$\delta = 2 \ln \frac{d_0}{d},$$  

(9-7)

where $d_0$ is the initial diameter and $d$ is the neck diameter of the bar.

As in the case of strain, approximate and exact definitions of stress are also in use. For small elastic deformations the stress is always very nearly

$$\sigma = \frac{F}{A_0},$$  

(9-8)

where $F$ is the load and $A_0$ is the original cross-sectional area of the specimen. This is also the definition of the nominal stress used in approximate stress-strain curves. However, since the actual area $A$ may be only a fraction of $A_0$ after severe plastic deformation, the exact definition

$$\sigma = \frac{F}{A}$$  

(9-9)

must be used to calculate the true stress. This definition of stress is employed in this chapter.

**Flow stress.** A striking characteristic of the relation between stress and plastic strain is that below a certain stress (the flow stress $S_0$), essentially no plastic strain is produced. Thus for elastic strain the stress-strain
Plasticity of Metals

Relation can be represented by the equation \( \varepsilon = \sigma / E \), where \( \varepsilon \) is the normal strain in the direction in which the stress \( \sigma \) is acting. However, for plastic strain a pair of equations is needed, such as *

\[
\begin{align*}
\delta &= 0 \quad \text{for } \sigma < S_0 \\
\delta &= f(\theta) \quad \text{for } \sigma > S_0
\end{align*}
\]  

(9-10)

That is, plastic strain occurs as some function \( f \) of the stress only when the stress is greater than the critical value \( S_0 \). Before we consider the nature of the function that relates stress and plastic strain, we should learn something of the stress \( S_0 \) at which plastic deformation begins.

In view of the complex nature of small plastic strains, it is not surprising that it is difficult to define precisely the stress at which plastic deformation begins even under the simple conditions of a tension test. Fortunately, there is general agreement among engineers that a useful, conventional definition of the beginning of plastic deformation is the 0.2 percent offset yield strength.† The method for determining this stress value is shown in Fig. 9-9. From the point representing a strain of 0.2 percent on the zero stress axis a line is drawn parallel to the elastic portion of the stress-strain curve. This line will intercept the stress-strain curve at the point at which the material being tested departs from elastic behavior by 0.2 percent. The stress at this point is the (0.2 percent offset) yield strength. Thus, for a metal plastically deformed in simple tension, the magnitude of the stress at which plastic deformation begins is the yield strength. It is shown below that this is also the value of \( S_0 \).

Actual engineering structures often are subjected not merely to a single tensile stress but to a combination of tensile, compressive, and torsional stresses. The question then arises: what is the condition for flow under such conditions of combined stresses? Extensive investigations of metal specimens subjected to complex stress combinations have shown that for isotropic, polycrystalline metals plastic deformation begins when the

\*

These equations are strictly valid only for a simple stress state, such as that in a tension test. More generally, not the single stress component \( \sigma \), but rather the stress function \( S \) is related to \( S_0 \), and the pair of equations is then written

\[
\begin{align*}
\mathcal{B} &= 0 \quad \text{for } S < S_0 \\
\mathcal{B} &= f(S) \quad \text{for } S > S_0
\end{align*}
\]

where \( S \) and \( \mathcal{B} \) are defined by Eqs. (9-17) and (9-18).

† Although 0.2 percent offset is the most widely used definition of yield strength, 0.1 percent is often employed for steels, and as much as 0.5 percent for cast iron.
FLOW STRESS

Fig. 9-9. Illustration of the method for determining the 0.2% offset yield strength from the stress-strain curve in tension.

shear-strain energy reaches a critical value. The corresponding equation is

\[ S = \frac{(S_1 - S_2)^2 + (S_2 - S_3)^2 + (S_3 - S_1)^2}{2} = S_0, \quad (9-11) \]

where \( S_1, S_2, \) and \( S_3 \) are the principal stresses, and algebraically \( S_1 > S_2 > S_3 \). Thus the flow stress \( S_0 \) is not represented by a single physical stress in the most general case. Rather, flow stress is the critical value of the stress function \( S \) at which plastic deformation begins.

It is easy to determine the magnitude of \( S_0 \) by means of a tension test. When a given material is tested in tension, \( S_1 = \sigma_1 \) and \( S_2 = S_3 = 0 \). When these values are substituted in Eq. (9-11), this equation reduces to

\[ \left( \sigma_1^2 + 0 + (\sigma_1)^2 \right)^{1/2} = \sigma_1 = S_0, \quad (9-12) \]

Chapter 8 showed that the use of principal axes permits the reduction of any stress state to one involving only three normal (tensile or compressive) stresses. The three stresses referred to the principal axes are the principal stresses. Stress problems that are described without the use of shear stresses are already referred to principal axes, for example in a tension test. That is, the stress \( \sigma_1 \) in a tension test is also the principal stress \( S_1 \). A torsion test, on the other hand, is usually described in terms of a torque (or the corresponding shear stresses), and a suitable conversion must be made in order to obtain the principal stresses. In this case the principal stresses consist of a tensile and a compressive stress.
That is, plastic flow begins in simple tension when the tensile stress $\sigma_1$ becomes equal to $\sigma_0$. In other words, the magnitude of $\sigma_0$ in Eq. 9-11 is just the yield strength determined in a tension test.

With this information it is possible to predict the stress at which flow will begin under any combination of applied stresses. For example, if a steel plate is subjected to tension in one direction and is compressed with an equal stress at right angles to the first direction, then $\sigma_2 = -\sigma_1$ and $\sigma_3 = 0$. Equation (9-11) then becomes

$$
\left(\frac{(\sigma_1)^2 + (\sigma_2)^2 + 4(\sigma_1)^2}{2}\right)^{1/2} = \sigma_0,
$$

(9-13)

That is, the steel plate will plastically deform at a tensile stress only about 58 percent as large as that required to produce plastic deformation in a tension test. This pronounced effect of the compressive stress can be explained qualitatively in terms of maximum shear stress. Slip, the principal mechanism of plastic deformation, occurs at a critical value of shear stress. Therefore we might expect plastic flow to begin when the maximum shear stress reaches a certain value, regardless of the magnitudes of the individual principal stresses. In the case of equal tensile and compressive stresses at right angles, the maximum shear stress is twice as great at a given value of the tensile stress as it is in simple tension. This visualization therefore gives the relation $\sigma_1 = 0.58\sigma_0$, rather than the more exact shear-strain energy criterion of Eq. (9-13). In spite of its lack of accuracy, the maximum shear-stress criterion of the beginning of plastic deformation is widely used.

In contrast to the decrease in flow resistance described above, a condition of biaxial tension generally leads to an increase in flow resistance compared with that found in a tension test. For example, if $\sigma_2 = 0$ and $\sigma_3 = 0$, the value of $\sigma_1$ at which plastic deformation begins can be shown by substitution in Eq. (9-11) to be $\sigma_1 = 2\sigma_0/\sqrt{3} = 1.15\sigma_0$. A state of combined stresses such as this can reduce the ductility of a metal in comparison with the ductility that the metal exhibits in a tension test. Since a larger tensile stress $\sigma_1$ must be exerted to produce initial plastic deformation, the stress for fracture will usually be reached after a smaller total amount of deformation has occurred.

Inasmuch as the flow stress (yield strength) is the practical limit on which design stresses are based, it is worth while to consider the more important factors that influence its value. Although the quantitative values vary greatly from one alloy to another, the following general statements can be made:
1. The flow stress of a solid solution is higher than that of the pure solvent metal. The effect of a given concentration of alloying element, say 1 a/o (atomic percent), tends to be larger in proportion to the dissimilarity between the solute and solvent atoms. When applied in commercial alloys, solid-solution strengthening can increase the yield strength severalfold.

2. The flow stress decreases with increasing temperature $T$. The quantitative relationship can be approximated in many cases by the exponential equation

$$S_0 = Ae^B/T,$$  \hspace{1cm} (9-14)

where $A$ and $B$ are constants. In practice the flow stress ceases to be of much significance at high temperatures, and the creep rate then becomes important.

3. An increase in flow stress is produced by an increase in rate of straining. Although the relation appears to be exponential, like Eq. (9-14) for temperature, the effect of strain rate is very small. An increase in flow stress corresponding to a $100\%$ decrease in temperature would be produced by about a $10^5$-fold increase in strain rate. Usually body-centered cubic metals are more strongly affected by a given change in strain rate or temperature than are face-centered cubic metals.

4. The microstructure of a given alloy has a strong influence on the flow stress value. Roughly, the relation is

$$S_0 = S + k \ln \frac{1}{d},$$  \hspace{1cm} (9-15)

where $S$ and $k$ are constants and $d$ is the mean free path in the matrix of the alloy. This mean free path is the average distance between grain boundaries or between particles of a dispersed phase. For example, with a decrease in the spacing $d$ of lamellar pearlite, the yield strength of steels increases according to Eq. (9-15). This equation does not apply when the dispersed phase is coherent with the matrix (see Chapter 13).

Effective stress-strain curve. In the preceding section only the first of the pair of Eqs. (9-10) was considered. That is, emphasis has been given to the magnitude of the stress $S_0$ at which plastic flow begins. There remains the task of describing the nature of the relation between the plastic strains and the stresses above the flow stress $S_0$. A useful, approximate treatment is given here. It is convenient to divide this stress-strain relation into two parts, namely, the flow curve

$$\mathcal{S} = kT^\alpha,$$  \hspace{1cm} (9-16)
Range of nonuniform plastic deformation

Linear relation between \( \varepsilon_p \) and \( \sigma_p \)

Uniform plastic deformation

\[ \sigma_p = K \]

Elastic range

\( \varepsilon_1 = \text{elastic strain} \)
\( \varepsilon_1 = \text{plastic strain} = 0 \)

Fig. 9–10. The regions of applicability of the relations used to calculate plastic deformation of metals subjected to a tension test. In this case \( \bar{D} = \varepsilon_1 \) and \( \bar{S} = \sigma_1 \). The amount of elastic strain shown is greatly exaggerated.

which applies in the region of uniform plastic deformation, and an essentially linear portion of the \( \bar{S} \) versus \( \bar{D} \) curve.* In Eq. (9–16) \( \bar{S} \) and \( \bar{D} \) are the effective stress and strain, respectively (defined below), and \( K \) and \( n \) are constants. Figure 9–10 is a schematic illustration of the range of stresses over which each of these two stress-strain relations can be used in an ordinary tension test. (It is shown below that in a tension test, \( \bar{S} \) is equal to \( \sigma_1 \), the normal stress in the direction of testing, and \( \bar{D} \) is equal to \( \varepsilon_1 \), the normal plastic strain in the direction of testing.) In Fig. 9–10 the range of elastic deformation extends to the stress \( S_p \), the yield strength. Uniform plastic deformation, which is described by the flow curve, begins at this stress and continues until the appearance of necking indicates the beginning of nonuniform plastic deformation. (The load corresponding to the stress at which necking begins is the maximum load the specimen supports during the tension test. It is shown later that this maximum load, referred to unit area, is the tensile strength of the material.) The true stress continues to increase as a linear function of strain in proportion as

* After necking begins, flow occurs under a combined stress state even in a simple tension test. Bridgman has shown that this factor can be taken into account by multiplying the stress \( \sigma_1 \) by the quantity

\[
\left(1 + \frac{4R}{d}\right) \ln \left(1 + \frac{d}{4R}\right)^{-1},
\]

where \( d \) is the minimum diameter of the neck and \( R \) is the radius of curvature of the neck profile.
necking becomes more pronounced, until finally the specimen breaks at the fracture stress, that is, the largest stress to which the specimen is subjected in the course of the tension test.

$\bar{S}$ and $\bar{D}$, the effective stress and effective strain, are defined in such a manner that Eq. (9-16) is valid for any arbitrary combination of principal stresses and strains:

$$\bar{S} = \frac{(S_1 - S_2)^2 + (S_2 - S_3)^2 + (S_3 - S_1)^2}{2}, \quad (9-17)$$

$$\bar{D} = \left[ \frac{2(D_1)^2 + (D_2)^2 + (D_3)^2}{3} \right]^{1/2}, \quad (9-18)$$

where $S_1, S_2,$ and $S_3$ are the principal stresses and $D_1, D_2,$ and $D_3$ are the principal strains. It is seen that for a simple tension test $S_1 = S_3 = \bar{S}$, since $S_2 = S_3 = 0$. It can also be shown that $D_1 = D_1 = D$, since there is no appreciable volume change during plastic flow in metals and therefore $D_1 = D_2 + D_3$. Thus, the strength coefficient $K$ and the strain-hardening exponent $n$ can be determined for a given alloy by means of a tension test. Table 9-2 gives representative values of $K$ and $n$ determined in this manner. Also, if a stress-strain curve such as Fig. 9-10 is

<table>
<thead>
<tr>
<th>Material</th>
<th>Flow stress $S_0$, lb/in$^2$</th>
<th>Strength coefficient $K$, lb/in$^2$</th>
<th>Strain-hardening exponent $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed low-carbon steel</td>
<td>30,000</td>
<td>65,000</td>
<td>0.3</td>
</tr>
<tr>
<td>Quenched and tempered 0.6% steel</td>
<td>75,000</td>
<td>184,000</td>
<td>0.15</td>
</tr>
<tr>
<td>Annealed copper</td>
<td>8,000</td>
<td>46,000</td>
<td>0.54</td>
</tr>
<tr>
<td>Annealed cartridge brass</td>
<td>12,000</td>
<td>130,000</td>
<td>0.49</td>
</tr>
<tr>
<td>Annealed 24S aluminum alloy</td>
<td>16,000</td>
<td>49,000</td>
<td>0.21</td>
</tr>
<tr>
<td>Precipitation-hardened 24S aluminum alloy</td>
<td>45,000</td>
<td>100,000</td>
<td>0.16</td>
</tr>
</tbody>
</table>
determined for a given alloy by means of a tension test, the same curve describes the behavior of the alloy when it is subjected to a complex combination of stresses. This is true because $\sigma_0$ and $\delta_1$ in a tension test are equal to $S$ and $D$, and the relations between $S$ and $D$, such as Eq. (9-16), are valid for any arbitrary stress state.

The variation of $K$ and $n$ with composition, temperature, rate of straining, and microstructure is much like that previously described for $S_0$. The behavior is by no means the same for all alloys, however. In particular, the yielding phenomenon that is especially prominent in certain steels merits attention. When deformation begins in these alloys, plastic deformation occurs nonuniformly, with the resulting production of markings on the surface called Luder's lines. This nonuniform yielding continues at nearly constant stress until the entire specimen has been deformed several percent. The over-all deformation is then uniform, and further plastic deformation occurs in a uniform manner until necking begins. The yielding phenomenon occurs because certain impurity elements (nitrogen and carbon in steel) locate themselves preferentially adjacent to dislocations and make the dislocations more difficult to move. However, once the necessary high stress, called the upper yield stress, has torn some of the dislocations away from their restraining impurity atoms, the dislocations can then continue to move under the usual stress, the (lower) yield stress. When yielding has begun in one portion of the specimen, stress concentration in adjacent portions causes yielding to spread gradually throughout the metal at the yield stress. It is to be noted that this yielding phenomenon is the exception rather than the rule in plastic deformation behavior of metals.

The portion of the effective stress-strain curve in which the flow curve, Eq. (9-16), is valid is characterized by a continuously increasing load $F$ applied to the specimen. Although the cross section decreases during this portion of a tension test, the metal is sufficiently strengthened as a result of plastic deformation to increase the load necessary to cause additional deformation. However, at a strain about equal to the strain-hardening exponent $n$ the rate of strain hardening is insufficient to compensate for the decrease in cross section, and localized deformation (necking) begins. Further reduction of the necked area proceeds with a continuous decrease in load until fracture occurs. It is evident that necking is undesirable both in forming operations on metals and in their deformation behavior as stressed members. Unlike the load on a necked specimen, the stress continues to increase to a maximum value at fracture.

**Fracture**

In contrast to the imperceptible gradualness with which plastic deformation begins, it ends with suddenness and finality in fracture. Cons-
Types of fracture. The simplest mode of fracture is cleavage along a crystal plane, shown for a single crystal in Fig. 4-1(b). Brittle fracture of this type occurs at low temperatures in crystals of body-centered cubic and close-packed hexagonal metals, but it has not been found in face-centered cubic crystals. The data of Table 9-3 show the critical value of stress normal to a given plane required for cleavage fracture. Ordinarily there is a preferred fracture plane, for example the (100) plane in iron, but the behavior of zinc crystals shows that fracture can occur on other planes if the stress is sufficiently high. The presence of 0.53 percent cadmium in solid solution in zinc crystals greatly increases the critical stress for cleavage. Typically, those metals that fracture in a brittle manner by cleavage at low temperatures show a more ductile behavior at higher temperatures. This change is especially pronounced in iron and leads to the concept of transition temperature that is discussed below. A second mode of fracture in single crystals is shear fracture. In some instances,

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cleavage plane</th>
<th>Temperature, °C</th>
<th>Critical stress normal to cleavage plane, kg/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe (body-centered cubic)</td>
<td>(100)</td>
<td>-100</td>
<td>26</td>
</tr>
<tr>
<td>Zn (close-packed hexagonal)</td>
<td>(0001)</td>
<td>-185</td>
<td>27.5</td>
</tr>
<tr>
<td>Zn + 0.53 Cd</td>
<td>(0001)</td>
<td>-185</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Fig. 9-11. Intercrystalline and transgranular fracture in a polycrystalline metal (low-carbon steel). (a) Fracture along grain boundaries (intercrystalline fracture), and (b) fracture through the grains (transgranular fracture) (both X15). (Courtesy J. R. Low, Jr., General Electric Research Laboratory.)
such as in magnesium crystals, the fractured surfaces clearly reveal that final rupture occurred by shearing along slip planes after much plastic deformation had occurred. Usually, however, the crystal simply deforms continuously until it necks down and breaks.

Fracture in ordinary polycrystalline metals involves several new features; the most obvious is the distinction between intercrystalline fractures (between the grains) and transgranular fractures (through the grains), Fig. 9-11. Intercrystalline fractures occur without appreciable deformation and often are caused by the presence of a second phase at the grain boundaries. An important example of this type of fracture is found in metals stressed for long times at high temperatures. In this case the cracks form at discontinuities such as grain junctions and progress along grain boundaries that are most nearly normal to the applied stress. The usual mode of fracture in polycrystalline metals is transgranular. Ordinarily it occurs by a ductile shear mechanism. Figure 9-12 shows the cup-and-cone fracture that is normally produced by this mechanism in a tension-test specimen. The initial crack forms at the center of the necked region of the specimen and spreads with increasing strain in a direction perpendicular to the applied stress. This behavior is interrupted when the final stage of fracture occurs by shearing at about 45° to the axis of the specimen.

Under some conditions transgranular fracture in polycrystalline metals may occur partly or entirely by cleavage. The fracture in Fig. 9-11(b) is of this type; the fracture surface follows certain crystal planes through the grains. Examination reveals large bright facets, and consequently the term granular is used to describe this type of fracture. A common
pattern observed in the fracture of impact specimens consists of a granular center portion surrounded by a "picture frame" of dull, fibrous fracture. In mixed fractures of this kind it is important to distinguish three different aspects of fracture: (1) the amount of deformation that precedes fracture (ductile or brittle behavior), (2) the appearance of the fracture (the amounts of fibrous and of granular areas), and (3) the crystallographic mode of fracture (the proportion of shear and of cleavage fracture). Although (2) and (3) are fairly closely related, the data of Fig. 9–14 show that the fracture appearance will not always indicate the crystallographic mode of fracture.

**Mechanism of fracture.** As in the study of plastic deformation, the basic problem in fracture is to explain why it occurs at only a small fraction of the theoretical stress calculated for a perfect crystal structure. The cause is now believed to be submicroscopic microcracks in the metal that cause local concentration of stress to values high enough to propagate the crack and eventually to fracture the metal. In the **Griffith theory** an energy method is used to estimate the stress necessary to cause a crack to spread. The surface energy associated with a flat crack of length 2C and unit width is $4C\gamma$, where $\gamma$ is the surface energy per unit area of the crack surfaces. In general there will also be some plastic deformation of the surfaces of the crack requiring energy $p$ per unit area, so the total energy needed to create the crack is

$$W_n = 4C(\gamma + p). \tag{9-19}$$

This energy is considered to be supplied by the elastic strain energy that is released by the formation of the crack (see Problem 11), that is,

$$W_n = \frac{\pi C^2 \sigma^2}{E}, \tag{9-20}$$

where $\sigma$ is the tensile stress acting normal to the crack and $E$ is Young's modulus. Now, an existing crack will grow spontaneously under the action of a given stress, if the change in $W_n$ with increase in $C$, $dW_n/dC$, is at least equal to the corresponding change in $W_n$, $dW_n/dC$. From Eqs. (9-19) and (9-20) this equality can be written

$$\frac{2\pi C \sigma^2}{E} = 4(\gamma + p). \tag{9-21}$$

The value of $\sigma$ given by this equation is the critical value required to
Fig. 9-13. A mechanism of crack formation. (a) Edge dislocations from an active Frank-Read source piling up at a barrier, and (b) the three piled-up dislocations in (a) form an incipient crack within the crystal lattice. (After Stroh.)

cause the crack to propagate:

$$\sigma_{\text{crit}} = \left[ \frac{2E(\gamma+p)}{\pi C} \right]^{1/2}.$$  (9-22)

It can be seen from this equation that the stress required to fracture a metal is lower the longer the existing cracks and the smaller the energy $p$ expended in plastic deformation.

In some cases it is believed that microcracks exist in the metal as a result of the previous history of solidification or hot-working. However, even an initially sound metal specimen can develop cracks on an atomic scale, for example by the mechanism shown in Fig. 9-13 involving the "piling up" of dislocations at a barrier. When a sufficient stress is applied, a few favorably oriented Frank-Read sources will generate a succession of dislocations on slip planes. A barrier, such as a grain boundary, will impede the motion of the leading dislocation as shown and will cause the following dislocations to pile up against the first one. Figure 9-13(b) shows the microcrack that forms if three unit dislocations combine to form a single dislocation having a Burger vector $b$ equal to three lattice spacings. Microcracks of this kind will propagate and cause brittle fracture if a critical tensile stress can be generated normal to the crack. The competing process that may prevent brittle fracture is prior slip in the
vicinity of the microcrack. This concept of crack formation explains the following important phenomena:

1. The increase of working temperature usually increases the amount of plastic deformation that occurs before fracture. This is reasonable, since the dislocations responsible for plastic flow are then more mobile.

Figure 9-14(a) shows the great increase in ductility of a low-carbon steel as the temperature is raised.

2. The tendency for brittle fracture to occur is greater at high rates of straining, because there is less time for plastic flow to occur near the microcracks and thus relieve the stress concentration.

3. The state of stress in a specimen greatly influences the likelihood of fracture, since tensile stresses cause propagation of the microcracks while shear stresses promote the competing process of plastic deformation. In the three important types of testing, the ratio of maximum tensile stress to maximum shear stress is approximately as follows:
Comparison of curves (a) and (b) in Fig. 9-14 clearly shows the embrittlement effect of the unfavorable stress state in notched Charpy specimens.

4. Like flow stress, fracture stress increases as the size of the microstructural detail decreases. However, an additional factor tends to operate. The fracture stress appears to be inversely proportional to the average size of nonhomogeneous particles, such as inclusions, measured on a plane perpendicular to the direction of testing. Thus, after a metal has been elongated in one direction by hot rolling, its fracture stress is higher in that direction than in a direction at right angles to the rolling direction.

**Tests of Plastic Properties**

It is a relatively easy matter to determine the two values essential in designing for static, room-temperature service. These values are Young’s modulus and the yield strength, both of which can be obtained from the initial portion of a tension test. In many instances, however, it is necessary to know the effect of high or low temperatures, pulsating loads, impact loading, or stresses in the plastic range. It is inevitable that a number of different test procedures are necessary to determine the variety of design information needed for industrial practice. A few of the more important tests are briefly described here.

Approximate stress-strain curve. The tension test, for which a (true) stress-strain curve is shown in Fig. 9-1, is widely used in industry. However, for reasons of precedent and convenience, it is customary to plot the results in terms of stress and strain calculated by means of equations like (9-6) and (9-8), which are strictly valid for the elastic region only. The resulting approximate stress-strain curve is illustrated in Fig. 9-15(a). Comparison of this curve with that of Fig. 9-1 shows that the two methods of plotting data obtained from a tension test give about the same initial portion of the curve. However, especially beyond the point of maximum load, the two curves differ greatly, and the approximate stress-strain curve cannot be taken at its face value. Thus the tensile strength of a metal is not a stress value; it is the maximum load that could be supported by a test specimen one square inch in area. A large amount of uniform plastic deformation has occurred in many metals when the tensile strength is reached, and in such cases the actual stress is greater than the approximate
Fig. 9-15. (a) A typical approximate stress-strain curve, and (b) an industrial testing machine that can be used in making a tension test. (Photograph courtesy Riehle Testing Machines.)
value given by the tensile strength. In other words, the load \( F \) has the same value in the equation \( \sigma' = F/A_o \) and in the equation for true stress \( \sigma = F/A \). However, the actual area \( A \) often becomes much smaller than the original area \( A_o \), so that \( \sigma \) is often much larger than the approximate stress \( \sigma' \). The area term in these equations is so important that the highest stress, which exists just before fracture in a tension test, may correspond to a relatively small load applied to a necked-down specimen.

In addition to information on strength, a tension test supplies data on the ductility of a metal. The percent elongation is the most widely used measure of ductility and is defined as

\[
\% \text{Elongation} = \frac{l_f - l_o}{l_o} \times 100, \tag{9-23}
\]

where \( l_o \) is the original gage length and \( l_f \) is the separation of the gage length markers measured on the reassembled bar after fracture. The percent elongation is the sum of uniform and nonuniform (necking) deformation. In test specimens with a long gage length the contribution of nonuniform deformation is relatively small, and in such specimens the percent elongation has nearly the value characteristic of uniform deformation alone. The reduction in area is a second common measure of ductility, but it is determined at the necked portion of the fractured specimen and so is practically independent of the gage length chosen. Its definition is

\[
\% \text{Reduction in area} = \frac{A_o - A_f}{A_o} \times 100, \tag{9-24}
\]

where \( A_o \) is the original cross-sectional area of the test bar, and \( A_f \) is the minimum area of the necked portion, measured on the reassembled bar after fracture. Adequate ductility is required not only for hot-and cold-working operations, but also as a guard against sudden fracture in the event of an overload in service.

**Hardness tests.** It is possible in many cases to substitute for the relatively slow and expensive tensile test a more convenient test of the plastic deformation behavior of metals, a hardness test. Hardness is usually defined as resistance to penetration, and the majority of commercial hardness testers force a small sphere, pyramid, or cone into the body of the metal by means of an applied load. A definite number is obtained as the hardness of the metal, and this number can be related to the yield strength.

*The effect of gage length, which is described here, is largely eliminated in practice by using for test specimens of all sizes the constant ratio \( l_o/d_o = 4 \), between the gage length \( l_o \) and the diameter \( d_o \) of the test section.*
Fig. 9-16. Two models of Rockwell hardness testing machines: (a) manual, (b) fully automatic. (Courtesy Wilson Mechan- 
ics Instrument Company.)
or tensile strength of the given metal as determined from a tension test. The tensile strength of a steel, for example, is roughly equal to 500 times its Brinell hardness number. Hardness tests are essentially of a practical control nature, but they are of great value both in the plant and in the laboratory.

Figure 9-16(a) shows the manual Rockwell hardness tester, an especially convenient machine. The following procedure is used in obtaining a hardness number with this machine. The specimen is brought into contact with the penetrator, the penetrator is then slowly forced into the specimen surface by weights acting through a system of levers, and when the load is released the dial pointer indicates the hardness number, which is determined by the depth reached by the penetrator. In automated production lines it is possible to measure the hardness of each piece at rates up to 1000 tests per hour, using the fully automatic Rockwell machine in Fig. 9-16(b). Specimens are fed to the testing unit, and on the basis of the hardness reading they are automatically sorted so that only acceptable pieces continue in the production line.

The characteristics of several types of hardness testers are summarized in Table 9-4 (see p. 338). The Brinell machine is widely used in production-line testing of large parts such as crankshafts, since a minimum of preliminary preparation of the test surface is needed. Microhardness tests can be made in individual pieces of each phase in an alloy. For example, the hardness of second-phase particles less than 0.01 inch in diameter can be determined by this means.

**Impact tests.** A metal may be very hard (and therefore presumably very strong, i.e., have a high tensile strength) and yet be unsuitable for applications in which it is subjected to sharp blows. Impact resistance is the capacity of a metal to withstand such blows without fracturing. Many different procedures are used to evaluate the impact resistance of metals, depending on the brittleness of the metal and on the nature of the application. Figure 9-17 shows five of the principal tests. The tension impact test can be used on the most ductile metals, while the torsion impact test is suitable for extremely brittle materials such as hardened tool steels.

The term notch-bend test is sometimes applied to those tests ( Izod and Charpy) involving a notched specimen, to emphasize that the effect of the notch is more important than the speed of testing in reducing the ductility of the metal. In the neighborhood of the base of the notch, bending of the specimen causes the appearance of radial and transverse tensile stresses as well as of the primary longitudinal tensile stress. This condition of triaxial tension raises the stress at which plastic deformation begins and tends to cause fracture with little plastic flow. For example,
Table 9-4  CHARACTERISTICS OF SEVERAL HARDNESS TESTS

<table>
<thead>
<tr>
<th>Type</th>
<th>C scale</th>
<th>Rockwell</th>
<th>Brinell</th>
<th>Vickers</th>
<th>Microhardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetrator</td>
<td>Diamond cone</td>
<td>T, F, medium</td>
<td>F, D, 10 mm</td>
<td>D, 50</td>
<td>Diamond pyramid</td>
</tr>
<tr>
<td>Usual range of hardness covered, kg</td>
<td>150</td>
<td>100</td>
<td>500-2000</td>
<td>5-100</td>
<td>0.01-50</td>
</tr>
<tr>
<td>Typical preparation before testing</td>
<td>Medium to very hard</td>
<td>Soft to medium</td>
<td>Soft to hard</td>
<td>Very soft to very hard</td>
<td></td>
</tr>
<tr>
<td>Typical applications</td>
<td>Production testing of finished parts</td>
<td>Production testing of finished parts</td>
<td>Production testing of unfinished parts</td>
<td>Laboratory investigations</td>
<td>Production testing of microstructures of alloys</td>
</tr>
</tbody>
</table>

PLASTICITY OF METALS [CHAP. 9]
ENDURANCE TESTS

Sudden blow struck here

Fixed end

Tension impact

Keyhole Charpy impact

Notched Izod impact

Unnotched Izod impact

Torsion impact

Suitable for specimens of increasing brittleness

Fig. 9-17. Impact tests suitable for testing metals of various degrees of brittleness.

if the radial and transverse stresses are assumed to be one-half as large as the longitudinal stress, Eq. (9-11) can be used to show that the longitudinal stress at which flow begins is equal to twice the stress $S_0$ necessary to cause flow in a simple tension test. In some metals local deformation can occur (without fracture) in the highly stressed area at the base of the notch. The sharpness of the notch is reduced by such deformation, and further ductile behavior is encouraged. Metals that behave in this manner are said to have low notch sensitivity. High notch sensitivity is characteristic of normally ductile metals that fracture in a brittle fashion in the triaxially stressed notch area. Initial cracking intensifies the stress concentration and causes rapid propagation of the crack across the entire specimen.

Endurance tests. The yield strength is a suitable basis for designs involving static loads, but for loads that are repeatedly applied and removed a different strength measure is needed. The endurance strength is the stress $S$ that will cause a metal to break after a large number $N$ of applications of that stress. It would be expected that the value of $S$ should depend on the exact value of $N$, and this dependence is found experimentally as shown in Fig. 9-18. An $S$-$N$ curve is a plot of stress versus the number of cycles of stress application required to fracture the given metal. Figure 9-18 shows that some metals can withstand an infinitely large number of stress reversals provided the stress is below a limiting stress, the endurance limit.

Although it would appear that endurance-strength values could be used directly as the permissible stresses in rapidly rotating shafts, the situation is quite otherwise. To clarify the proper use of endurance-strength data, the testing procedures will first be considered. Figure 9-19(a) shows the
Fig. 9-18. S-N curve for a metal that shows an endurance limit.

(a) An R. R. Moore-type rotating beam endurance testing machine. (b) Typical S-N curves, showing the experimental points, for several commercial alloys. (After H. F. Moore.)
most common method of determining endurance strength. A highly polished specimen of circular cross section is subjected to a bending moment by means of a static (weight) load. However, the stresses in the outer fibers of the specimen are not static. As the specimen is rotated, the outer fibers are subjected to longitudinal stresses that vary from a maximum value in tension to a maximum value in compression and back again to tension during each cycle. A counter records the number of stress cycles that the specimen withstands before it fractures. Figure 9-19(b) shows the experimental points that were used to determine the $S-N$ curves for four commercial alloys. The aluminum alloy is representative of materials that do not seem to have a definite endurance limit.

Actual operating conditions differ significantly from those used in the standard endurance tests, and the performance of an alloy may be greatly affected by the changed conditions. The influence of some of these service factors can be estimated roughly as follows:

1. **Effect of surface conditions.** Rarely is an industrial machine component given the high polish that is used on a laboratory endurance test specimen. Figure 9-20 shows the effect of surface condition in reducing the actual endurance limit of steel. It is noteworthy that the endurance limit of a low-strength steel is only slightly affected by a given surface imperfection, compared with the decrease suffered by a high-strength steel. This behavior is a result of the higher notch sensitivity of stronger, less ductile materials. Since the ratio of the endurance limit to the tensile strength, the *endurance ratio*, is about 0.5 for steels, it is easy to show (Fig. 9-20) that there is no advantage in using a high-strength steel for an application requiring endurance strength in a corrosive environment.

2. **Effect of range of stress.** Frequently a part is subjected in service to a range of stresses in which the ratio $r$ of the minimum stress to the maxi-
mum stress is not $-1$, as in the case of the reverse bending employed in the usual endurance test. For example, the ratio may be $r = 0$ if the stress range is from zero to a maximum tensile stress. It has been determined that the endurance limit $S_r$ corresponding to a certain value of $r$ is given by an equation of the form

$$S_r = S_i \left( \frac{3}{2 - r} \right),$$  \hspace{1cm} (9-25)

where $S_i$ is the endurance limit determined in reverse bending.

3. Effect of complex stresses. In brittle alloys, such as gray cast iron, the behavior in an endurance test is determined only by the largest tensile stress. The significant stress in ductile materials, on the other hand, is determined by the combination of all the principal stresses that act on the specimen, Eq. (9-11). In particular, if permanent compressive stresses can be produced in the surface layer by such a means as shot-peening, the endurance limit can be increased by about 25 percent.

4. Effect of section size. Larger specimens of a given material have a lower endurance limit than the small laboratory specimen. If the diameter of a machine part is more than about $\frac{1}{2}$ inch, it is customary to assume that the endurance limit will be about 20 percent below that usually determined.

5. Effect of temperature and frequency. Endurance strength and tensile strength are affected in approximately the same manner by changes in temperature or rate of straining. Therefore changes in frequency have little effect on the endurance limit at ordinary temperatures, but increasing the temperatures causes a pronounced decrease in endurance strength compared with the room-temperature value.

The fracture surfaces produced by endurance (fatigue) failures have a characteristic appearance. In the fractured shaft shown in Fig. 9-21 the crack began at the keyway. During the slow spreading of the crack into

![Fig. 9-21. Typical endurance (fatigue) failure in a motorboat shaft containing a keyway. (Courtesy International Nickel Company.)](image-url)
the body of the shaft, rubbing of the two surfaces of the cracked portion produced a smooth area. The "clamshell" markings indicate successive boundaries of the crack. Final brittle failure of the reduced cross section produced the granular portion of the fracture surface.

**Damping.** It is common knowledge that if a metal rod is set in vibration by hitting it with a hammer, the amplitude of this vibration will slowly decrease as time goes on. This characteristic is called the **damping capacity**. One of the many proposed measures of this property is the **damping decrement Δ**, defined as

\[ \Delta = \frac{\Delta W}{W}, \]  

(9-26)

where \( W \) is the total vibrational energy per cycle, and \( \Delta W \) is the amount of vibrational energy lost in the form of heat during one cycle. Plastic

<table>
<thead>
<tr>
<th>Material</th>
<th>Damping decrement Δ (room temp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>( 144 \times 10^{-4} )</td>
</tr>
<tr>
<td>Tin</td>
<td>( 108 \times 10^{-4} )</td>
</tr>
<tr>
<td>Lead</td>
<td>( 93 \times 10^{-4} )</td>
</tr>
<tr>
<td>Copper</td>
<td>( 70 \times 10^{-4} )</td>
</tr>
<tr>
<td>95% Cu, 5% Sn</td>
<td>( 14 \times 10^{-4} )</td>
</tr>
<tr>
<td>70% Cu, 30% Zn</td>
<td>( 4 \times 10^{-4} )</td>
</tr>
<tr>
<td>Iron</td>
<td>( 40 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.2-1.5% C steel, annealed</td>
<td>( 10 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.6% C steel, hardened</td>
<td>( 40 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.2% C steel, hardened and tempered</td>
<td>( 30 \times 10^{-4} )</td>
</tr>
<tr>
<td>Gray cast iron</td>
<td>( 60 \times 10^{-4} )</td>
</tr>
<tr>
<td>Zinc</td>
<td>( 15 \times 10^{-4} )</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>( 10 \times 10^{-4} )</td>
</tr>
<tr>
<td>Magnesium</td>
<td>( 4 \times 10^{-4} )</td>
</tr>
<tr>
<td>Aluminum</td>
<td>( 1 \times 10^{-4} )</td>
</tr>
</tbody>
</table>
deformation is the principal source of damping in the usual range of stresses and frequencies, but it is known that many other factors also contribute to damping. The name *internal friction* is usually applied to the broader study of damping from all possible causes.

With the exception of the bronzes used in bells, a high damping capacity is almost always desirable in industrial metals. Turbine blades, for example, are subjected to thousands of impulses per minute and will build up significantly greater stresses at critical resonant speeds if their damping capacity is not sufficient to dissipate energy quickly. Because of the large number of factors that influence damping capacity, it is difficult to list quantitative values that can be used directly in design calculations. A more feasible procedure is to list relative damping capacities that have been determined under similar conditions for a number of materials. Such a tabulation is given in Table 9-5 for small amplitudes of vibration, that is, for low stresses. Under these conditions nickel is one hundred times better than aluminum in damping out vibrations. The damping decrement increases rapidly with increasing stress; for example the $\Delta$ value for gray cast iron increases from 0.006 to 0.3 as the stress increases from a value near zero to about 10,000 lb/in$^2$. Less pronounced increases in damping capacity are caused by cold-working, by precipitation of a second phase from solid solution, and by ordering of a solid solution.

**High-temperature strength.** The need for materials that can operate for long periods at the high temperatures encountered in internal combustion engines, steam-power machines, and gas turbines has led to extensive study of the properties of metals at these temperatures. Although knowledge of many properties is necessary for designing a complex industrial machine, only the high-temperature strength is considered here. The effect of temperature on other properties, such as Young’s modulus and corrosion resistance, is treated in other chapters. At moderate temperatures the ordinary yield strength is the property that limits the application of engineering alloys. For steels these temperatures are in the range below about 700°F. The rate of straining or the duration of loading has little effect on the yield strength or tensile strength, and it is therefore permissible to use a (rapid) tension test to determine the strength that a metal will exhibit on being stressed for many years in such a part as a bridge member or an automobile frame. At very high temperatures the situation is completely different, and it is necessary to determine the precise dependence both of tensile strength (rupture strength) and of yield strength (creep strength) on the time of application of the stress. The procedure and equipment for both creep and stress-rupture testing are similar, Fig. 9-22, but the treatment of the test data are sufficiently different that each of the tests will be described separately.
A stress-rupture test determines the constant approximate-stress value \((F/A_0)\) that causes a metal to break in a definite time at a given temperature. The specimen is loaded as shown in Fig. 9-22, and the elongation is automatically recorded from the time of the beginning of the test until the time of fracture. A typical set of three curves for tests at 1500°F is shown in the lower part of Fig. 9-23 plotted as log (percent elongation) versus log (time). To estimate closely the load that would cause rupture to occur in a certain time, say 1000 hours, it is convenient to plot the experimentally determined pairs of stress-rupture time values in the manner shown in the upper curve of Fig. 9-23. The points in such a plot form a straight line that is useful both for interpolation and extrapolation. An ordinary tensile test at a high temperature is evidently similar to a very short time rupture test. The good correlation between extrap-
PLASTICITY OF METALS

It will be recalled that yield strength is a practical measure of the stress necessary to start plastic deformation at room temperature. At high temperatures, on the other hand, plastic deformation (creep) appears to occur at all stresses, but the rate at which it occurs increases with increasing stress at a given temperature. Therefore the quantity that is used in design, the creep strength, is chosen so that plastic deformation occurs at a suitably low rate. Thus an objectionable amount of deformation will not occur during the expected life of the machine.

It is evident that careful measurements are required to determine the small rates of plastic deformation involved in creep. The principle of measuring creep strength is the same as that shown in Fig. 9-22, but special means are used to increase the precision of the strain measurement. Figure 9-24 shows the characteristics of the usual creep curve in which the applied stress causes a constant rate of creep to continue for the time of interest in the engineering design being considered. The relatively constant second-stage creep is preceded by a brief first stage of creep, and it would be followed eventually by accelerated creep and final fracture in the third stage of creep. The usual creep strength values, such as those listed in Table 9-6 (pp. 348–49), represent the rate of elongation during second-stage creep at a given temperature and under a given stress.

It can be seen from Fig. 9-24 that the total elongation experienced by a...
Fig. 9-24. Typical creep behavior showing the relation of the useful portion of a creep curve to the eventual fracture of the alloy.

Fig. 9-25. Design data for alloy N-155 (Table 9-6) at 1200°F. (After Grant and Buchlin.)

specimen during creep of an engineering structure is the sum of the initial elastic and plastic strains plus the rapid first-stage creep deformation and the elongation calculated from the creep rate. Design data based on total elongation are given in Fig. 9-25 for a high-temperature alloy. The lower curves in this figure show the time required for 0.1 to 1.0 percent elongation to occur when the alloy is subjected to given tensile stresses at 1200°F. Data from stress-rupture tests on this alloy are summarized in the top curve, which shows the time for rupture to occur under various tensile stresses. For applications in which only small deformations are permissible, creep resistance determines the maximum design stress. However, when large deformations can be tolerated, the rupture strength may be the limiting factor.

The alloying principles and structural considerations that apply to strength at normal temperatures are also generally valid for high-tempera-
<table>
<thead>
<tr>
<th>Alloy (balance of composition is essentially iron)</th>
<th>Temp., °F</th>
<th>Short-time tensile strength, lb/in²</th>
<th>1000-hr rupture strength, lb/in²</th>
<th>Creep strength, lb/in² (0.1% per 1000 hr)</th>
<th>Creep strength, lb/in² (0.01% per 1000 hr)</th>
<th>Approximate relative cost, carbon steel = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel 0.15% C</td>
<td>800</td>
<td>50,000</td>
<td>11,700</td>
<td>20,000</td>
<td>14,000</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>30,000</td>
<td>11,700</td>
<td>4,000</td>
<td>2,700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,200</td>
<td>15,000</td>
<td>2,000</td>
<td>1,000</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>Carbon-molybdenum steel 0.15% C 0.55% Mo</td>
<td>800</td>
<td>60,000</td>
<td>25,000</td>
<td>600</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>45,000</td>
<td>4,400</td>
<td>10,800</td>
<td>6,700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,200</td>
<td>27,000</td>
<td>2,000</td>
<td>200</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>18-8 Stainless steel 18% Cr 8% Ni</td>
<td>1,000</td>
<td>55,000</td>
<td>35,000</td>
<td>18,000</td>
<td>11,000</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>1,200</td>
<td>42,000</td>
<td>14,000</td>
<td>7,000</td>
<td>4,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>21,000</td>
<td>3,500</td>
<td>2,000</td>
<td>1,300</td>
<td></td>
</tr>
<tr>
<td>Timken alloy (hot-rolled) 16% Cr 25% Ni 6% Mo 0.1% C 0.15% N₂</td>
<td>1,200</td>
<td>86,000</td>
<td>35,000</td>
<td>18,000</td>
<td>10,000</td>
<td>8</td>
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<tr>
<td></td>
<td>1,350</td>
<td>60,000</td>
<td>20,000</td>
<td>13,000</td>
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<tr>
<td></td>
<td>1,500</td>
<td>41,000</td>
<td>10,000</td>
<td>6,000</td>
<td>3,000</td>
<td></td>
</tr>
<tr>
<td>N-155 (low carbon) 20% Cr 20% Ni 20% Co 3% Mo 2% W 1% Cb 0.12% C 0.12% N₂</td>
<td>1,200</td>
<td>91,000</td>
<td>32,000</td>
<td>20,000</td>
<td>17,000</td>
<td>50</td>
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<td></td>
<td>1,350</td>
<td>65,000</td>
<td>22,000</td>
<td>15,000</td>
<td>11,000</td>
<td></td>
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<tr>
<td></td>
<td>1,500</td>
<td>56,000</td>
<td>13,000</td>
<td>9,000</td>
<td>6,000</td>
<td></td>
</tr>
<tr>
<td>Material Description</td>
<td>Tensile Strength (ksi)</td>
<td>Tensile Strength (MPa)</td>
<td>Elongation (%)</td>
<td>Reduction of Area (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>----------------</td>
<td>-----------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-816</td>
<td>1,200</td>
<td>110,000</td>
<td>52,000</td>
<td>28,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,350</td>
<td>105,000</td>
<td>45,000</td>
<td>20,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>120,000</td>
<td>40,000</td>
<td>14,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,600</td>
<td>140,000</td>
<td>35,000</td>
<td>12,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inconel “X” (solution heat treated and aged)</td>
<td>1,200</td>
<td>110,000</td>
<td>52,000</td>
<td>28,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,350</td>
<td>120,000</td>
<td>65,000</td>
<td>62,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>130,000</td>
<td>70,000</td>
<td>54,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,600</td>
<td>140,000</td>
<td>75,000</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cupronickel 68.9% Cu 30.0% Ni 0.5% Mn 0.5% Fe</td>
<td>750</td>
<td>40,000</td>
<td>18,500</td>
<td>9,200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-4V Titanium alloy 6% Al 4% V bal. Ti</td>
<td>800</td>
<td>70,000</td>
<td>48,000*</td>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>80,000</td>
<td>10,000*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2024 Aluminium alloy (naturally aged) 4.5% Cu 1.5% Mg 0.6% Mn bal. Al</td>
<td>200</td>
<td>92,000</td>
<td>50,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>100,000</td>
<td>55,000</td>
<td>21,000*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>110,000</td>
<td>60,000</td>
<td>3,600*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HK31A Magnesium alloy (artificially aged) 3.0% Th 0.7% Zr</td>
<td>400</td>
<td>23,000</td>
<td>5,400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>25,000</td>
<td>3,100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>28,000</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 1% per 100 hours
FIG. 9-26. The spheroidization that occurred during creep of a steel containing 0.15% carbon and 0.5% molybdenum. (a) Initial condition of the steel. The carbide is present as pearlite in a ferrite matrix. (b) After 30,000 hours of service at 1100°F the carbide appears as coarse spheroids and fine precipitate. (×1000; reproduced at three-fourths size.) (Courtesy U. S. Steel Corporation Research Laboratory.)

PLASTICITY OF METALS [CHAP. 9]

ture strength, with one important qualification. It is essential that the microstructure be relatively stable at the operating temperature, since the process of microstructural change usually accelerates deformation of the alloy and may also decrease the toughness. For example, cold-working can be used to increase the creep strength of many iron-base alloys for service at 1000°F, but at 1500°F this treatment would be harmful, since the cold-worked alloy would recrystallize during service. Similarly, a finely dispersed microstructure, such as pearlite, gives greater strength than a coarser spheroidized structure, provided the pearlite is stable under the service conditions. Figure 9–26 illustrates a case in which this condition was not fulfilled, and the pearlite spheroidized during use. An initially spheroidized structure would have been a better choice in this instance.

Low-temperature properties. In designing equipment to operate at low temperatures, it is sometimes necessary to consider the decrease in ductility produced in some alloys by these low temperatures. Practically all alloys show an increase in yield strength and tensile strength at low temperatures. This behavior is shown for nickel and for two steels in the
FIG. 9-27. The effect of low temperatures on the impact resistance and yield strength of a face-centered cubic metal (nickel) and two essentially body-centered cubic alloys.

lower part of Fig. 9-27. In addition, all metals and alloys that have a face-centered cubic lattice appear to maintain their ductility substantially unimpaired at very low temperatures (−400°F). However, nonface-centered cubic metals and alloys, such as ordinary pearlitic steels, usually suffer a marked decrease in ductility and impact strength at even moderately low temperatures. Figure 9-27 shows how the impact strength curve for steels falls off at low testing temperatures. The impact strength of nickel, on the contrary, remains essentially unchanged down to −400°F. The transition temperature used here in describing the change from ductile to brittle behavior in steels will be recognized as the “average energy transition” of Fig. 9-14.

Since ductile behavior is essential for the satisfactory operation of many alloys in service, the high transition temperature of ordinary carbon steel makes it unsuitable for use under unfavorable conditions of stress even
at only moderately low temperatures. Fortunately, it is possible to use steels at subzero temperatures if their transition temperatures are lowered by the addition of about 4 percent nickel, by hardening and tempering, by complete decarburization, or by refinement of grain size. Figure 9-27 shows the pronounced lowering of the transition temperature produced by the combination of heat treatment and the addition of nickel. The transition temperature of the heat-treated nickel steel is more than 100°F lower than that of the normalized carbon steel.

APPLICATIONS OF PLASTIC DEFORMATION

There are many examples of plastic deformation in the commercial use of metals. For example, Chapter 12 will be devoted to one important aspect, the strengthening of metals by cold deformation and the effect of temperature on the resulting structure. There are also many metallic properties not so directly associated with deformation that are largely determined by the plasticity of the metal. Two examples that will be considered here are wear resistance and machinability. The most dramatic application of plasticity is in the hot-working of metals, the technology of which was briefly described in Chapter 2. Several of the structural aspects of this topic will now be discussed.

Hot-working. When metals are deformed at high temperatures, the strained grains instantly re-form during hot-working and essentially return to their initial condition. One important consequence of this constancy of structure is the fact that the stress required to deform the metal, the flow stress $\sigma_f$, remains essentially constant during a hot-working operation. This fact greatly simplifies the estimation of the forces required in commercial forming processes such as forging, extrusion, and rolling. A first approximation to the force $F$ required in a simple forming operation (such as press forging) for a block of metal of cross-sectional area $A$ is simply

$$ F = \sigma_f A. \quad (9-27) $$

The corresponding work required to reduce the height of the block from the initial value $h_0$ to a final height $h_f$ is conveniently written

$$ \text{Work} = \int_{h_0}^{h_f} F \times dh = \sigma_f A \int_{h_0}^{h_f} \frac{dh}{h} = \sigma_f A \ln \frac{h_f}{h_0}. \quad (9-28) $$

where use has been made of the fact that the volume $V = Ah$ remains constant during plastic deformation. Since the quantity $\ln (h_f/h_0)$ is the
Fig. 9-26. Illustration of good (a) and of poor (b) grain flow lines in a forged blank for the compressor wheel of a jet aircraft. Note that in (a) the grain flow parallels the finished part outline much more closely than in (b). The arrow points to an especially critical area. (Courtesy S. M. Jablonski, Wyman-Gordon Company.)
true strain $\Delta$, according to Eq. (9-4), the ideal work of plastic deformation is

$$\text{Work} = S_0V\Delta.$$ (9-29)

Negative values of $\Delta$ are produced by compressive stresses (negative $S_0$), so that the work is always a positive quantity.

The actual work required in hot-forming operations is always greater than the ideal value because of several factors that were neglected in the above treatment. The most important of these are (1) friction between the metal and the forming device, and (2) nonuniform flow of the metal. Both phenomena are useful in many processes, for example in producing desirable grain flow lines in forgings, Fig. 9-28. However, they cause the work of deformation to be larger than the ideal value by a factor $\alpha$ that ranges from about 2 for press forging to 10 or more for extrusion.

Some of the general characteristics of hot-working processes that contribute to their wide use are:

1. The energy necessary to form a metal to a desired shape decreases rapidly as the temperature of forming increases.
2. The ability of an alloy to flow without cracking usually reaches a maximum value at a temperature near its solidus temperature.
3. The inhomogeneities associated with the cast, ingot structure of an alloy are more quickly removed at high temperatures, where diffusion occurs rapidly.

This third factor is involved in the distinction between wrought and cast alloys. The tensile strength of the cast material is usually equal to that of the wrought alloy. However, the impact strength of a casting is relatively low, presumably because of inhomogeneities in the grain boundaries and elsewhere. After sufficient hot-working, about 50 percent reduction, the new set of grains produced by recrystallization usually has much higher impact strength and somewhat better ductility.

**Wear resistance.** In wear of a metal or alloy, small particles are torn from its surface by materials moving against it. Although the mechanism of wear is not completely understood, it is likely that the following processes occur to some extent in the wearing of metals:

1. *Seizing or penetration of the metal surface.* Depending on the nature of the wearing agent, the first step in removing a metal particle may be digging into the metal surface or local welding because of intimate contact on an atomic scale. High hardness tends to prevent both penetration of the surface and the deformation necessary to permit relatively large contact areas. There is usually an excellent correlation between hardness and wear resistance.
2. *Deformation of the metal.* Small pieces of the metal must be deformed
WEAR RESISTANCE

WEAR RESISTANCE

and torn loose if the process of wear is to take place. A tough metal tends to resist this action and so exhibit good wear resistance. In practice, toughness is often sacrificed in favor of high hardness.

3. Corrosion of the metal surface. A corrosion product, such as an oxide or a sulfide, is usually quickly removed from the metal surface by the wearing agent. Corrosion resistant metals, therefore, show superior wear resistance in many applications.

4. Heating of the metal surface. Although actual melting of the metal occurs only in rare cases, less severe heating can reduce wear resistance by speeding corrosion reactions and by decreasing mechanical properties. Metals with a high melting point tend to have good wearing properties. Although the qualitative significance of these four processes can often be estimated in a given instance, a quantitative theory of wear resistance is lacking. In fact, the conditions under which wear occurs in practice are so varied that it is necessary to divide the subject into more or less isolated sections for effective study. The following are important types of wear:

<table>
<thead>
<tr>
<th>Type of Wear</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal-to-metal, lubricated</td>
<td>Shaft in bearing</td>
</tr>
<tr>
<td>Metal-to-metal, not lubricated</td>
<td>Wheel on track</td>
</tr>
<tr>
<td>Metal-to-nonmetal, dry friction</td>
<td>Belt on pulley</td>
</tr>
<tr>
<td>Metal-to-nonmetal, particle impact</td>
<td>Sandblast nozzle</td>
</tr>
<tr>
<td>Metal-to-fluid, liquid particle</td>
<td>Wet steam in turbine</td>
</tr>
</tbody>
</table>

Wear testing is a difficult problem. A useful device for rating materials for a given application must closely duplicate service conditions, and the results must be verified by checking them against actual performance. Although most wear-testing machines are custom-made for a given purpose, the Amsler machine is a versatile device for testing metal-to-metal wear, and the Brinell machine is useful for testing metal-to-nonmetal wear.

Hard-surfaced metals. The rate of wear under many industrially important conditions can be reduced to an acceptable value by the use of high hardness at the wearing surface. Hardening an entire cross section has the disadvantage of decreasing the over-all ductility, and frequently limits the surface hardness to relatively low values. It is therefore common practice to harden just the surface layer, often by means of an extremely hard, brittle phase embedded in a more ductile matrix. The principal surface hardening methods are briefly described in Table 9-7.

Carburizing, nitriding, cyaniding, and carbonitriding all depend on the diffusion of carbon or nitrogen or both into the steel surface. The diffusion process is considered in a later chapter, but the end result in the case of
<table>
<thead>
<tr>
<th>Method</th>
<th>General nature of surface-hardening process</th>
<th>Metals usually hardened by this method</th>
<th>Process used</th>
<th>Characteristic of the process</th>
<th>Typical use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carburizing</td>
<td>A high-carbon surface is produced on a low-carbon steel and is hardened by quenching.</td>
<td>Plain carbon or alloy steel containing about 0.30 percent carbon.</td>
<td>Low-carbon steel is heated at 1600-1700°F in contact with gaseous, solid, or liquid carbon-containing substances for several hours. The high-carbon steel surface is hardened by quenching from above the A_3 temperature.</td>
<td>Case depth is about 0.005 inch. Hardness after heat treatment is R_c 65. Negligible dimensional change caused by carburizing. Distortion may occur during heat treatment.</td>
<td>Gears, Camshafts, bearings</td>
</tr>
<tr>
<td>Nitriding</td>
<td>A very hard nitride-containing surface is produced on the surface of a strong, tough steel.</td>
<td>Nitroloy steel containing aluminum: Nitroloy 120 contains 0.25% C, 1.1% Cr, 0.3% Ni, and 1.5% Al. Nitroloy 130 contains 0.35% C, 1.1% Cr, 0.5% Mo, and 1.0% Al. The steel is hardening and then tempered at 1000-1050°F before being nitrided.</td>
<td>The steel is heated at 900-1000°F in an atmosphere of ammonia gas for about 50 hours. No further hardening is necessary.</td>
<td>Case depth is about 0.015 inch. Extreme hardness (Vickers 1000). Growth of 0.001-0.002 inch occurs during nitriding. Case is not softened by heating for long times at 900°F. Case has improved corrosion resistance.</td>
<td>Valve seals, guides, gear wheels</td>
</tr>
<tr>
<td>Cyaniding</td>
<td>A carbon-and-nitride-containing surface is produced on a low-carbon steel and is hardened by quenching.</td>
<td>Plain carbon or alloy steel containing about 0.30 percent carbon.</td>
<td>Low-carbon steel is heated at 1000°F in a molten 30 percent sodium cyanide bath for about one hour. Quenching in oil or water from this bath hardens the surface of the steel.</td>
<td>Case depth is about 0.010 inch. Hardness is about R_c 65. Negligible dimensional change is caused by cyaniding. Distortion may occur during heat treatment.</td>
<td>Screws, nuts and bolts, small gears</td>
</tr>
<tr>
<td>Carbonitriding</td>
<td>Carbons and nitrogens are added to the surface of a low-carbon steel and permit hardening by an oil quench.</td>
<td>Plain carbon steel containing about 0.20 percent carbon.</td>
<td>Low-carbon steel is heated at 1300-1500°F for several hours in a gaseous hydrogen and ammonia atmosphere. Nitrogen in the surface layer increases hardness and permits hardening by an oil quench.</td>
<td>Case depth is about 0.020 inch. Hardness after heat treatment is R_c 65. Negligible dimensional change occurs. Distortion is less than in carburizing or cyaniding.</td>
<td>Gears, nuts, bolts</td>
</tr>
<tr>
<td>Process</td>
<td>Description</td>
<td>Steel Properties</td>
<td>Case depth</td>
<td>Surface Hardness</td>
<td>Distortion</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------</td>
<td>------------</td>
<td>------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Siliconizing (Brightening)</td>
<td>A moderately hard, corrosion-resistant surface containing 14 percent silicon is produced on low-carbon steels.</td>
<td>Plain carbon steel containing 0.1 to 0.2 percent carbon. The steel parts are heated at 1700-1850°F in contact with silicon carbide and chlorine gas for two hours. No further heat treatment is required.</td>
<td>Case depth is about 0.025 inch. Hardness is Rockwell C 88. Case has good corrosion resistance. Growth of 0.001-0.002 inches during siliconizing.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard chromium plating</td>
<td>A hard chromium plate is applied directly to the metal surface. Generally a steel, low or high carbon, hardened or soft.</td>
<td>The steel parts are plated in the usual plating bath, but without the usual undercoat of nickel. The plating is a thousand times thicker than the decorative chromium plating. Plating thickness is about 0.005 inch. Extreme hardness (Vickers 900). Plating has good corrosion resistance. Plating has a low coefficient of friction.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard facing</td>
<td>A hard, high-alloy layer is welded to the surface of a steel or cast iron. Almost any steel or cast iron, but usually a medium carbon steel. A fusion welding process is used to weld the hard surfacing alloy and weld it to the base metal. Typical hard surfacing alloy is composed of chromium, tungsten and cobalt. Surface layer is about 1/16 inch thick. Variety of hardness and toughness given by various alloys. Building up worn or broken parts. Excavating equipment. Metal-working dies.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flame hardening</td>
<td>The surface of a hardenable steel or iron is heated by a gas torch and quenched. Steel containing 0.4 to 0.8 percent carbon; cast iron containing 0.4 to 0.8 percent carbon. An oxygen-acetylene flame quickly heats the surface layer of the steel, and a water spray or other type of quench hardens the surface.</td>
<td>Hardened layer is about 1/32 inch thick. Hardness is Rockwell C 50 to 60. Distortion can often be minimized. Gear teeth, Sliding ways, Bearing surfaces.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Induction hardening</td>
<td>The surface of a hardenable steel or iron is heated by a high-frequency electromagnetic field and quenched. Steel containing 0.4 to 0.8 percent carbon; cast iron containing 0.4 to 0.8 percent carbon. The section of steel to be hardened is placed inside an induction coil. A heavy induced current heats the steel surface in a few seconds. A quenching operation, such as spraying with water, hardens the heated section.</td>
<td>Hardened layer is 1/8 inch thick or more. Hardness is Rockwell C 50 to 60. Distortion can often be minimized. Surface remains clean.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Austenitic (Stainless)</td>
<td>A tough, strong austenitic structure is converted to a hard martensitic structure by surface deformation. This steel contains 1.2 percent carbon and 12 to 13 percent manganese. The cast or rolled steel is toughened by an austenitizing heat treatment of water quenching from 1850°F. Deformation in service causes a martensitic structure to form in the surface layer.</td>
<td>Hardened layer is of variable thickness depending on severity of deformation. Hardness is Rockwell C 50.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Valve, Tubing, Shafts

Dies, Gages, Tools

Building up worn or broken parts. Excavating equipment. Metal-working dies.

Gear teeth, Sliding ways, Bearing surfaces.

Bearing surfaces, Gear teeth, Hubs

Overhead cranes, Railroad cars, and switchers.
Fig. 9-29. The effect of carburizing a one-inch diameter bar of 0.24% carbon, 1.32% manganese steel. (a) Gradient in carbon content near the surface. (b) Microstructure of the same portion of the annealed bar. (c) Hardness after oil quenching from 1550°F. (Courtesy F. E. Harris, Buick Motor Division, General Motors Corporation.)
carburizing can be easily seen in Fig. 9-29. Gas carburizing caused the carbon content near the surface to increase from 0.24 percent to the values shown in Fig. 9-28(a). The microstructure of this surface region of the annealed bar, Fig. 9-29(b), varies from a mixture of iron carbide (white) and pearlite (black) to mostly ferrite (white) with increasing distance below the surface. The desired high hardness of the surface region is obtained only after a hardening heat treatment. Figure 9-29(c) shows the hardness values that are finally obtained in the hardened, carburized region.

Bearing metals. A bearing supports a moving part of a machine. Since motion is essential to the proper working of almost all machines, the problem of ensuring dependable action with minimum frictional losses and at low cost is a most important one for engineers. This problem is complex, and there are almost as many solutions to it as there are conditions of service (conditions that range from the slow-moving, heavily loaded boom of a fifty-ton power shovel to the delicately balanced shaft of a small, high-speed electric motor). The solution of bearing problems lies largely in mechanical design, but intimately associated with this design are the characteristics of the available bearing materials.

Bearings are usually classified as (1) rolling contact bearings and (2) plain bearings. The self-lubricating bearing made by the powder-metallurgy process is a type of plain bearing. Rolling contact bearings have a number of advantages over plain bearings: (1) the starting friction is lower; (2) the shaft is held more precisely in the desired position; (3) maintenance costs are lower; (4) a combination of radial and thrust loads can be carried. The principal advantage of plain bearings is their lower cost, but in addition they may be chosen for conditions involving shock loading, or occasionally for more quiet operation.

Ball bearings and roller bearings are almost invariably made of steel that can be hardened after machining. SAE 1090,* a plain carbon steel containing 0.90 percent carbon, is an inexpensive and frequently used material, but alloy steels are required for many applications. Greater toughness at the high hardness needed for wear resistance is obtained by using a few percent of one or more of the alloying elements chromium, nickel, and molybdenum, and by lowering the carbon content to about 0.50 percent. A carburized, low-carbon alloy steel can be used to achieve a combination of hard, wear-resistant surfaces and a tough core. For applications in which corrosion resistance is essential, a 17 percent chromium stainless steel is often chosen.

An extremely wide range of materials can be used for plain bearings; in fact, the subject of bearing metals usually deals only with alloys for use in

* The SAE and AISI classifications of steel are described in Chapter 14.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tin-base babbit</th>
<th>Lead-base babbit</th>
<th>Bearing bronze</th>
<th>Copper-lead</th>
<th>Cadmium-silver</th>
<th>Silver with a thin coating of lead and indium</th>
<th>Aluminum-base</th>
<th>Self-lubricating bearing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>91% Sn 4.5% Cu</td>
<td>75% Pb 15% Sb</td>
<td>85% Cu 10% Sn 10% Pb</td>
<td>70% Cu 30% Pb</td>
<td>95% Cu 1% Ag 0.5% Cu</td>
<td>91.5% Al 6.5% Sn 1% Cu 1% Ni</td>
<td>88% Cu 10% Sn 1% graphite</td>
<td></td>
</tr>
<tr>
<td><strong>0.1% offset compressive yield strength, lb/in²</strong></td>
<td>4,600 2,700</td>
<td>3,000 1,600</td>
<td>14,000</td>
<td>3,000</td>
<td>14,000</td>
<td></td>
<td>16,000</td>
<td>13,000</td>
</tr>
<tr>
<td><strong>Fatigue strength</strong></td>
<td>2,000 (3 X 10⁶ cycles)</td>
<td>4,200 (5 X 10⁶ cycles)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Approximate order of merit in a bearing; No. 1 is lowest</strong></td>
<td>1</td>
<td>2</td>
<td>8</td>
<td>5</td>
<td>4</td>
<td>7</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td><strong>Thermal conductivity, Btu/ft²/hr/°F</strong></td>
<td>7 X 10⁻⁴ 4 X 10⁻⁴</td>
<td>17 X 10⁻⁴ 10 X 10⁻⁴</td>
<td>50 X 10⁻⁴</td>
<td>24 X 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Coefficient of thermal expansion per °F</strong></td>
<td>13 X 10⁻⁶ 14 X 10⁻⁶</td>
<td>11 X 10⁻⁶ 12 X 10⁻⁶</td>
<td>16 X 10⁻⁶</td>
<td>11 X 10⁻⁶</td>
<td>14 X 10⁻⁶</td>
<td>11 X 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum $Z/N/p^*$</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Maximum $p/F^*$</td>
<td>40,000</td>
<td>40,000</td>
<td>90,000 *</td>
<td>90,000 *</td>
<td>100,000</td>
<td>900 *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion resistance (using ordinary lubricants)</td>
<td>very good</td>
<td>good</td>
<td>fair</td>
<td>poor</td>
<td>poor</td>
<td>fair</td>
<td>excellent</td>
<td>good</td>
</tr>
<tr>
<td>Sliding temperature, °F</td>
<td>433</td>
<td>464</td>
<td>1,735</td>
<td>622</td>
<td>598</td>
<td>Max. useful temp. 400°F</td>
<td>440</td>
<td></td>
</tr>
<tr>
<td>Conformability to journal</td>
<td>good</td>
<td>good</td>
<td>poor</td>
<td>fair</td>
<td>fair</td>
<td>fair</td>
<td>fair</td>
<td>poor</td>
</tr>
<tr>
<td>Ability to embed dirt</td>
<td>good</td>
<td>good</td>
<td>poor</td>
<td>fair</td>
<td>fair</td>
<td>fair</td>
<td>good</td>
<td>poor</td>
</tr>
<tr>
<td>Seizure resistance</td>
<td>excellent</td>
<td>very good</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Journal hardness</td>
<td>not critical</td>
<td>not critical</td>
<td>hardened steel</td>
<td>300 Brinell minimum</td>
<td>250 Brinell minimum</td>
<td>hardened steel</td>
<td>300 Brinell minimum</td>
<td>250 Brinell minimum</td>
</tr>
<tr>
<td>Cost</td>
<td>medium</td>
<td>lowest</td>
<td>medium</td>
<td>high</td>
<td>high</td>
<td>highest</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>Remarks</td>
<td>Used only in pre-fit bearings</td>
<td>Generally used in the cold-worked temper with a thin coating of pure tin</td>
<td>Usually saturated with oil before use</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $Z =$ viscosity in centipoises; $N =$ revolutions per minute;
* $p =$ average unit pressure, lb/in²; $V =$ peripheral speed, ft/sec.
plain bearings. The correct application of a bearing metal requires the matching of such bearing properties as cost, fatigue strength, compressive strength, ease of fabrication, antiseizure characteristics, and corrosion resistance, with such service conditions as type of load, amount of load, shaft speed, conditions of temperature, dirt and corrosion, oil supply, and shaft hardness. Table 9-8 lists a number of representative bearing metals and some of their properties. The minimum value of $Z_n/p$ at which complete film lubrication exists is known as the bearing modulus. This modulus depends on such factors as the smoothness of the journal.

Fig. 9-30. Microstructures of three types of bearing metals. (a) Tin-base babbitt, 85% Sn, 7.5% Cu, 7.5% Sb (X100); (b) copper-lead alloy, 70% Cu, 30% Pb (X100); (c) self-lubricating alloy, 85% Cu, 10% Sn, 1% graphite (X250). (All reproduced three-fourths size.) (Courtesy Research Laboratories and Moraine Products Divisions, General Motors Corporation.)
and of the bearing surface, and it may decrease by a factor of ten during the running-in period of a bearing. The values given in the table are approximate steady-state values. The bearing load factor $pV$ is also only approximate and depends on such variables as the type of lubrication and the conditions of loading.

Various alloy microstructures appear to be suitable for a bearing metal. The classical structure, hard particles in a soft matrix, is illustrated by a tin-base babbitt in Fig. 9-30(a). The phase relations in the ternary system represented by this alloy are not completely known, but it is believed that solidification proceeds in the following manner. The rod-shaped particles of the hard intermetallic compound CuSn form initially in the liquid alloy. Next the cube-shaped particles of the SbSn phase begin to form; probably their formation is promoted by the existence of CuSn crystals. Finally, the remaining liquid solidifies as a fine ternary eutectic of CuSn, SbSn, and a tin-rich solid solution. The eutectic microconstituent, which is relatively soft, forms the dark background material in the photomicrograph. The structure of copper-lead eutectics, Fig. 9-30(b), consists of soft pockets of lead (dark) in a matrix of hard copper dendrites. Some bearing metals, like silver, are basically single-phase, homogeneous structures, while the powder metallurgy product, Fig. 9-30(c), is a mixture of metallic and nonmetallic components. Essentially all the black areas in Fig. 9-30(c) are voids, which are usually filled with oil before the bearing is used. The background structure is largely alpha solid solution in which both a second phase (delta) and minute graphite particles can be expected to be present.

**Machinability.** Another commercially important and many-sided property is machinability. An industrial machining operation has many objectives, such as rapid cutting, good surface finish, and long tool life, but an adequate definition of the machinability of a metal is the following: the most machinable metal is the one which permits the removal of material with a satisfactory finish at lowest cost. However, the actual value of lowest cost is determined (as well as by the quality of finish required) by such factors as: (1) the metal being cut (the work piece), (2) the metal of the cutting tool (the tool material), (3) the size and shape of the tool, (4) the kind of machining operation (drilling, planning, etc.), (5) the size, shape, and velocity of the cut, (6) the type and quality of the machine (lathe, shaper, etc.), (7) the conditions of lubrication. Although these factors are closely interrelated, attention is given here mostly to the work piece and to the tool material.

**Chip formation.** Figure 9-31(a) shows the formation of discontinuous chips in the machining of a work piece by a tool. In every such machining process the following steps occur:
Fig. 9-31. Illustration of chip formation in machining operations. (a) The formation of a continuous chip. The photomicrographs show the character of: (b) a continuous chip; (c) a continuous chip with a built-up edge; (d) a discontinuous chip. (Courtesy M. E. Merchant and Hans Ernst, Cincinnati Milling Machine Company.)

1. The metal is severely stressed just ahead of the cutting edge of the tool.
2. The metal (a) fractures approximately perpendicular to the tool face and forms discontinuous chips, or (b) plastically deforms sufficiently so that fracture does not occur; that is, a continuous chip is produced. Continuous chips may form with or without a built-up edge.
3. The metal flows up the face of the tool.

Photographs of discontinuous chips and of the two types of continuous chips are shown in Fig. 9-31(b). Some of the characteristics of the three kinds of chips are given in Table 9-9. Discontinuous chips are desirable for automatic screw machine work because of their easy disposal. Continuous chips with a minimum of built-up edge are preferred when the best finish is needed, and these chips may readily be broken artificially because they curl tightly in the absence of built-up edge. The tendency

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Discontinuous Without built-up edge</th>
<th>Continuous With built-up edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface finish</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>Face of chip disposal</td>
<td>good</td>
<td>fair</td>
</tr>
<tr>
<td>Type of tool failure</td>
<td>Wear of cutting edge</td>
<td>Wear of cutting edge and abrasion of tool face</td>
</tr>
<tr>
<td>Tendency to heat tool</td>
<td>small</td>
<td>small</td>
</tr>
<tr>
<td>Conditions for obtaining a given type of chip</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimum work-piece ductility</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Optimum chip thickness</td>
<td>large</td>
<td>small</td>
</tr>
<tr>
<td>Optimum cutting speed</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Optimum rake angle</td>
<td>small</td>
<td>large</td>
</tr>
</tbody>
</table>

Table 9-9

Characteristics of Chip Types
PLASTICITY OF METALS

Region of poor machinability

Ductility

Variation of finishability of alloys caused by changing their structures.

Table 9-10

Relative Machinabilities of Alloys

<table>
<thead>
<tr>
<th>Machinability</th>
<th>Ferrous</th>
<th>Nonferrous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>Leaded steel screw stock</td>
<td>Magnesium alloys</td>
</tr>
<tr>
<td></td>
<td>Low-carbon steel screw</td>
<td>Aluminum alloys</td>
</tr>
<tr>
<td></td>
<td>stock</td>
<td>Led brass</td>
</tr>
<tr>
<td></td>
<td>Ferritic malleable cast</td>
<td>Silicon-bronze</td>
</tr>
<tr>
<td></td>
<td>iron</td>
<td>Lead phosphor-bronze</td>
</tr>
<tr>
<td></td>
<td>Ferritic gray cast iron</td>
<td>Yellow brass</td>
</tr>
<tr>
<td></td>
<td>Free-cutting 12% Cr iron</td>
<td>Cast copper</td>
</tr>
<tr>
<td></td>
<td>Low alloy steel</td>
<td>Nickel</td>
</tr>
<tr>
<td></td>
<td>Ingot iron</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wrought iron</td>
<td>Monel metal</td>
</tr>
<tr>
<td></td>
<td>Free-cutting 18-8 stainless steel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Austenitic manganese steel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High-speed steel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18-8 Stainless steel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>White cast iron</td>
<td>Stellite</td>
</tr>
<tr>
<td>Unmachinable</td>
<td></td>
<td>Sintered carbides</td>
</tr>
</tbody>
</table>
to form a built-up edge is decreased by using a keen cutting edge, a highly polished tool face, and a tool material with a low coefficient of friction against the work piece. Suitable cutting fluids also aid materially in reducing the built-up edge.

**Work-piece characteristics.** Since the cutting edge of the tool must penetrate the work piece in a machining operation, it is usually desirable that the metal being cut have low resistance to penetration. Hardness is defined as resistance to penetration, and therefore low hardness is an almost universal requirement for easy machinability of a metal. The need for low hardness applies on a micro- as well as a macroscale, since hard, abrasive constituents in the microstructure will quite evidently produce rapid wear of the cutting tool. The second important characteristic of a work piece is low ductility, which promotes easy breaking of the chips in discontinuous chip formation. When continuous chips are formed, low ductility also increases the ease of cutting by decreasing the built-up edge and the deformation of the metal.

Some alloys, such as those of magnesium, naturally possess a desirable combination of low strength and low ductility. Other materials can have their properties changed by suitable treatment to bring them within the range of good machinability. Figure 9-32 is a schematic illustration of the improvement of the machinability of a low-carbon steel by decreasing its ductility (and incidentally increasing its hardness). This figure also shows the effect of malleableizing a white cast iron. It will be recalled, Fig. 6-41, that this treatment changes the hard, brittle carbide phase into soft ferrite and graphite. Machinability can also be improved by suitable additions to alloys during manufacture. Lead is used for this purpose in a number of alloys, and steels can be treated with sulfur as well. The action of constituents such as these is to reduce the rubbing friction between the chip and tool, since they act as a solid lubricant at that interface.

Since so many factors enter into a machinability rating, it is difficult to list the machinability of alloys in a definite order. The arrangement given in Table 9-10 can be considered only approximate.

**Tool-material characteristics.** The substances used as tool materials are conveniently divided into the five groups shown in Table 9-11. Because of their low cost, low-alloy steels are used when their properties are adequate for the application. However, production machining the use of the more expensive materials is well justified for most by the higher cutting rates they permit. For example, carbide-tipped tools maintain their cutting efficiency at 1300°F. The maximum temperature for high-speed steel is about 1000°F, and for carbon tool steel it is considerably lower. The nonsteel tool materials tend to produce a better finish in machining ferrous materials because of a lower friction coefficient. Sintered carbides, made by the powder-metallurgy process, consist of hard carbide particles
### Table 9-11

**Characteristics of Tool Materials**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Tool material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low-alloy steels</td>
</tr>
<tr>
<td>Typical alloy</td>
<td>Plain carbon tool steel</td>
</tr>
<tr>
<td></td>
<td>1% C</td>
</tr>
<tr>
<td></td>
<td>balance Fe*</td>
</tr>
<tr>
<td>Relative cost</td>
<td>low</td>
</tr>
<tr>
<td>Permissible metal cutting rate</td>
<td>low</td>
</tr>
<tr>
<td>Resistance to softening by heat</td>
<td>poor</td>
</tr>
<tr>
<td>Toughness</td>
<td>good</td>
</tr>
<tr>
<td>Wear resistance</td>
<td>poor</td>
</tr>
<tr>
<td>Typical uses</td>
<td>Pipe cutters, Roll threading dies</td>
</tr>
</tbody>
</table>

*Plus small amounts of Mn, Si, etc.*
bonded with 3 to 15 percent of cobalt metal. In addition to their extensive use as tips for cutting tools, sintered carbides are used in such devices as wire-drawing dies, in which very good wear resistance is needed. The new aluminum-oxide tool materials permit very high cutting speeds and suffer little wear. However, lack of toughness limits their application to the finer machining operations.

REFERENCES


PROBLEMS

1. Give two examples of metal parts in which plastic deformation behavior is important.

2. The total deformation of metals during creep is often less than one percent. Discuss the possibility of reducing (a) the elastic, (b) the anelastic, (c) the permanent plastic components of this total deformation by special treatment, such as periodic removal of the load.

3. Sketch a unit cell of the copper crystal structure (face-centered cubic). Show on it (a) the plane on which slip occurs, (b) the direction in which slip occurs. (c) What statement can be made about the density of atoms on the slip plane compared with other planes such as the [100] planes? (d) What statement can be made about the atomic spacing along the slip direction compared with other directions?

4. Consider the compression at room temperature of a single crystal of magnesium oriented so that the [0001] direction coincides with the axis of compression. Assuming that the stress for twinning on the (1012) plane is 10 times $\tau_0$ for slip on the (0001) plane, determine whether the crystal will twin or slip.

5. The approximate strain $\delta'$ differs increasingly from the true strain $\delta$ with increasing plastic deformation. Show that $\delta'$ is 5 percent larger than $\delta$ when $\delta'$ has reached a value of about 0.1. [Recall the useful approximation for small values of $x$, in $(1 + x) = x = \frac{1}{x}$]

6. Consider a small cylindrical volume of metal in the necked region of a tension test specimen. Taking the diameter of the necked region as the diameter of the small volume, and assuming that no volume change occurs during plastic deformation, show that the equation

$$\delta = 2 \ln \frac{d_0}{d}$$

gives the true strain at the neck of the specimen.

7. (a) Does the equation of Problem 6 also apply during the early stages of the tension test when uniform deformation is occurring? (b) Why?

8. For a given material the yield strength (which is determined by a tension test) and the flow stress have the same numerical value. What is the difference in the significance of these two terms with regard to mechanical design?

9. The central portion of a long steel rod passes through a liquid that is under 10,000 lb/in$^2$ pressure. What is the maximum tensile stress that the rod can sustain without plastic deformation? The yield strength of the steel is 30,000 lb/in$^2$. [Hint: Make an analysis at a point in the central portion of the rod. Note that $S_1$ is along the axis of the rod. $S_2$ and $S_3$ are equal, are at right angles to each other, and lie in a plane that is perpendicular to the axis of the rod.]

10. (a) What is the difference, if any, between the fracture stress and the tensile strength? (b) Compare the direct design significance of these two values.

11. (a) Apply the equation Work $= \int force \times dx$ to show that $\frac{1}{2}E$ is the work of elastic deformation. Consider that the tensile stress $\sigma$ is gradually applied to unit volume of a bar of metal whose Young's modulus is $E$. (b) Explain by analogy with gravitational potential energy why this calculation gives the strain energy per
PROBLEMS

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unit volume. (c) Show that the strain energy $W$, in Eq. (9-20) can be considered to come from a cylindrical region surrounding the crack, the diameter of the cylinder being slightly larger than the crack length $2C$.

12. Assume that the heat-treated alloy steel of Fig. 9-19(b) is to be used as a 1½ inch shaft containing a keyway. (a) What is the (laboratory) endurance limit of this steel? (b) List the factors that would tend to decrease the endurance limit value in this case. (c) Make an estimate of the actual endurance limit of steel under these conditions.

13. What are the service conditions for which (a) yield strength, (b) creep strength, (c) rupture strength is the most useful design value?

14. Consider the press forging of a block of 0.45 percent carbon steel at 1800°F, where the flow stress $S_0$ is 10,000 lb/in². (a) Calculate the ideal work required to compress a block 4 X 2 inches in cross-sectional area from an initial height of 2 inches to a final height of 1 inch. (b) Describe with the aid of sketches the action of the two factors that would cause the actual work to be about twice the ideal work obtained in (a). (c) If a 3 horsepower motor drives the hydraulic press, and assuming an over-all mechanical efficiency of 70 percent, calculate the maximum number of pieces that could be formed per minute. Use $a = 2$.

15. Discuss the interdependence of metallurgical and mechanical factors in bearing design. (For example, consider the fact that the stress in any bearing can be made smaller, for the same total load, by increasing the size of the bearing.)

16. List the steps that might be taken to make a low-carbon steel more suitable for machining in an automatic screw machine by (a) changes in the work pieces, and (b) changes in the machining procedure.
CHAPTER 10
CORROSION AND OXIDATION

"With sharpen'd sight pale Antiquaries pore,
Th' inscription value, but the rust adore.
This the blue varnish, that the green endears;
The sacred rust of twice ten hundred years."
ALEXANDER POPE

INTRODUCTION

The esthetic value of the corrosion products on ancient plaques and statues is small compensation for the enormous economic loss caused by environmental attack on metals. Moreover, it is typical of the complex factors governing corrosion processes that the green patina on weathered copper alloys is generally admired, while iron rust is almost always looked upon with disfavor. These two aspects of corrosion, its great financial waste and its complexity, have produced an unusual situation. Extensive research has resulted in a good understanding of many phases of corrosion, and thousands of new investigations are conducted each year. Nevertheless, in many important applications engineers must rely on the empirical results of service tests, since actual performance may differ markedly from the predictions of laboratory investigations.

Although corrosion theory cannot be applied rigorously to all practical problems, in many cases its basic principles offer a guide to corrosion control. Most of the subsequent discussion is devoted to these principles. Chemical behavior is fundamentally important, but other factors also influence the choice of corrosion-resistant materials for engineering applications. For example, although tantalum has excellent corrosion resistance, it is expensive and often difficult to fabricate in the required form. The usual criteria for selecting an alloy for a given application are adequate strength, ease of fabrication, low initial and maintenance costs, and corrosion resistance in a specific environment.

The prime cause of all reactions between metals and their environments is a decrease in the free energy of the system as a result of the reaction. In only a few instances is it economical to reverse this driving force by the use of noble metals such as gold or platinum. In most practical situations corrosion is controlled by reducing the rate at which the corrosion reaction proceeds. As a background for studying this control of corrosion rates, we shall consider here the main types of corrosion.
ELECTROCHEMICAL CORROSION

TYPES OF CORROSION

It is customary to classify the multitude of possible corrosion reactions into a few broad types such as direct corrosion, electrochemical corrosion, and high-temperature oxidation. Although this classification has many practical advantages, its theoretical justification is not so evident, since practically all corrosion is electrochemical; that is, anodic and cathodic regions on the metal surface are involved. It is convenient, however, to reserve the term electrochemical corrosion for corrosion reactions in which there are electric currents through parts of the metal in which corrosion is not taking place. In direct corrosion, on the other hand, the electrical effects involved occur in the immediate vicinity of the reaction. Reactions of the oxidation type exhibit a variety of electrochemical behaviors, but they all involve reaction with oxygen or the halogens, usually in the absence of moisture.

**Direct corrosion.** This form of corrosion is essentially ordinary chemical attack. The corrosive agent, such as an acid pickling solution used to clean steel surfaces, dissolves the surface uniformly without the formation of protective layers and without selective attack of a certain phase or component. The attack continues at an almost constant rate that can be conveniently measured in standard units, e.g., inches penetration per year (ipy) or milligrams per square decimeter per day (mdd). A typical direct corrosion reaction is

\[
Fe + 2H^+ \rightarrow Fe^{++} + H_2 \text{(gas)},
\]

which describes the direct attack of iron by hydrogen ions in the acid pickling* of steel. This reaction differs significantly from the indirect process of electrochemical corrosion, shown in Fig. 10-1, in which iron is dissolved as the anodic reaction and hydrogen takes part in a separate cathodic reaction.

The rate of direct corrosion tends to be relatively high compared with that of other corrosion mechanisms. One means of controlling direct corrosion is to force a change in the reaction mechanism. Often a suitable addition to the corroding medium causes the formation of a protective layer of the corrosion reaction product, and this in turn alters the process by which corrosion occurs.

**Electrochemical corrosion.** The type of corrosion most frequently encountered takes place at or near room temperature as a result of the

* To remove surface oxides, steels are immersed for a suitable period in a pickling solution (5-10% H₂SO₄) at about 150°F.
reaction of metals with water or with aqueous solutions of salts, acids, or bases. These reactions are part of the broad field of electrochemical corrosion. Although there are many variations of this type of corrosion, the action of an aerated salt solution at the junction between a piece of iron and a piece of copper* illustrates the essential characteristics, Fig. 10-1.

It is seen that there are two principal reactions, one at the anode and another at the cathode. Anodic reactions are always oxidation reactions and therefore tend to destroy the anode metal by causing it to dissolve as an ion or to revert to a combined state such as an oxide. Cathodic reactions are always reduction reactions and usually do not affect the cathode metal, since most metals cannot be further reduced. The electrons that are produced by the anodic reaction flow through the metal and are used up in the cathodic reaction. The disposition of the reaction products is often decisive in controlling the rate of corrosion. They may go into solution or be evolved as a gas and thus not inhibit further reaction. In other cases an insoluble compound is formed that may cover the metal surface and be effective in reducing the rate of additional corrosion. However, in the example of Fig. 10-1 the insoluble compound is formed at a distance from the corroding area and has little protective value.

A number of factors other than the presence or absence of protective layers influence the course and rate of electrochemical corrosion under given conditions. One of the most important is the relative chemical natures of the anodic and cathodic regions of the corroding material. When these two regions are represented by two different metals, the electromotive series (Table 10-1) determines which of the metals will be

* Strictly speaking, this is an example of galvanic corrosion, but other types of electrochemical corrosion involving only a single metal occur in a similar manner.
Table 10-1

Comparison of the Galvanic Series in Sea Water and the Electromotive Series

<table>
<thead>
<tr>
<th>Galvanic series in sea water</th>
<th>Electromotive series†</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anodic (corroded) end</strong></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>Li, Li⁺</td>
</tr>
<tr>
<td>Magnesium alloys</td>
<td>K, K⁺</td>
</tr>
<tr>
<td>Zinc</td>
<td>Na, Na⁺</td>
</tr>
<tr>
<td>Galvanized steel</td>
<td>Mg, Mg⁺⁺</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al, Al⁺⁺⁺</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Zn, Zn⁺⁺</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>Cr, Cr⁺⁺⁺</td>
</tr>
<tr>
<td>Steel</td>
<td>Fe, Fe⁺⁺</td>
</tr>
<tr>
<td>Wrought iron</td>
<td>Cd, Cd⁺⁺</td>
</tr>
<tr>
<td>Cast iron</td>
<td>Co, Co⁺⁺</td>
</tr>
<tr>
<td>50-50 Solder</td>
<td>Ni, Ni⁺⁺</td>
</tr>
<tr>
<td>18-8 Stainless steel (active)</td>
<td>Sn, Sn⁺⁺</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb, Pb⁺⁺</td>
</tr>
<tr>
<td>Tin</td>
<td>H₂, H⁺</td>
</tr>
<tr>
<td>Muntz metal</td>
<td>Bi, Bi⁺⁺⁺</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu, Cu⁺⁺</td>
</tr>
<tr>
<td>Yellow brass</td>
<td>Hg, Hg⁺⁺</td>
</tr>
<tr>
<td>Red brass</td>
<td>Ag, Ag⁺⁺</td>
</tr>
<tr>
<td>Copper</td>
<td>Pt, Pt⁺⁺</td>
</tr>
<tr>
<td>70-30 Cupronickel</td>
<td>Au, Au⁺⁺</td>
</tr>
<tr>
<td>18-8 Stainless steel (passive)</td>
<td>Au⁺⁺</td>
</tr>
<tr>
<td><strong>Cathodic (protected) end</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Adapted from the Corrosion Handbook.
† Voltages are for oxidation reaction.

Anodic under the standard conditions for which the electromotive series is determined. However, the actual conditions under which corrosion is

† The voltages in Table 10-1 are called standard half-cell potentials because each of them is a potential associated with a portion of a cell composed of two parts, the half cell in question and a standard half cell. For example, the potential of Cd, Cd⁺⁺ which is reversible with respect to Cd⁺⁺ in an electrolyte of unit Cd⁺⁺ activity is called the standard half-cell potential of the Cd, Cd⁺⁺ electrode. Cell potentials are usually referred to a standard hydrogen half-cell consisting of gaseous hydrogen H₂ at one atmosphere pressure and hydrogen ions H⁺ at unit activity in contact with a specially prepared platinum electrode. This subject is fully treated in standard textbooks on physical chemistry.
occurring may result in different relative positions of the two metals in a corresponding series. Therefore galvanic series, such as that given in Table 10-1 for sea water, have been determined for practical corroding environments. The galvanic series for sea water can be used to predict that iron will corrode in contact with copper and that the copper will be protected. If zinc is substituted for copper in a couple with iron, the galvanic series shows that the iron will become cathodic relative to the zinc and will tend not to corrode. Thus the relation of two metals in the galvanic series plays an important part in determining the course of corrosion when the metals are in contact in a corroding environment.

If care is taken to prevent direct contact of dissimilar metals in a corroding medium, the severe local attack shown in Fig. 10-1 can be prevented, but electrochemical corrosion may still occur on each metal independently. Small anodic and cathodic regions form on the exposed surface of each metal as the result of slight inhomogeneities in the metal or in the corroding environment. Some of the causes of electrochemical differences in metals and alloys are impurities, a second phase, grain boundaries, variation in grain orientation or in grain size, and nonuniform thermal treatments. Also, the corroding liquid may contribute to the formation of local corrosion cells because of differences in local velocity, intensity of illumination, bacteria count, temperature, solute concentration, or degree of aeration. For example, if dirt or scale hinders the access of oxygen to a portion of an iron surface, this portion will tend to become anodic, since the surrounding areas are able to undergo the cathodic reaction shown in Fig. 10-1. Attack at the anodic areas then occurs in the manner described above. The use of high-purity metals minimizes inhomogeneity in the surface of the metal and tends to reduce the rate of corrosion. Table 10-2 gives typical corrosion data for several materials in a common environment, quiet sea water.

<table>
<thead>
<tr>
<th>Material</th>
<th>Average corrosion rate, ipy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum alloy 2024-T3</td>
<td>2.24 x 10^{-3}</td>
</tr>
<tr>
<td>Acelad 2024-T3</td>
<td>0.61 x 10^{-3}</td>
</tr>
<tr>
<td>302 Stainless steel</td>
<td>0.15 x 10^{-3}</td>
</tr>
<tr>
<td>347 Stainless steel</td>
<td>1.43 x 10^{-3}</td>
</tr>
<tr>
<td>Monel</td>
<td>1.88 x 10^{-3}</td>
</tr>
<tr>
<td>Inconel</td>
<td>0.49 x 10^{-3}</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.00 x 10^{-3}</td>
</tr>
</tbody>
</table>

A remarkable aspect of the corrosion of iron is the fact that direct reaction with hydrogen ions in aqueous solutions does not occur to a serious extent unless oxygen is present. A layer of atomic hydrogen quickly forms on the surface of a bar of iron that is immersed in a salt solution. This reaction is

\[ \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{++} + 2\text{H}. \]  

However, it is difficult for these hydrogen atoms to combine to form a gas and thus escape from the surface of the iron. A bar of iron is therefore essentially unattacked by a salt solution from which oxygen is excluded. The corrosion of iron in ordinary salt solutions is made possible by the combination of dissolved oxygen with the atomic hydrogen to form water. This removal of hydrogen atoms is called depolarization and permits continuing corrosion of the iron to take place. The corrosion rate of iron is thus controlled not by the primary reaction with hydrogen ions but by the depolarization reaction involving oxygen. This explains why in many instances the rate of corrosion is determined by the rate at which oxygen can diffuse to the reacting metal.

An opposite characteristic of oxygen and oxidizing media is their ability to make certain metals and alloys passive. (For example, concentrated nitric acid makes iron passive, and the iron is then virtually unattacked by strong solutions of this acid.) A metal is less reactive in the passive condition than in the normal or active condition. Passivity is a relative term, however, and a metal may be passive under one set of conditions but corrode rapidly under another. This behavior is shown for stainless steel in sea water in Table 10-1. Under most conditions stainless steel is passivated by sea water and acts like a more noble metal, but if a pit develops on the surface of the steel the metal in that local area becomes active, and corrosion is accelerated. The exact mechanism is uncertain, but passivity is believed to be caused by the presence of complex oxide films at the metal surface.

Liquid-metal corrosion. Corrosion of metals and alloys at high temperatures by liquid metals flowing past them is a form of corrosion that has recently come into prominence because of its occurrence in devices for nuclear power. The corrosion reaction is essentially a process of mass transfer and is not dependent upon local cell potentials for its driving force. Usually the driving force for this form of corrosion is the tendency of the solid to dissolve in the liquid up to the solubility limit at the given temperature. The specific types of liquid-metal attack include the follow-

* On the other hand, Fig. 10-12 shows that hydrogen gas can form during the corrosion of steel in a moderately acid solution, pH = 4.
The most serious cases of damage by liquid-metal attack occur in heat exchangers carrying liquid-metal coolants. As the solid container, usually iron or copper tubing, approaches equilibrium with the liquid-metal coolant in the hot zone of the heat exchanger, a portion of the solid goes into solution in the liquid. When the liquid moves to a cooler part of the heat exchanger, the solubility limit decreases and deposition of solids takes place, usually on the walls of the exchanger tubes. In a thermal loop of this kind the hot zone is continually corroded, and the cold zone becomes plugged with the deposited corrosion products. Shutdown of liquid-metal heat exchangers may be necessary after less than one month of continuous operation unless specific preventive measures are taken. The most promising technique for prolonging the life of exchangers is the addition of certain inhibitors to the liquid alloy. It is believed that the inhibitors adsorb on the walls of the solid vessel or form protective films that hinder the corrosion processes at elevated temperatures.

Specific corrosion types. While the general corrosion mechanisms (direct corrosion, electrochemical corrosion, and liquid-metal corrosion) represent convenient divisions of the subject for some purposes, more specific descriptions are widely used for certain types of industrially important corrosion. The broadest of these descriptions is the term uniform attack. This term is applied to any form of corrosion in which the whole surface of the metal is corroded to the same degree. One type of uniform attack is shown in Fig. 10-4. Under these conditions the useful life of a given material is easily estimated and unexpected failure need not be feared. Pitting and intergranular corrosion, on the other hand, are types of non-uniform corrosion that can proceed in otherwise undamaged metal. Both are initiated by inhomogeneities in the metal, but may be accelerated by such additional factors as a localized change from the passive to the active state after corrosion has begun. The deep, isolated holes caused by pitting (Fig. 10-2) are especially difficult to avoid, but improving the
homogeneity of the metal and of the corroding medium is often helpful.

Intergranular corrosion occurs when a pronounced difference in reactivity exists between the grain boundaries and the remainder of the alloy. In stainless steel such a difference is set up when chromium carbides form at the grain boundaries during heating of the steel in the range 900–1400°F. The grain-boundary region is thereby depleted in chromium and becomes anodic with respect to the surrounding alloy. Corrosion can then occur along the grain boundaries and produce serious damage like that shown (Fig. 10-3) for welded stainless steel subjected to a corrosive environment. Usually corrosion in welded stainless steels is not a serious problem, since corrosion resistance can be restored by a heat treatment that dissolves the chromium carbides precipitated during welding. However, when stainless steel assemblies are too large to be heat treated or are to be subjected in service to temperatures in the 900–1400°F range, it is then necessary to prevent the depletion of chromium by special means. The use of very low carbon contents (about 0.03 percent) is one remedy, but generally the customary 0.08 percent carbon is stabilized by the addition of titanium or columbium. In Fig. 10-3 note that the stainless steel stabilized by the addition of 0.5% titanium has not been attacked. Table 6-1 shows that these elements are extremely strong carbide formers, and they leave almost no carbon available for combination with chromium.

Single-phase alloys usually have better corrosion resistance than similar two-phase alloys. Electrochemical corrosion is encouraged by the presence of two dissimilar constituents, and one of them tends to be preferentially attacked. Moreover, even in certain single-phase solid-solution alloys, preferential corrosion of one of the component metals may occur. The best known example of this type of behavior is the dezincification that takes place in brasses containing more than 15 percent zinc. Figure 10-4 shows this kind of corrosion in a brass pipe. Ordinary water is capable of dissolving the zinc and leaving the copper, perhaps by redeposition, as a spongy mass that has almost no strength. Plug-type (localized) dezincification is especially severe. The addition of small amounts of alloying elements, such as tin or arsenic, to high-zinc alloys effectively controls this type of corrosion in some cases. A second type of preferential loss of zinc (that is also termed dezincification) occurs when brasses are heated to high temperatures at which the zinc vaporizes rapidly.

Stress-corrosion refers to greatly accelerated corrosion that takes place
in certain environments when metals contain internal tensile stresses. Well-known examples are *season cracking* that occurs in brasses, especially in the presence of moisture and traces of ammonia, and *caustic embrittlement* of steel exposed to solutions containing sodium hydroxide. The most effective control is in elimination of the tensile stresses. Usually this is accomplished by a stress-relief anneal that need not greatly decrease the strengthening effect of a previous cold-working operation. Occasionally it is possible to produce unobjectionable compressive stress by a means such as shot-peening. Since a specific environment is often necessary for rapid stress corrosion, adequate control may sometimes be obtained by treating the corroding medium.

*Corrosion fatigue* is the combined action of corrosion and repeated stresses and is far more serious than the sum of these two factors acting individually. To express the influence of corrosion on fatigue strength, the damage ratio is frequently used:

\[
\text{Damage ratio} = \frac{\text{corrosion fatigue strength}}{\text{normal fatigue strength}}
\]

This ratio for salt water as a corroding medium is about 0.2 for carbon steels, 0.5 for stainless steels, 0.4 for aluminum alloys, and 1.0 for copper. Suitable protective measures against corrosion fatigue include treatment of the corroding medium and surface protection of the metal. Nitriding of steels is often useful for this purpose.

Because most corrosion testing is done in liquids and gases at rest, the data are usually not applicable to service conditions with rapid movement past the metal surface. Such *erosion-corrosion* causes accelerated attack because it mechanically removes the protective layer that normally builds up on the corroding surface. Impingement attack of elbows in pipelines, Fig.
10^-5, is typical of this type of corrosion. Improved mechanical design is often a sufficient remedy for erosion-corrosion, but treatment of the corroding medium or choice of a different alloy may be necessary.

**Oxidation**

This type of corrosion involves the reaction of metals with oxygen at high temperatures, usually in the absence of moisture. (It is noteworthy that a type of oxide formation, such as the rusting of iron, that occurs in the presence of moisture is not considered to belong to this category, since a different mechanism is involved.) The nature of the oxide that is formed plays an important part in the oxidation process:

1. The oxide may be unstable, as in the case of gold oxide, and oxidation does not occur.
2. The oxide may be volatile, as in the case of molybdenum oxide, and oxidation occurs at a constant, relatively high rate.
3. One or more oxides may form a layer or layers at the metal surface.

The third occurrence is the most common, and various aspects of its behavior are considered here.

**Oxide films.** Surface oxide layers are called *films* when their thickness is less than about 3000 Å, and they are called *scales* when their thickness exceeds this value and is more easily measured. Since films are so thin, their destructive effect on most metal parts can be neglected. However, under certain conditions of wear, the rate of metal loss is greatly increased as a result of the removal by abrasion of the thin protective film. Films usually decrease the rate of additional oxidation and may, as in the case of the invisible film on aluminum, be almost completely protective. An example of film formation in steel heat treatment is the formation of *temper colors* during the heating of steels in the range 450 to 600°F. These colors range from light straw to dark blue and are the interference effects produced as the oxide film increases in thickness as a function of time and temperature. The laws governing the growth of films are similar to those for scale formation.

**Scale formation.** Thick oxide layers or scales are divided into two categories, protective and nonprotective, on the basis of the *Pilling-Bedworth rule*. According to this rule an oxide is protective if the volume of the oxide is at least as great as the volume of metal from which it formed. If the volume of oxide is less than this amount, the scale is not continuous and hence is comparatively ineffective in preventing the access of oxygen to the metal surface. Although there are many exceptions to the Pilling-Bedworth rule, it is a useful guide when the specific oxidation character-
Time of Oxidation, hours

FIG. 10-6. The oxidation of pure magnesium in oxygen. (After Leontis and Rhines.)

Oxidation reaction
(Generally near oxygen surface)

\[ M^{++} + O^--\rightarrow MO \]

\[ \frac{1}{2}O_2 + 2e^- \rightarrow O^--\]

FIG. 10-7. The course of oxidation of a metal through a protective oxide layer.

Characteristics of a metal are unknown. Metals that have these nonprotective oxides tend to increase the weight, \( W \), of their scale at a linear rate according to the equation

\[ W = At, \quad (10-3) \]

where \( A \) is a constant that depends on the temperature and \( t \) is the time. Data on the oxidation of magnesium are given in Fig. 10-6. Some of the alkali and alkaline earth metals also oxidize in accordance with Eq. (10-3). Usually the mechanism of growth of nonprotective films involves the passage of gaseous oxygen through pores or fissures in the oxide film.

When a protective oxide forms on the exposed metallic surface, diffusion must occur through the scale for additional growth to take place. Figure 10-7 is a schematic representation of the process of oxidation under these conditions. This figure shows that the metal ionizes at the oxide-metal surface, and then both the metal ion \( M^{++} \) and the electrons diffuse through the oxide layer to the oxygen surface. Here the electron aids in
forming the oxygen ion. This ion reacts near the gas-oxide surface with the metal ion to form the oxide, represented by \( MO \). It is shown in Chapter 11 that the rate of oxidation in this case should follow the \textit{parabolic law},

\[
W^2 = Bt,
\]  
(10-4)

where \( B \) is a constant that depends on the temperature. This behavior is observed experimentally in many instances, and Fig. 10-8 shows typical data for copper and several binary alloys.

The oxidation of iron to \( Fe_2O_3 \) occurs by a different mechanism than that shown in Fig. 10-7. In this case the oxygen ion is more mobile and diffuses inwardly from the gas-oxide surface to the oxide-metal boundary. Consequently, the \( Fe_2O_3 \) lattice grows outwardly from the oxide-metal boundary. Regardless of whether it is the oxygen ion or the metal ion that diffuses, it is necessary that the crystal lattice of the oxide contain defects in the form of vacancies or interstitial ions. The most common defect structure contains cation (metal ion) vacancies; however, anion vacancies and cation interstitialcies are also known to occur. Thus these oxidation products must deviate slightly from stoichiometry in order to form.

Some metals with protective oxides have reaction rates that diminish more rapidly with time than Eq. (10-4) predicts. For example, under many conditions the oxide layer on aluminum approaches a constant thickness with increasing time and so obeys an \textit{asymptotic law}. A logarithmic increase in the weight of oxide,

\[
W = C \log (Dt + E),
\]  
(10-5)

where \( C, D, \) and \( E \) are constants that depend on temperature, is observed.
in other cases, such as the oxidation of iron or nickel at moderate temperatures.

When the oxidation of an alloy (rather than a pure metal) is considered, several new features may appear. The separate oxides may form a solid solution; a multiphase scale may appear; or only a single component in the alloy may be oxidized, a process called selective oxidation. When the oxides which form are highly soluble in each other, certain generalizations regarding the oxidation behavior of the alloy system can be made. For example, NiO is basically a cation deficient structure and has high mutual solubility with Cr$_2$O$_3$. It is observed that additions of Cr to pure Ni increase the oxidation rate, while additions of Ni to pure Cr decrease the oxidation rate. The general rule for this type of behavior is that additions of a higher valence species tend to be deleterious, while additions of a lower valence species are usually beneficial. On the other hand, in oxides which have excess cations and electrons in interstitial positions, such as ZnO, the reverse is true. Aluminum additions to zinc lower the oxidation rate of zinc, while lithium additions have been shown to increase the oxidation rate.

When the oxide scale consists of more than a single phase, the oxidation characteristics of the alloy are generally governed by the properties of that oxide phase which is continuous. For example, in the oxidation of some Cu-Zn alloys, islands of ZnO are found in a matrix of Cu$_2$O, and the oxidation process is governed by diffusion through Cu$_2$O. A notable exception to this rule is the case of dilute additions of vanadium and molybdenum to steels. The oxides of these components form a low-melting eutectic with the oxides of iron, and catastrophic oxidation results. In the case of selective oxidation of one component at the surface of an alloy, great benefit can be derived from certain surface films if they are adherent, have poor electrical conductivity, and possess a complex crystal structure that hinders diffusion through them. A special case of selective oxidation is discussed below.

**Internal oxidation.** Under special conditions oxidation of an alloying element may occur below the surface of the base metal, and this internal oxidation may take place in the absence of appreciable film or scale formation at the surface. Such oxidation usually requires the following conditions:

1. The alloying element must have a greater affinity for oxygen than does the base metal.
2. Oxygen must diffuse rapidly in the base metal, compared with the diffusion of the alloying element.
3. Scaling of the base metal must not be so rapid as to destroy the surface region in which internal oxidation is occurring.
In some cases internal oxidation is useful as a method of surface hardening (see Chapter 13). More often it is the cause of difficulties, for example when certain copper or silver alloys are given high-temperature treatments in mildly oxidizing atmospheres. The internal oxidation produced under these conditions may cause processing problems or mar the surface of the metal. Compared with ordinary oxide layers these subscales are difficult to remove by the usual cleaning methods.

Oxidation rarely occurs in only one of the ways described here. Combinations of two or three types of reaction may occur in turn or simultaneously in different parts of the metal. The stress condition and the orientation of the oxide layer may vary with time or thickness, and discontinuous cracking or spalling of the layer may cause sudden changes in the reaction rate. If more than one oxide is stable under the conditions existing during oxidation, a series of oxide layers is formed, corresponding to the diffusion layers described in Chapter 11. For example, at temperatures above 500°C the scale on iron consists of layers of FeO, Fe₃O₄, and Fe₂O₃.

CORROSION AND OXIDATION CONTROL

Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so extremely varied, it is not surprising that many methods are used to deal with corrosion problems. The method or combination of methods used in a given instance is determined largely by economic considerations. In some cases it is cheaper to replace a low-cost metal at more frequent intervals than to use a somewhat superior, higher-cost alloy. However, when corrosion resistance is vitally important, a larger investment in corrosion control is usually advisable. Corrosion control measures can be considered under three general headings: (1) improving the characteristics of the metal, (2) protecting the metal with a coating substance, and (3) treating the corroding medium to reduce its corrosive action.

Characteristics of the metal. It is obviously impossible to describe here the corrosion tendencies of hundreds of different alloys under thousands of different service conditions. An excellent summary is contained in the Corrosion Handbook, and the answers to many corrosion problems can be found there. To give a brief, over-all view of metal characteristics, qualitative information on the corrosion of representative materials is presented in Table 10-3 (p. 386).* but it must be pointed out that even these qualitative relations may change as conditions of service, such as the operating temperature, are altered.

* Adapted from a Data Sheet in Metal Progress for November, 1946.
# Table 10-3

## Relative Corrosion Resistance of Several Metals and Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosion environment</th>
<th>Atmosphere</th>
<th>Water</th>
<th>High-temperature gases</th>
<th>Oxidizing gases</th>
<th>Reducing gases</th>
<th>Gases</th>
<th>Food products</th>
<th>S-15% Acid solutions</th>
<th>1-20% solutions of alkalis</th>
<th>Salt solutions (condensate concentration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingot iron or wrought iron</td>
<td>P</td>
<td>P</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>FG</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>Low-carbon steel</td>
<td>P</td>
<td>P</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>FG</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>Low-alloy, high-strength</td>
<td>F</td>
<td>F</td>
<td>G</td>
<td>F</td>
<td>FG</td>
<td>F</td>
<td>FG</td>
<td>F</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Structural steel</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>FG</td>
<td>F</td>
<td>FG</td>
<td>F</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Gray cast iron</td>
<td>F</td>
<td>F</td>
<td>G</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>FG</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>316% Nickel cast iron</td>
<td>FG</td>
<td>FG</td>
<td>F</td>
<td>FG</td>
<td>F</td>
<td>F</td>
<td>FG</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>17% Chromium-iron</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>18% Cr-8% Ni stainless steel</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>FG</td>
<td>E</td>
<td>150</td>
<td>FG</td>
<td>E</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>30% Cr-25% Ni stainless steel</td>
<td>E</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>E</td>
<td>2100</td>
<td>FG</td>
<td>E</td>
<td>F</td>
<td>E</td>
<td>FG</td>
</tr>
<tr>
<td>Nickel (99.99%)</td>
<td>E</td>
<td>E</td>
<td>F</td>
<td>G</td>
<td>E</td>
<td>1000</td>
<td>FG</td>
<td>E</td>
<td>F</td>
<td>E</td>
<td>FG</td>
</tr>
<tr>
<td>Inconel (80% Ni, 14% Cr, 6% Fe)</td>
<td>E</td>
<td>E</td>
<td>F</td>
<td>E</td>
<td>E</td>
<td>2000</td>
<td>FG</td>
<td>E</td>
<td>F</td>
<td>E</td>
<td>FG</td>
</tr>
<tr>
<td>Hastelloy C (65% Ni, 17% Mo, 14% Cr, 5% W, 3% Fe)</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>2100</td>
<td>FG</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>FG</td>
</tr>
<tr>
<td>Copper (99.99%)</td>
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<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>FG</td>
<td>G</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
</tr>
<tr>
<td>99% Tin-brass</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>FG</td>
<td>G</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
</tr>
<tr>
<td>Aluminum (99.9%)</td>
<td>G</td>
<td>E</td>
<td>FG</td>
<td>G</td>
<td>G</td>
<td>800</td>
<td>FG</td>
<td>F</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>2024 Aluminum alloy</td>
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<td>FG</td>
<td>F</td>
<td>P</td>
<td>F</td>
<td>1500</td>
<td>FG</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>Magnesium</td>
<td>G</td>
<td>G</td>
<td>F</td>
<td>P</td>
<td>P</td>
<td>400</td>
<td>FG</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>Wrought magnesium alloys</td>
<td>G</td>
<td>F</td>
<td>G</td>
<td>P</td>
<td>P</td>
<td>400</td>
<td>FG</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>FG</td>
</tr>
<tr>
<td>Tin</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
</tr>
<tr>
<td>Lead (99.99%)</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>G</td>
<td>G</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
<td>FG</td>
</tr>
</tbody>
</table>

* Service temperature is always an important variable, and in this instance the rating applies only for temperatures below 120°F.  
E = Excellent   G = good   F = fair   P = poor
The corrosion resistance of a given metal may be improved by increasing its purity, but the low strength of pure metals is often a disadvantage. It is more common to increase both strength and corrosion resistance by the use of suitable alloying elements. Examples of such alloying can be found for almost all metals, but iron-base alloys are especially significant because of the wide use of stainless steels. Many alloying elements are useful in giving iron limited corrosion resistance. For example, small amounts of phosphorus and copper improve the resistance of structural steels to atmospheric corrosion, high silicon contents are useful in acid-resistant cast alloys, and about 10 percent aluminum renders iron extremely resistant to high-temperature oxidation but also makes it brittle. However, chromium dwarfs all other alloying elements in importance. The reasons are many, but the primary one is the effect of chromium in increasing corrosion resistance in almost all environments. Figure 10-9 shows the relation between chromium content and the corrosion rates under three different conditions.
### Table 10-4

**Some Properties of Typical Stainless Steels**

<table>
<thead>
<tr>
<th>Description of steel</th>
<th>Composition, %</th>
<th>Yield strength, 1000 lb/in²</th>
<th>Tensile strength, 1000 lb/in²</th>
<th>% Elongation in 2 inches</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>Grade</td>
<td>Condition</td>
<td>C</td>
<td>Cr</td>
</tr>
<tr>
<td>Martensitic</td>
<td>420</td>
<td>Annealed</td>
<td>Heat-treated</td>
<td>0.15</td>
<td>13</td>
</tr>
<tr>
<td>Ferritic</td>
<td>405</td>
<td>Annealed</td>
<td></td>
<td>0.06</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>446</td>
<td>Annealed</td>
<td></td>
<td>0.35</td>
<td>25</td>
</tr>
<tr>
<td>Austenitic</td>
<td>301</td>
<td>Annealed</td>
<td></td>
<td>0.15</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>304</td>
<td>Work-hardened</td>
<td>Annealed</td>
<td>0.06</td>
<td>18-</td>
</tr>
<tr>
<td></td>
<td>304</td>
<td>Work-hardened</td>
<td></td>
<td>0.06</td>
<td>18-</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>Annealed</td>
<td></td>
<td>0.35</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>321</td>
<td>Annealed</td>
<td></td>
<td>0.06</td>
<td>17-</td>
</tr>
<tr>
<td>17-7PH</td>
<td>Cold-rolled</td>
<td></td>
<td></td>
<td>0.07</td>
<td>17</td>
</tr>
<tr>
<td>17-7PH</td>
<td>Age-hardened</td>
<td></td>
<td></td>
<td>0.07</td>
<td>17</td>
</tr>
<tr>
<td>201</td>
<td>Annealed</td>
<td></td>
<td></td>
<td>0.15</td>
<td>17</td>
</tr>
<tr>
<td>202</td>
<td>Annealed</td>
<td></td>
<td></td>
<td>0.15</td>
<td>18</td>
</tr>
</tbody>
</table>

*The endurance strength is usually about half of the tensile strength, corresponding to an endurance ratio of 0.5.*
chromium or more consist of ferrite under all conditions, Fig. 10-10. Such stainless irons are used primarily for high-temperature service as furnace parts and turbine blades. The sigma phase that appears at very high chromium contents is almost always undesirable in stainless steels because it has an adverse effect on corrosion resistance and impact strength. However, the hardness of this phase has been found useful in applications such as automobile engine valves, where both wear and moderate corrosion problems are encountered.

Certain aspects of the corrosion resistance of chromium alloys can be further improved by the addition of other elements, especially nickel; the standard stainless steel, 18-8, contains about 18% chromium and 8% nickel. When nickel is added to iron-chromium alloys a new factor enters the problem of phase constitution. This factor is the retention of metastable austenite at room temperature. Thus the vertical section through the iron-chromium-nickel equilibrium diagram, Fig. 10-11, shows that 18-8 stainless steel should be completely ferritic at room temperature, but in practice this steel remains austenitic on being cooled from high temperatures. Such austenitic stainless steels cannot be hardened by quenching, since the austenite does not transform to martensite. However, even in the unhardened condition these steels have a very useful combination of strength and ductility (Table 10-4).

The degree of metastability of the austenite in stainless steels depends on the composition. Elements such as manganese, carbon, and nitrogen act
with nickel to stabilize austenite, while molybdenum aids chromium in producing the ferritic condition. In many commercial stainless steels only the effects of nickel and chromium need be considered. At a composition of 17% chromium and 7% nickel it is possible by cold-working to cause a portion of the metastable austenite to decompose into a martensitelike structure, particularly at subatmospheric temperatures. An exceptionally high degree of work hardening results in this case. The amount of austenite decomposition produced by cold-working decreases with increasing nickel content and is almost zero in the 18% chromium-12% nickel alloy.

The strength of certain stainless steels, such as 17-7PH, can be increased not only by work hardening but also by age hardening. If about 1.2% aluminum is added to a 17-7 stainless steel, the austenite can be retained at room temperature. This structure can then be transformed to martensite by cold-working or heat-treating. Further hardening and strengthening result from a precipitation reaction during heating at about 900°F. The corrosion resistance of hardened 17-7PH is somewhat inferior to that of standard 18-8, but it is adequate for many applications.

Protective coatings. The choice of an engineering material involves many factors, including cost. In the majority of applications of metals the importance of the corrosion factor does not warrant the use of expensive corrosion-resistant alloys. However, in general, when an easily corroded alloy like steel is used, some provision is made to prolong its life or improve its appearance by protecting it from its surroundings. By far the most important protective measure is some kind of coating.

Nonmetallic coatings. Paint is the most widely used protection against corrosion. For adequate protection of steel surfaces, paint must provide not only a continuous barrier against the corroding environment but also a rust-inhibiting action. A pigment such as red lead (Pb₃O₄) satisfies the second requirement. It tends to maintain an alkaline, corrosion-retarding environment at the metal surface, and it also acts to make the metal passive. Other nonmetallic coatings include porcelain, plastics, and rubber. Bituminous coatings such as pitch are especially useful for protecting underground tanks and pipe.

A second type of nonmetallic coating is sometimes called a chemical coating, since its formation involves chemical reaction with the metal on which it is formed. Anodic coatings on aluminum consist of a layer of aluminum oxide about 0.0005 inch thick. They are formed when the metal is made the anode in an acid electrolyte. Because these coatings are about 1000 times thicker than the natural oxide film, they improve resistance to corrosion as well as to mechanical injury. Chromate coatings are widely used on magnesium alloys and to a smaller extent on zinc. These thin coatings are produced by many different procedures, but one of the
simplest merely requires dipping the metal in a chromate solution. The protective value of these coatings is a result of some mechanical protection plus the action of the chromate ion in decreasing the anodic reaction in electrochemical corrosion. Phosphate coatings (Parkerizing, Bonderizing) are produced on steels by dipping them in suitable phosphate solutions. They are used principally as an adherent base for paint or a protective oil.

Metallic coatings. Two factors are involved in the protection of the underlying metal by a metallic coating. One is mechanical isolation of the metal from the corrosive environment; the other is the galvanic relation of the coating metal and the base metal. If the coating metal is higher in the galvanic series than the base metal, discontinuities in the coating are not a serious problem, since the base metal is cathodic and is protected. Zinc and cadmium are examples of metals that afford galvanic protection to steel. The superior properties of cadmium coatings under such conditions as attack by salt spray or alkalies may justify their higher cost. Tin, nickel, and chromium are below steel in the galvanic series for most service conditions. Consequently, corrosion of the underlying steel occurs at small discontinuities that may be present in the protective coating. This disadvantage is outweighed for some applications by the attractive appearance of nickel and chromium plating, and by the excellent corrosion and fabricating qualities of tin plate for use in food containers.

A number of methods are used to apply metallic coatings. Zinc coatings on steel (galvanized coatings) and tin plate are usually produced by dipping clean sheet steel into a molten zinc or tin bath. The character of the resulting metallic layer is described in Chapter 11. Thinner, uniform coatings of zinc and tin can be obtained by electroplating, and this process is becoming increasingly important for these metals. Cadmium coatings and decorative nickel and chromium plates are almost always produced by electroplating. Diffusion coatings can be formed on steel by high-temperature treatment in the presence of powdered aluminum (calorizing), chromium (chromizing), ferrosilicon (therigizing), zinc (sherardizing), and other metals. These coatings are relatively thick and are usually applied to cast or machined parts such as bolts, valve guides, and turbine buckets. Thick coatings of almost any metal can be produced by metal spraying. In this process a special gun melts and atomizes the coating metal and then uses compressed air to drive the small particles against a prepared surface. Since the metal particles solidify in the air, the bond they form is primarily mechanical, and the coating is somewhat porous. However, the coating is sufficient for many purposes in addition to corrosion protection; for example, thick sprayed metal coatings can be used to build up worn shafts and other damaged parts.

Metal cladding is the joining of two different metals or alloys by forming a strong alloy bond between plates of the two materials. The bond may
be formed in many ways (by casting one alloy against a solid plate of the
other, for example). This thick, composite ingot is then hot worked to
reduce it to a convenient form such as clad sheet. The production of a
corrosion-resistant surface is the principal objective for cladding; for ex­
ample, Aiclad aluminum alloys (see Chapter 13) are used when superior
corrosion resistance is required. Cladding is also used for such purposes as
making bimetal strips for temperature-control devices.

Environment control. Sometimes the rate of corrosion can be greatly
reduced by small changes in the corroding environment. Since the rate of
corrosion is usually an exponential function of temperature, a slight
decrease in the temperature of the corroding medium may cause a pro­
nounced decrease in the amount of corrosion. Also, if the velocity of the
corroding medium can be diminished by a change in operating conditions
or in design, the rate of corrosion is usually lowered. This factor is espe­
cially important when erosion-corrosion is occurring.

Treatment of liquid media. Changes in the chemical composition of
the corroding medium may have a great effect on corrosion behavior.
Figure 10-12, for example, shows that in distinctly acid solutions steel
corroses rapidly with the evolution of hydrogen gas. In mildly acid or
basic solutions, on the other hand, the cathodic reaction involves the
formation of water rather than of hydrogen, and the reaction is relatively
slow. Since oxygen is necessary for this second process, the corrosive ac­
tion of ordinary water in boilers can be greatly decreased by removing its
dissolved oxygen. Although lowering the hydrogen ion or oxygen concen­
tration of solutions in contact with steel effectively reduces corrosion,
such radical changes in composition are frequently impractical. More
useful in most instances are small additions of inhibitors to the corrod­
ing medium. Inhibitors are organic or inorganic substances that dissolve
in the corroding medium but are ca­pable of forming a protective layer
of some kind at either the anodic or
cathodic areas. Anodic inhibitors,
such as chromates and phosphates,
are those that stifle the destructive
anodic reaction. Although this type
of control is effective, it may be
dangerous, since severe local attack
can occur if certain areas are left
unprotected by depletion of the inhibitor. Magnesium and calcium salts are examples of cathodic inhibitors that act by forming a deposit on iron through which oxygen must diffuse to take part in the cathodic reaction. The more effective anodic inhibitors are most often used to treat boiler water, and care is taken to ensure that an adequate amount of inhibitor is always present.

Electric currents exist between the (dissolving) anodic regions and the (protected) cathodic regions during the course of corrosion. One method of stopping the flow of these local currents and thereby controlling corrosion is the imposition of opposing potentials, a procedure known as cathodic protection. The metal to be protected, such as a buried pipeline, is connected to external anodes that are in the same corroding environment. The anodes may be a reactive metal like zinc, which is replaced at intervals, or they may be essentially unreactive like graphite, and the protective potential is then supplied by a suitable direct current source such as a rectifier. To neutralize adequately the corrosion currents in iron, a system of anodes must supply on the order of $10^{-2}$ amp/ft$^2$. Cathodic protection has been applied extensively to buried tanks and pipelines, and to water storage tanks.

Protective atmospheres. The use of protective atmospheres in heat-treating furnaces is an important example of industrial control of corrosive environments. Two defects may be introduced when alloys are heated at high temperatures. The first of these is scaling or discoloration of the surface as the result of reaction of the base metal with the surrounding gases, especially oxygen, water vapor, or carbon dioxide. A second, less easily observed defect is a change in the chemical composition of the alloy (for example the loss of carbon from the surface of steel), a process known as decarburization. Since the reactivity of alloying elements is different from that of the base metal, a given atmosphere may protect metal parts from only one of these two types of damage. Many unfinished metals, such as steel ingots, are heated in ordinary air or in the oxidizing combustion products of the gases which heat the furnace. Under these conditions the surface layer that is changed in alloy content is effectively removed by scale formation. The poor surface appearance and the dimensional changes produced by these untreated atmospheres are often objectionable in finished metal parts. By heating such parts in a controlled-atmosphere chamber (called a muffle or retort) that is isolated from the air and from the combustion products of the heating gases, it is possible to surround them with a protective atmosphere that leaves the parts clean (unsealed) or even bright after a high-temperature treatment. Changes in alloy composition can also be minimized.

Many different types of protective atmospheres are used. An inert gas like helium is ideal, but its high cost limits its use to special applications
such as research problems. Hydrogen and the mixture of hydrogen and nitrogen produced by dissociating ammonia (NH₃) are moderate-cost atmospheres that are successfully used in the heat treatment of stainless steel and in sintering many types of powder-metal compacts. Low-cost atmospheres for heat treating steel, brass, and other alloys are prepared from the products of combustion of fuel gases. By removing water vapor and carbon dioxide from partly or completely burned natural gas, an atmosphere can be obtained that prevents both decarburization and discoloration during the hardening of plain carbon and alloy steels. Liquid salt or lead baths also are frequently used as inert atmospheres in the heat treatment of steel.

An example of a gaseous controlled atmosphere, employed to prevent both oxidation of steel and change in its surface carbon content, is a mixture of carbon monoxide and carbon dioxide. The use of this atmosphere is governed by the curves of Fig. 10–13. Two reactions are considered in this figure: (1) the oxidation of iron by CO₂ occurs for gas compositions and temperatures below the sloping line labeled with this reaction; (2) the carburization of a given steel occurs for gas compositions and temperatures above and to the left of the curve labeled with the composition in question. For example, an atmosphere of 90% CO and 10% CO₂ at 1700°F (point A) would carburize a steel containing 0.10% carbon. Under the same condi-
tions a steel containing 0.40% carbon would be decarburized, while a 0.20% carbon steel would be in equilibrium with the gas and would be unaffected. It should be noted that the data of Fig. 10-13 are for dry atmospheres. Oxidation of steel will also occur if appreciable water vapor is present in a furnace atmosphere.

REFERENCES


PROBLEMS

1. (a) How does electrochemical corrosion differ from other types of corrosion? (b) What possible control measures does the mechanism of electrochemical corrosion suggest?

2. Compare the corrosion that occurs (a) when iron and copper are in electrical contact in a dilute sodium chloride solution containing dissolved oxygen; (b) when isolated pieces of iron and copper are in the sodium chloride solution containing oxygen.

3. Explain the following phenomena: (a) a piece of iron sealed in a small glass tube filled with water showed no signs of rusting over a long period, but it began to rust almost immediately when air was allowed to come in contact with the water; (b) a specimen of an iron pillar that was almost unaffected by weathering in an arid climate for hundreds of years was found to corrode rapidly in England.

4. Explain why an oxide that is unprotective according to the Pilling-Bedworth rule should increase in amount at a linear rate.

5. Explain the statement that for parabolic oxidation, Eq. (10-4), "the rate of oxidation is inversely proportional to the instantaneous oxide film thickness."
6. Test the following data for "fit" to the parabolic, linear, or cubic rate laws for the oxidation of a metal.

<table>
<thead>
<tr>
<th>Oxide thickness, Å</th>
<th>Time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>1000</td>
<td>40</td>
</tr>
<tr>
<td>2000</td>
<td>160</td>
</tr>
</tbody>
</table>

7. If a first-order interference color of yellow is seen on a slightly oxidized tool steel, estimate the oxide thickness \( t \). Assume a representative blue radiation of 4700 Å, and that first-order extinction of blue occurs when \( t = \frac{\lambda}{4\pi} \), where \( \lambda \) is the wavelength being destroyed and \( \eta \) is the index of refraction of the oxide film (\( \eta = 3 \)).

8. Is internal oxidation more likely to occur in aluminum- or in copper-base alloys? Why?

9. A widely used measure of corrosion is the weight loss per unit area per unit time, for example mmdd (the loss in milligrams per square decimeter per day). Contrast the usefulness of this measure when applied to uniform corrosion and when applied to pitting.

10. Often a second phase forming within a solid solution tends to be localized at the grain boundaries. Explain whether this effect can cause intergranular corrosion.

11. (a) Name three applications in which special corrosion-resistant alloys are used. (b) Name three applications in which the corrodible alloys used must be protected from the corroding environment.

12. Compare the three general types of stainless steels (martensitic, ferritic, and austenitic) with respect to (a) composition, (b) possible phases, and (c) typical uses.
CHAPTER 11

DIFFUSION IN METALS

"... there has long been a prevalent belief that diffusion can take place in solids, and the practice in conducting important industrial operations supports this view."

ROBERTS-AUSTEN (1896)

INTRODUCTION

A massive, rigid block of metal has some unexpected characteristics. In the chapter on atomic structure it was shown that this dense body is mostly empty space. Here an equally surprising fact will be discussed, that there is continuous, long-range motion of the atoms that form such a rigid body. This motion or diffusion of atoms occurs under all conditions, for example in a bar of pure aluminum at room temperature, but it is of greatest interest when it causes pronounced changes in alloys. Several examples of these changes have already been considered: the homogenization of a cast alloy as the result of movement of metal atoms from regions of high concentration to regions of low concentration, and the addition of carbon to the surface of a low-carbon steel for the purpose of surface hardening. Many of the reactions in metals that are treated in the following chapters are also strongly dependent on diffusion for their progress. The most noteworthy of these is in the heat treatment of steels.

THEORY

The cause of diffusion is easily understood; it is simply that the atoms in a solid are continually jumping from one position in the structure to a neighboring position. The mechanism by which jumping occurs will be explained later, but it will be helpful first to consider how atomic jumping is related to large-scale diffusion phenomena. In a pure metal, since all the atoms are alike, it is difficult to detect any evidence of diffusion. However, if certain atoms are distinguishable by virtue of being radioactive isotopes of the metal in question, then it is possible to measure the rate of self-diffusion at which the atoms diffuse among themselves.

Figure 11-1 is a schematic illustration of self-diffusion between a central region containing a uniform concentration $c_1$ of radioactive atoms and
Fig. 11-1. The process of self-diffusion in metals: Atomic distributions (above) and the corresponding concentration curves (below) for three stages in the diffusion process. (a) Condition before diffusion. (b) Condition after brief diffusion (one jump per atom). (c) Uniform condition produced by prolonged diffusion.
two adjoining regions initially containing only normal atoms. It is known that the diffusion behavior of normal and of radioactive atoms is essentially the same. By the mechanisms discussed below, each of the atoms will tend to jump from its position, as shown in Fig. 11-1(a), to one of the neighboring positions. The atomic distribution shown in Fig. 11-1(b) might exist after an average of one jump per atom. In the case of the radioactive atoms, for example, there were initially four such atoms in each column, and each atom had the possibility of jumping up, down, left, or right. It is easy to verify that random jumping would leave the number of radioactive atoms unchanged in columns 4 and 5. However, a radioactive atom would leave column 3 and enter column 2, and similarly an atom would leave column 6 and enter column 7. The concentration curve in Fig. 11-1(b) is a convenient method for recording this spreading of radioactive atoms through the specimen. With further jumping the atoms continue to spread (see Problem 1) until a uniform distribution of atoms is finally produced, Fig. 11-1(c). Although the atoms then continue to jump about as before, the concentration curve remains unchanged and it is no longer possible to observe diffusion as a change in the concentration curve.

First Fick law. It can be seen from Fig. 11-1 that the concentration gradient \( \frac{dc}{dx} \) determines whether or not (observable) diffusion occurs. Thus, where \( \frac{dc}{dx} = 0 \), as in Fig. 11-1(c), diffusion does not occur. However, in the portion of Fig. 11-1(b) where \( \frac{dc}{dx} \) is positive (\( \frac{dc}{dx} > 0 \)), a net flow of radioactive atoms occurs across plane I in the negative \( x \)-direction, while where \( \frac{dc}{dx} \) is negative the net flow is in the positive \( x \)-direction. A quantitative relation between the concentration gradient and the amount of material transported by diffusion is given by the first Fick law:

\[
dm = -D \frac{dc}{dx} A \, dt,
\]

(11-1)

where \( dm \) is the number of grams of metal that cross a plane perpendicular to the direction of diffusion, \( D \) is a diffusion coefficient whose value depends on the metal being considered and other factors to be mentioned later, \( A \) is the area (in \( cm^2 \)) of the plane across which diffusion is occurring, and \( dt \) is the time in seconds during which diffusion occurs. The units of \( x \) are centimeters and of \( c \) are grams/cm\(^3\).

After this brief description of the nature of diffusion, it is pertinent to inquire why an atom should jump about in the lattice at all. In Chapter 4 it was pointed out that all atoms are constantly vibrating about their equilibrium positions in the lattice and that the amplitude of vibration increases with increasing temperature. The energy associated with these
thermal vibrations, often referred to as thermal energy, is sufficient to cause an atom to jump out of its lattice position under suitable conditions. Temperature is obviously an important factor determining whether jumping is likely to occur, but another factor is the barrier that an atom must overcome in the act of jumping. For example, atoms in a perfect crystal lattice would be faced by almost insuperable barriers to diffusion. Not only would the forces of atomic cohesion tend to hold each atom in its own position in the lattice, but also the physical problem of squeezing between closely packed neighboring atoms would further increase the barrier to diffusion. Therefore it is believed that in a perfect region of the lattice, Fig. 11-2(c), direct interchange of two atoms does not actually occur. Instead, diffusion occurs through imperfections in the lattice, using mechanisms for which the energy barrier is low.

Mechanism of diffusion. It will be recalled from Chapter 4 that vacant lattice sites are a normal feature of a crystal lattice at any temperature above absolute zero. Imperfections of this type greatly facilitate the jumping of adjoining atoms. For example, Fig. 11-2(a) indicates how a radioactive atom might advance one atomic spacing to the right by jumping into a vacancy. The vacancy simultaneously moves to the left, occupies the former position of the radioactive atom, and is ready for another random interchange. The average vacancy has only a limited lifetime in a metal, since vacancies are continually being created and destroyed at surfaces, grain boundaries, and suitable interior positions such as dislocations.

Although it is believed that self-diffusion in metals almost always occurs by the vacancy mechanism, in some cases it is possible that interstitialcies are partially or exclusively involved. The mechanism in this case (Fig. 11-2b) involves the presence of an atom in an interstitial position. The jumping process and the lifetime of interstitialcies are similar to those for vacancies. For simplicity, the remaining discussion will be based on the vacancy mechanism, but the essential results are not affected by neglecting the possibility of interstitial diffusion.

In addition to diffusion within the crystal lattice, which is called volume diffusion, it is possible to study grain-boundary diffusion and surface diffusion. Ordinary grain boundaries are regions of pronounced imperfection in crystal structure, and therefore it is not surprising that diffusion may occur a million times faster here than within the grain proper. Furthermore, in agreement with the picture of low-angle grain boundaries shown in Fig. 5-8, the grain-boundary diffusion coefficient decreases as the angle

*It is equally probable, of course, that any one of the other atoms neighboring the vacancy would have made the jump.
Fig. 11-2. Possible mechanisms for self-diffusion in metals. (a) Vacancy mechanism. (b) Interstitial mechanism. (c) Atom interchange mechanism.

of tilt of the two grains across the grain boundary decreases below a critical value of about 20°. Atoms at the surface of a metal are only weakly bound to a given position in the lattice, so that surface diffusion is even faster than grain-boundary diffusion. Although the specific rates of surface and grain-boundary diffusion are much higher than the rate of volume diffusion, their actual contribution to the total diffusion process is usually small because of the small numbers of atoms in the surface and grain-boundary regions. Special conditions in which grain-boundary diffusion may become important are discussed in Problem 2. Only volume diffusion will be considered in the remainder of this chapter.

Diffusion in alloys. The use of radioactive atoms permits the determination of self-diffusion rates in homogeneous alloys in the same manner as described for a pure metal in Fig. 11-1. For example, in an alloy of equal numbers of gold and nickel atoms it is possible to determine the rate of diffusion of gold atoms $D_{Au}$ if (Fig. 11-1a) the central layer of the homogeneous alloy initially contains radioactive gold atoms. At 900°C this value is found to be $D_{Au} = 7 \times 10^{-10}$ cm²/sec. On the other hand, if radioactive nickel atoms are initially present in the central layer, then the rate of self-diffusion of nickel in the homogeneous alloy can be determined. This value is found to be $D_{Ni} = 5 \times 10^{-10}$. Self-diffusion data for the entire range of compositions in the gold-nickel system are given in Fig. 11-3, and it can be seen that the gold atoms diffuse more rapidly than the nickel atoms at all compositions. It should be noted that self-diffusion data apply for a homogeneous alloy in which there is no gradient in chemical composition.

Since diffusion in commercial practice usually has a concentration gradient, it is necessary to take this additional factor into account. It
can be shown that the appropriate diffusion coefficient is then given by the equation

\[ D_{Ni} = D_{Ni}^* \left( 1 + \frac{d \ln f_{Ni}}{d \ln X_{Ni}} \right), \]  

(11-2)

where \( D_{Ni} \) is called the intrinsic diffusion coefficient for nickel and \( f_{Ni} \) is the thermodynamic activity coefficient of nickel in the gold-nickel alloy containing an atomic fraction \( X_{Ni} \) of nickel. A similar equation can be written for \( D_{Au} \), the intrinsic diffusion coefficient for gold. The factor in parentheses in Eq. (11-2) ordinarily differs from unity by a factor of less than 10.

Like the self-diffusion coefficients, the intrinsic diffusion coefficients for the two components in an alloy have different values. Consequently, when two metals interdiffuse there is a net transport of material across the plane that initially separated the two specimens. This phenomenon, known as the Kirkendall effect, can be revealed by the type of experiment.
DIFFUSION IN ALLOYS

Fig. 11-4. The Kirkendall effect during interdiffusion of gold and nickel.

shown schematically in Fig. 11–4. A specimen is made by joining a gold and a nickel bar so that diffusion will occur across the marked interface. The inert markers may be pieces of very fine tungsten wire lying in the plane of joining. During a diffusion anneal of many hours at a sufficiently high temperature, such as 900°C, interdiffusion of the gold and nickel will occur and will change the concentration distribution as shown. However, since $D_{Au}$ is greater than $D_{Ni}$, more gold atoms than nickel atoms will have diffused past the inert markers. Consequently, the inert markers will no longer be at their original position but will have moved toward the gold end of the specimen. This movement is known as the Kirkendall shift.

The plane at the position of the original joining of the gold and nickel is called the Matano interface and has the important property that the two areas $A_1$ and $A_2$ are equal.* $A_1$ and $A_2$ represent the amounts of nickel and of gold, respectively, that have crossed this interface. Therefore if the Matano interface is used in describing diffusion behavior, only a single diffusion coefficient $D$ need be used. It can be shown that the relation between $D$ and $D_{Au}$ and $D_{Ni}$ is

$$D = X_{Ni}D_{Au} + X_{Au}D_{Ni},$$  \hspace{1cm} (11-3)

*This treatment neglects such effects as the condensation of vacancies to form microscopic voids in the diffusion zone or possible changes in length because of alloying.
and between $D$ and $D_{Au}$ and $D_{Ni}$ is

$$D = (X_{Ni}D_{Au} + X_{Au}D_{Ni}) \left(1 + \frac{\ln f_{Au}}{\ln X_{Ni}}\right)$$  \hspace{1cm} (11-4)

The values of $D$ for various compositions in the gold-nickel system are shown in Fig. 11-3. To distinguish $D$ from the other two types of diffusion coefficient, it may be called the interdiffusion or mutual diffusion coefficient. However, since it is the quantity usually employed in diffusion calculations, it is most often referred to simply as the diffusion coefficient.

Although a special mechanism, involving vacancies for example, is necessary for explaining diffusion in substitutional solid solutions, this is not true of diffusion in interstitial solid solutions. In this case the small solute atom is able to slip from one interstitial position to the next when the solvent atoms are vibrating sufficiently vigorously. The first Fick law, Eq. (11-1), describes the quantitative aspects of diffusion in interstitial as well as substitutional solid solutions.

**Second Fick law.** The first Fick law is not in a convenient form for application to certain problems, for example the diffusion of carbon into the surface of steel, which is discussed below. By means of a derivation that considers the net gain of atoms in a vanishingly small volume (see Problem 4), we obtain the second Fick law,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D\frac{\partial c}{\partial x}\right)$$  \hspace{1cm} (11-5)

This form of the equation takes account of the variation of $D$ with concentration. However, it is quite difficult to apply, and therefore a simplification is usually introduced by assuming that $D$ is constant. Equation (11-5) then becomes

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.$$  \hspace{1cm} (11-6)

This form of the second Fick law is used in later examples.

**ILLUSTRATIVE EXAMPLES**

Since the rate at which many metallurgical processes occur is determined by diffusion, adequate control of these processes often requires quantitative handling of pertinent diffusion data. As is typical of engineering calculations, it is impractical to obtain an exact solution of the diffusion equation, and it is necessary to introduce various simplifying assumptions. The nature of these assumptions is illustrated in the following examples of diffusion processes.
GROWTH OF OXIDE LAYERS

Diffusion of metallic atoms

Oxidizing atmosphere

Metal

Diffusion of metallic atoms

FIG. 11-5. The oxidation of metals, a diffusion process. (a) The process of oxidation of a metal. (b) A typical parabolic relation between the thickness of the oxide layer and time of oxidation.

Growth of oxide layers. The mechanism of one type of metallic oxidation can be explained using the first Fick law. Experimental data on the high-temperature oxidation of metals frequently show a parabolic relation between the time of oxidation and the amount of oxide formed. With the aid of Fig. 11-5(a), this behavior can be explained in terms of a diffusion process. It is assumed that diffusion of only the metal atoms need be considered. Furthermore, the difference between the metal concentration $c_o$ at the oxide surface and the concentration $c_m$ at the metal surface has a constant value $\Delta c$. Therefore, at any thickness $x$ of the oxide layer the rate of transfer of metal atoms per unit area is

$$ dm = - D \frac{\Delta c}{x} \frac{dx}{dt}. \quad (11-7) $$

However, $dm$ and the change in thickness, $dx$, are related by some constant; that is, $dx = K dm$. Therefore Eq. (11-7) can be written

$$ dx = - D' \frac{\Delta c}{x} \frac{dx}{dt}, \quad (11-8) $$

where $D'$ is $KD$ and is a constant when $D$ is assumed to be constant. This equation can be solved as follows:

$$ \int_{x=0}^{x} x \, dx = - D' \Delta c \int_{t=0}^{t} dt, \quad (11-9) $$

$$ x^2 = -2 D' \Delta c t, \quad (11-10) $$

$K'$ is positive, since the minus sign cancels the minus sign of the concentr-
Diffusion of carbon atoms

(a) Schematic representation of the procedure used in carburizing an iron plate. (b) Carbon penetration curve near the beginning of the carburizing process, and (c) after 10 hours.

Fig. 11-6. The diffusion of carbon in iron during carburizing. (a) Schematic representation of the procedure used in carburizing an iron plate. (b) Carbon penetration curve near the beginning of the carburizing process, and (c) after 10 hours.

Carburizing of steel. As an example of the application of Eq. (11-6) the carburizing of an iron plate by means of the interstitial diffusion of carbon will be discussed. Ordinary weight percent concentrations will be used for convenience. Figure 11-6(a) shows the carburizing procedure in which a low-carbon material (carbon-free iron, in this case) is held for several hours at a high temperature in contact with an atmosphere, such as natural gas, capable of supplying carbon to the metal. The initial carbon content of the iron plate is zero at all distances from the surface. As the carbon atoms go into solution at the surface of the iron, they are free to begin diffusing farther into the plate. The maximum concentration,
$C_1$, of carbon atoms in solution in iron at 1700°F can be read from the iron-carbon diagram, and is about 1.3% carbon. The carburizing atmosphere can build up this carbon concentration at the surface almost immediately, so that the carbon penetration curve shortly after the beginning of carburizing is of the form shown in Fig. 11-6(b).

The general problem is to predict the penetration curve, such as that given in Fig. 11-6(c), that is produced by carburizing for a number of hours at a given temperature (1700°F in this case). Since Eq. (11-6) relates concentration to time and distance, it is reasonable to expect that this equation can be used to obtain the desired curve. It can be shown† that the appropriate solution in this case is

$$C - C_0 = (C_1 - C_0) \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right], \quad (11-11)$$

where $C$ is the carbon concentration at a distance $x$ centimeters below the surface after diffusion has occurred for $t$ seconds, $C_1$ is the surface concentration, and $C_0$ is the initial carbon concentration in the steel plate ($C_0 = 0$ in this example); erf $(x/2\sqrt{Dt}) = \text{erf} (y)$ is a function of the variable $y = x/2\sqrt{Dt}$ and is obtainable in the form of mathematical tables like logarithms and trigonometric functions. Some values of erf $(y)$ are given in Table 11-1. The value of the diffusion coefficient $D$ for carbon diffusing in dilute solution in iron at 1700°F is about $1.5 \times 10^{-7}$ cm$^2$/sec.

<table>
<thead>
<tr>
<th>$y$</th>
<th>erf $(y)$</th>
<th>$y$</th>
<th>erf $(y)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>0.8</td>
<td>0.742</td>
</tr>
<tr>
<td>0.112</td>
<td>0.112</td>
<td>0.9</td>
<td>0.797</td>
</tr>
<tr>
<td>0.223</td>
<td>0.223</td>
<td>1.0</td>
<td>0.843</td>
</tr>
<tr>
<td>0.323</td>
<td>0.323</td>
<td>1.2</td>
<td>0.890</td>
</tr>
<tr>
<td>0.428</td>
<td>0.428</td>
<td>1.4</td>
<td>0.952</td>
</tr>
<tr>
<td>0.521</td>
<td>0.521</td>
<td>1.6</td>
<td>0.976</td>
</tr>
<tr>
<td>0.624</td>
<td>0.624</td>
<td>2.0</td>
<td>0.995</td>
</tr>
<tr>
<td>0.728</td>
<td>0.728</td>
<td>2.4</td>
<td>0.999</td>
</tr>
</tbody>
</table>

*This assumes that the natural gas has sufficient carburizing power or carbon activity to build up and maintain an incipient amount of cementite at the surface of the iron.

When $C_0 = 0$, Eq. (11-11) reduces to the form

$$C = C_1 \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right].$$  \hspace{1cm} (11-12)

Using this equation, it is easy to determine the carbon penetration curve that will be produced by a ten-hour carburizing treatment. The time $t$ is then $10 \times 60 \times 60 = 3.6 \times 10^4$ sec, and the quantity $y = x/2\sqrt{Dt}$ can be written

$$y = \frac{x}{2\sqrt{1.5 \times 3.6 \times 10^{-3}}} = 6.8x.$$  \hspace{1cm} (11-13)

The steps used in calculating the value of $C$ at 0.04 centimeter intervals below the surface of the steel plate are summarized in Table 11-2. A plot of these results gives the curve of carbon concentration versus distance below the surface, which is shown in Fig. 11-6(c).

Because the value of $D$ actually increases with carbon concentration, this plot does not coincide exactly with experimental data, but it gives an approximation that is useful for many purposes.

In practical carburizing operations it is usually required that a certain minimum carbon content be produced at a given depth below the surface. From the form of the variable $y = x/2\sqrt{Dt}$ it can be concluded that the time of carburizing necessary to produce the given carbon content at the given depth increases with the square of the depth and is inversely proportional to the diffusion coefficient.

**Table 11-2**

Summary of Calculations for Plotting the Curve of Figure 11-6(c)

<table>
<thead>
<tr>
<th>Distance $x$ below the surface, cm</th>
<th>$y = x/2\sqrt{Dt}$ = 6.8x</th>
<th>erf ($y$)</th>
<th>$1 - \text{erf} (y)$</th>
<th>Carbon concentration, $C = 1.3 {1 - \text{erf} (y)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
<td>1.30</td>
</tr>
<tr>
<td>0.04</td>
<td>0.272</td>
<td>0.300</td>
<td>0.700</td>
<td>0.91</td>
</tr>
<tr>
<td>0.08</td>
<td>0.544</td>
<td>0.558</td>
<td>0.442</td>
<td>0.57</td>
</tr>
<tr>
<td>0.12</td>
<td>0.816</td>
<td>0.752</td>
<td>0.248</td>
<td>0.32</td>
</tr>
<tr>
<td>0.16</td>
<td>1.088</td>
<td>0.876</td>
<td>0.124</td>
<td>0.16</td>
</tr>
<tr>
<td>0.20</td>
<td>1.360</td>
<td>0.946</td>
<td>0.054</td>
<td>0.07</td>
</tr>
<tr>
<td>0.24</td>
<td>1.632</td>
<td>0.979</td>
<td>0.021</td>
<td>0.03</td>
</tr>
<tr>
<td>0.28</td>
<td>1.904</td>
<td>0.993</td>
<td>0.007</td>
<td>0.01</td>
</tr>
<tr>
<td>0.32</td>
<td>2.176</td>
<td>0.998</td>
<td>0.002</td>
<td>0.00</td>
</tr>
</tbody>
</table>
TEMPERATURE

VARIABLES THAT INFLUENCE DIFFUSION

The diffusion coefficient $D$ is usually not a constant. Ordinarily $D$ is a function of many variables such as temperature, concentration, and crystal structure. In a given instance all these variables are assumed to have specified values, and the diffusion coefficient is then a definite number. However, in arriving at this number it is frequently necessary to consider the individual effects of one or more of these variables.

Temperature. An idea of the tremendous influence of temperature on diffusion is given by the rule of thumb that the diffusion constant doubles for every twenty-degree centigrade increase in temperature. More exactly, the diffusion constant is related to the absolute temperature ($^\circ C + 273$) by the equation

$$D = Ae^{-Q/RT},$$

(11-14)

where $A$, $Q$, and $R$ are independent of temperature. When the activation energy $Q$ is given in calories per gram-mol, then the gas constant $R$ has the value 1.987 calories per gram-mol per degree Kelvin. The frequency factor $A$ is related to the frequency of vibration of the diffusing atoms, while $Q$ is a measure of the energy barrier that tends to prevent diffusion from occurring. Values of $A$ and $Q$ for the determination of an approximate diffusion coefficient in several binary systems are given in Table 11-3.

### Table 11-3

**Approximate Values of $A$ and $Q$ for Several Diffusion Systems**

<table>
<thead>
<tr>
<th>Diffusing metal</th>
<th>Matrix metal</th>
<th>$A$, cm$^2$/sec</th>
<th>$Q$, calories per gram-mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>$\gamma$-iron</td>
<td>0.21</td>
<td>33,800</td>
</tr>
<tr>
<td>Carbon</td>
<td>$\alpha$-iron</td>
<td>0.0079</td>
<td>15,100</td>
</tr>
<tr>
<td>Iron</td>
<td>$\alpha$-iron</td>
<td>5.8</td>
<td>59,700</td>
</tr>
<tr>
<td>Iron</td>
<td>$\gamma$-iron</td>
<td>0.5</td>
<td>60,000</td>
</tr>
<tr>
<td>Nickel</td>
<td>$\gamma$-iron</td>
<td>0.35</td>
<td>67,500</td>
</tr>
<tr>
<td>Nickel</td>
<td>$\gamma$-iron</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>Aluminum</td>
<td>2.0</td>
<td>33,900</td>
</tr>
<tr>
<td>Copper</td>
<td>Copper</td>
<td>0.033</td>
<td>38,000</td>
</tr>
<tr>
<td>Silver</td>
<td>Silver</td>
<td>0.72</td>
<td>45,000</td>
</tr>
<tr>
<td>Silver</td>
<td>(volume diffusion)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>Silver</td>
<td>0.14</td>
<td>21,500</td>
</tr>
<tr>
<td>Silver</td>
<td>(grain-boundary diffusion)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Concentration. Since it is common practice to assume for mathematical convenience that the diffusion coefficient is independent of concentration, it is useful to know the error involved in this assumption. The data of Fig. 11-3 for the gold-nickel system show an extreme variation of $D$ with concentration, while Fig. 11-7 shows that there is only a relatively small change in the diffusion coefficient of carbon in austenite up to 1.3% C, the limit of solubility at the temperature in question. Even in systems for which $D$ is strongly concentration-dependent, little error is involved in assuming that $D$ is constant, provided diffusion occurs in a dilute solution or over a small range of concentration. For example, diffusion in a solution of a few atomic percent gold in nickel at 900°C can be calculated adequately using $D = 1 \times 10^{-11}$, while the value $D = 9 \times 10^{-10}$ would be a good approximation for a calculation of diffusion in a dilute solution of nickel in gold.

Crystal structure. Because of the importance of the allotropic transformation of iron from body-centered cubic to face-centered cubic at high temperatures, the effect of this change in crystal structure on the rate at which solute atoms diffuse in iron has been studied. At a given temperature these diffusion processes and self-diffusion of the iron occur about one hundred times more rapidly in ferrite (body-centered cubic) than in austenite.

Another effect of crystal structure is the variation of the diffusion coefficient with crystal direction in a single crystal of the solvent metal. Such anisotropy is nearly or completely absent in cubic metals, but bismuth (rhombohedral space lattice) shows a ratio of about one thousand in its self-diffusion constants measured parallel and perpendicular to the c-axis. Moreover, if a crystal structure is distorted either by elastic strains or by extensive plastic deformation, the rate of diffusion is usually increased.

Impurities. The presence of small amounts of additional metals usually has a relatively small effect on the diffusion of solute atoms in a solvent metal. This fact is often useful in treating problems in which diffusion is only one of several possible variables. For example, it can be concluded that the strong influences of alloying elements on the hardenability of
steel (Chapter 14) must be the result of factors other than large changes in the rate of carbon diffusion.

Grain size. Since grain-boundary diffusion is faster than that within the grains, it is to be expected that the over-all diffusion rate would be higher in a fine-grained metal. However, in the usual range of grain sizes it is not necessary to take grain size into account in making diffusion calculations.

Applications

Metal bonding. The bonding of metals, which includes such processes as galvanizing, welding, and metal-cladding, is a good example of an industrial application of diffusion principles. Although a continuous metallic bond may be formed under many different conditions between two different metals, in every case it is necessary that some diffusion occur. Since diffusion can take place only in a solid solution, only two metals that have appreciable solid solubility can be bonded. Thus, because lead is practically insoluble in iron, it is possible to heat steel in molten lead baths without danger of forming an adherent lead layer on its surface. The opposite problem arises when it is desirable to protect sheet iron with a thin coating of lead. To obtain adequate bonding it is necessary to add to the molten lead a small amount of a second metal that alloys with iron.

![Fig. 11-8. Correlation of the phases present in a galvanized coating produced at 450°C and the phases present in the corresponding temperature section of the iron-zinc diagram. (×1000; reproduced at two-thirds size.) (Courtesy D. H. Rowland, Carnegie-Illinois Steel Corporation.)](image-url)
### Table 11-4

**Characteristics of Typical Solders and Brazing Filler Metals**

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Melting range, °F</th>
<th>Typical uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solder: 35-65</td>
<td>Sn 65Pb</td>
<td>351–473</td>
<td>Wiping solder</td>
</tr>
<tr>
<td>45-55 solder</td>
<td>Sn 55Pb</td>
<td>361–439</td>
<td>For automobile radiator cores; general-purpose solder</td>
</tr>
<tr>
<td>60-40 solder</td>
<td>Sn 40Pb</td>
<td>361–398</td>
<td>For use where temperature requirements are critical</td>
</tr>
<tr>
<td>Cd-Ag solder</td>
<td>95Cd 5Ag</td>
<td>630–734</td>
<td>High-temperature solder</td>
</tr>
<tr>
<td>Braze BCuZn-2</td>
<td>Cu 42Zn 1Sn</td>
<td>1630–1850</td>
<td>General-purpose alloy for steel, copper alloys, and nickel alloys</td>
</tr>
<tr>
<td>filler metals:</td>
<td></td>
<td></td>
<td>Furnace brazing alloy</td>
</tr>
<tr>
<td>BCu</td>
<td>Cu 99+</td>
<td>1305–1485</td>
<td>For self-drying brazing of copper alloys</td>
</tr>
<tr>
<td>CuP-2</td>
<td>Cu 93Cu 7P</td>
<td></td>
<td>Low-melting, free-flowing braze for general-purpose work</td>
</tr>
<tr>
<td>BAg-1</td>
<td>Ag 25Cd 15Zn 15Cu</td>
<td>1125–1145</td>
<td>For applications, such as vacuum tubes, where volatile elements are harmful</td>
</tr>
<tr>
<td>BAg-8</td>
<td>Ag 28Cu</td>
<td>1435</td>
<td>General-purpose alloy for brazing aluminum</td>
</tr>
<tr>
<td>BAISi-1</td>
<td>Si 9Si</td>
<td>1070–1165</td>
<td>General-purpose alloy for brazing magnesium</td>
</tr>
<tr>
<td>BMg</td>
<td>Mg 9Al 2Zn</td>
<td>770–1110</td>
<td>Heat-resistant alloy used for fabricating stainless steels or high-nickel alloys for jet engines.</td>
</tr>
<tr>
<td>BNiCr</td>
<td>Ni 16Cr</td>
<td>1850–1950</td>
<td></td>
</tr>
</tbody>
</table>
The most popular addition is tin, and the resulting alloy is widely used in making terne plated sheet steel for roofing.

A complicating factor in some bonding processes is the presence of brittle intermetallic compounds between the two metals being joined. When diffusion occurs between two metals, the primary solid solutions are formed; and in addition, those intermediate phases that exist at the diffusion temperature also form. This behavior is shown in Fig. 11-8 for the coating of steel with zinc to produce a galvanized sheet. The galvanized coating is produced in about fifteen seconds, while the carefully prepared sheet steel is passed through a molten zinc bath at 450°C. During this time the three intermediate solid phases indicated by the iron-zinc diagram are developed as so-called diffusion bands. Two-phase regions do not form in the course of the growth of diffusion bands; they merely constitute the interface between the one-phase regions. The resistance to flaking of a galvanized sheet when it is bent is improved by decreasing the amount of the brittle intermediate phases present. This can be accomplished by decreasing the total coating thickness or by adding a suitable alloying element, such as aluminum, to the molten zinc bath.

Many different methods are used to attach a layer of one metal to a different base metal. In making Alclad or Pureclad sheets, a protective layer of pure aluminum is bonded to a strong aluminum alloy by hot rolling a "sandwich" made of slabs of the two materials. Care must be taken to prevent excessive diffusion in this case, since the good corrosion resistance of the pure aluminum is lost if it is contaminated by the additional elements present in the strong alloy. No problem of brittle compound formation is met in producing Alclad, but when a layer of copper is to be attached to aluminum, special precautions must be taken to ensure a ductile product. One successful procedure is hot rolling the bimetal combination to disintegrate the brittle layer as it begins to form.

Welding is the bonding of metals by the application of heat. Arc welding and gas welding produce local melting of the metals to be joined, while forge welding and resistance welding result in plastic deformation of the base metals. There are two types of welding operations, however, that can bond metals without appreciably altering them. These are the soldering and brazing processes, in which a molten alloy partially diffuses into the solid metals and produces bonding. Solders have melting ranges below 800°F, while brazes melt above this temperature. Typical compositions and applications are listed in Table 11-4. The low-melting solders are convenient to use and produce little distortion. However, their shear strength is only about 5000 lb/in². The brazes are about ten times stronger and are widely used for such purposes as fastening sintered carbide inserts in machine tools. In most cases the presence of intermediate alloy layers is not objectionable in these joints, as high ductility is not necessary.
Homogenization. A chemically inhomogeneous solid solution tends to become homogeneous through diffusion. This process has a vanishingly small rate at low temperatures, however, and in practice a special heat treatment is used to produce homogenization. In many commercial alloys homogenization is achieved rather easily. Examples of this treatment were given in Chapter 6 for cast aluminum-copper and magnesium-aluminum alloys. In some instances the diffusion coefficient of the alloying element plays a decisive role. Thus, at a moderate temperature the rapid diffusion of zinc in copper produces effective homogenization of cast brasses, while at the same temperature nickel diffuses so slowly in copper that it is difficult to eliminate segregation in cast cupronickels. Only by plastically deforming cupronickels, and thereby decreasing the diffusion distance, can rapid homogenization be obtained at this temperature.

As an example of the application of diffusion data to the problem of eliminating chemical inhomogeneity, the subject of banding* in steel will be considered. The use of the term "banding" to describe chemical heterogeneity in rolled steels arises from the presence of closely spaced light and dark bands in the microstructure of some of these steels. These bands represent areas of segregation of alloying elements during freezing of the ingot. During rolling the segregated areas are elongated and compressed into narrow bands. This segregation can be eliminated only if the alloying elements diffuse from regions in which their concentration is high to regions in which their concentration is low.

The mathematical treatment of diffusion between adjacent regions of high and low alloy content is simplified if it is assumed that the alloy concentration varies sinusoidally with distance about the average value, so that

\[
c = c_m \sin \frac{\pi x}{l},
\]

where \(c\) is the variation from the average concentration at the point \(x\), \(c_m\) is the initial maximum variation from the average concentration, \(x\) is the distance in centimeters, and \(l\) is the distance between a region of maximum concentration and an adjacent region of minimum concentration. Using this expression for concentration, it can be shown that a solution of the second Fick law (Eq. 11-6) is

\[
c = c_m \sin \frac{\pi x}{l} e^{-\alpha D u / l^2}
\]

In this equation, \(c_m\) is a constant. \(\sin \pi x / l\) represents the sinusoidal varia-

tion of concentration that was assumed in using Eq. (11-15). For the present purpose only a maximum value of this function need be considered; that is, \( \sin \frac{\pi x}{l} \) can be set equal to unity. Evidently, then, the factor that controls the decrease in degree of inhomogeneity with increasing time \( t \) is

\[ e^{-Dl^2t} \]

which decreases from unity toward zero with increasing time. Thus the time required to produce a given degree of homogenization increases with the square of the diffusion distance \( l \) and is inversely proportional to the diffusion constant \( D \) of the segregated alloying element. If banding due to manganese segregation occurs, it is extremely difficult to produce effective homogenization in large ingots because of the large diffusion distance involved. After the ingot has been rolled, the value of \( l \) in Eq. (11-16) is reduced to about 0.003 cm, and diffusion is greatly accelerated. Even in this case, however, many hours of heating at an excessively high temperature (1200°C) are required to remove banding.

REFERENCES

PROBLEMS

1. Predict a possible concentration curve that might exist after a second round of jumps in Fig. 11-1. Start with Fig. 11-1(b) and use the same argument that was employed in obtaining this figure from Fig. 11-1(a). It is convenient to use fractional parts of atoms to express the probabilities in this case.

2. It is usually assumed that diffusion occurs by the grain-boundary mechanism in a region only about 5 A wide. (a) Show that the ratio of the grams of metal transported across a given plane by grain-boundary diffusion to the grams of metal transported by volume diffusion is roughly $(10^{-7}/d)(D_b/D_v)$, where $d$ is the average grain diameter in centimeters and $D_b$ and $D_v$ are the coefficients of grain-boundary and volume diffusion, respectively. (b) Using the data of Table 11-3, calculate the ratio $D_b/D_v$ for silver at 927°C and at 727°C. (c) For a grain size of $10^{-2}$ cm, could the effect of grain-boundary diffusion be detected? Assume that experimental error is ± 5%.

3. Hydrogen diffuses through metals so rapidly that it is often difficult to keep this gas under pressure at high temperatures. (a) Set up the first Fick law for the general problem of hydrogen storage in a metallic container. [Hint: Assume that the container has a surface area $A$ and a wall thickness $b$, and let $D_h$ represent the diffusion coefficient of hydrogen in the metallic wall. Recall Eq. (6-10) for the variation with pressure of the solubility of a gas in a metal.] (b) Explain what each term in the equation means. (c) Suggest conditions for minimizing the loss of hydrogen by diffusion.

4. To derive the second Fick law, consider the diffusion of a substance during a time $dt$ across 1 cm$^2$ of each of two planes separated by a distance $dz$. (a) Use Eq. (11-1) to obtain an expression for the amount of substance $dm$ that diffuses across the first plane. Let $D$ and $\partial c/\partial x$ represent the values of these two quantities at the first plane. (b) Obtain the corresponding expression for $dm'$, the amount of substance that diffuses across the second plane. Note that the value of the concentration gradient at this plane is $(\partial c/\partial x) + (\partial c/\partial x) (\partial x)/(\partial z) dz$, and that the value of $D$ is similarly altered. (c) Determine the amount of substance that accumulates in the volume $(dz \text{ cm}) \times (1 \text{ cm}^2)$ during the time $dt$ by subtracting the amount of substance that leaves this volume from the amount that enters it. (d) Complete the derivation of Eq. (11-5) by showing that the expression in (e) is the amount by which the concentration (in gm/cm$^3$) changes during the time $dt$. (e) Explain the significance of the partial derivatives in view of the dependence of concentration on both time and distance.

5. There is an advantage in carburizing steel parts at 1600°F rather than at 1700°, since a finer grain size can be obtained in the finished parts. (a) Calculate the diffusion coefficient of carbon in 7-iron at this temperature. [Use the data of Table 11-3.] (b) What carburizing time gives the same results at 1600°F that 10 hours gives at 1700°F? (Neglect the change in carbon solubility.) (c) Using 0.3% carbon as a measure of the depth of carburizing, what fraction of the depth at 1700°F is produced by 10 hours' carburizing at 1600°F? Use 1.2%
carbon as the maximum solubility at 1600°F, and neglect the effect of the lower limit of solubility of carbon in austenite.

6. Equation (11-11) can be used to make quantitative calculations of the degree of decarburization (see p. 393) that a steel will experience. (a) Since the surface carbon concentration \( C_1 \) in this case is lower than the initial carbon concentration \( C_0 \) in the steel, find a convenient rearrangement of Eq. (11-11) for treating problems of decarburization. (b) If \( C_1 = 0 \), show that the equation reduces to \( C = C_0 \text{erf} \left( \frac{z}{2\sqrt{D}t} \right) \). (c) Use the data of Table 11-2 to plot the curve of carbon concentration versus distance that would exist at the surface of a 1.3% carbon steel that had been decarburized for 10 hours under condition (b).

7. Consider the problem of increasing the chemical homogeneity of a solid solution of zinc in copper.

(a) Can inhomogeneity be completely removed by diffusion in a practical time?
(b) Why?
(c) Use the data of Table 11-3 to calculate the diffusion coefficient for zinc diffusing in copper at 1500°F.
(d) If the maximum variation from the average zinc content is 5% zinc, and if the distance between a region of maximum zinc content and a region of minimum zinc content is 0.01 cm, use Eq. (11-16) to estimate the time necessary to decrease the maximum variation to 1% zinc.
(e) Would cold-working a cast alloy before a high-temperature treatment increase or decrease the rate of homogenization?
(f) Why?

8. As an economy measure it might be suggested that lead be substituted for the usual lead-tin solders used in joining iron. Would such substitution be practical? Why?
"Every work of gold and silver, as well as copper, may be worked either hot or cold, only you must be careful to anneal the thing at every hammering or when it needs it."

Biringuccio (1540)

In plastic deformation of metals by hot-working, discussed in Chapter 9, the final microstructure consists of undeformed grains. For example, Fig. 12-1(b) shows that the structure of hot-rolled brass is essentially the same as that of the initial, wrought alloy, Fig. 12-1(a). If, however, the brass is plastically deformed at room temperature, the microstructure is greatly changed by the deformation, Fig. 12-1(c). The temperature of working for which this behavior is observed may be considerably higher than room temperature for some metals, but in all cases a metal is said to have been cold-worked if its grains are in a distorted condition when plastic deformation is completed. When a cold-worked metal is heated for a sufficient time at a high temperature, the distorted microstructure is changed to undeformed grains equivalent to the initial structure, Fig. 12-1(d).

Metals and alloys experience important changes in properties during cold-working and also as a result of heating the cold-worked structure. These changes must be taken into account in many metal-forming operations, in the use of alloys strengthened by cold work, and in the production of desirable microstructures. Since the changes in properties are a reflection of basic changes in structure, it is helpful to start with a picture of the structure of cold-worked metals and later to consider the changes in this structure during heating.

**Cold-Working**

It will be recalled that deformation of metals occurs principally by the motion of existing dislocations and by the creation of many additional dislocations, for example through the action of Frank-Read sources. In some single crystals it is possible for extensive deformation to occur by single slip on a single set of parallel slip planes. This process is called **COLD-WORKING**.
easy glide because the metal deforms extensively under a relatively constant stress. In polycrystalline specimens the mutual interference of adjacent grains causes slip to occur on many intersecting slip planes with accompanying strain hardening of the metal. This progressive strengthening with increasing deformation is caused by the interaction of the dislocations on intersecting slip planes. Depending on whether the dislocations that cut across one another are of edge or screw type, the result may be the creation of a line of vacancies or interstitialities in the lattice or the displacement of part of a dislocation into a slip plane parallel to the initial

Fig. 12-1. Illustration of the fact that the structure of a wrought metal need not be changed by hot-working but is strongly influenced by cold-working. Note that microstructures (a), (b), and (d) are alike except for incidental differences in grain size. (Photomicrographs at X75; reproduced at two-thirds size.) (Courtesy American Brass Company.)
slip plane. In the latter case the discontinuity between the two portions of the dislocation is called a "jog."

Thus the structure of a cold-worked metal must be pictured as being seriously disturbed by excess point defects, as well as by an increase in number of dislocations by a factor of about $10^4$, and the occurrence of jogs. Nevertheless, there is evidence that fragments of the metal lattice survive maximum deformation with only a moderate distortion. Figure 12-2 shows that severe disruption and plastic bending occur within the slip bands, but that fragments of relatively perfect lattice exist in the spaces between slip bands. Even after extreme cold-working, the size of the fragments is about 10,000 Å. This picture of the structure of cold-worked metals is useful in interpreting behavior during subsequent heating. It also is consistent with the property changes accompanying cold-working, which will now be considered.

By far the most important result of cold-working is strengthening of the metal. With increasing amounts of deformation the resistance of the metal to further deformation constantly increases, a phenomenon called strain hardening (work hardening), and the ductility of the metal simultaneously decreases. Strain hardening is a characteristic property of a metal and can be expressed quantitatively in terms of the exponent $n$, given in Eq. (9-16) and Table 9-2. The rate of strain hardening is usually lower for close-packed hexagonal metals than for face-centered cubic or body-centered cubic metals; also, increasing the temperature of cold-working decreases the rate of strain hardening. The addition of a soluble alloying element may either increase or decrease the rate of strain hardening, but the final
FIG. 12-3. The changes in hardness and ductility produced by cold-working copper and cartridge brass. (70% Cu, 30% Zn.)

hardness of a cold-worked alloy is almost always greater than that of the similarly cold-worked pure metal because of the higher yield strength of the alloy. Figure 12-3 shows typical changes in hardness and ductility produced by cold-working a pure metal and one of its solid solutions.

Other effects of cold-working include the slight decrease in electrical conductivity that was considered in a previous chapter. Corrosion resistance is sometimes drastically reduced by cold-working, and the resulting stress corrosion (see Chapter 10) is of industrial importance. Preferred orientation of the metal grains is an inevitable result of the slip and twinning processes that occur during cold-working. During the cold drawing of aluminum wire, for example, grains that were initially oriented at random are deformed in such a way that they have a [111] crystal direction along the wire axis. Steps are often taken to control the degree of preferred orientation produced in a given alloy, sometimes to increase its magnitude, as in magnetic materials, but more often to prevent its leading to inhomogeneous deformation in later working operations.

Recovery

When metals are cold-worked most of the energy expended in the process appears as heat, but a few percent is stored in the deformed metal structure. This stored energy acts as the thermodynamic driving force which tends to return the metal to the undeformed state, provided the metal is at a temperature where the required reactions can occur at an
Value after complete recrystallization

Time of annealing

Fig. 12-4. The course of recovery at three constant temperatures.

It is convenient to distinguish two types of changes that can be produced by heating a cold-worked metal: (1) a pronounced alteration in grain structure (recrystallization) may take place, accompanied by marked changes in properties; or (2) more gradual property changes may take place in the absence of appreciable change in microstructure. This second phenomenon is recovery, which may be defined as property changes produced in cold-worked metals by heat-treating times and temperatures that do not cause appreciable change in microstructure. Microstructural changes will therefore not be considered in the following discussion of recovery, since they are more appropriate to recrystallization.

When cold-worked metals are heated at the relatively low temperatures used for recovery treatments, only the more mobile imperfections can undergo rearrangement in the lattice. It is believed that vacancies and interstitials existing in the slip bands are eliminated first and that some dislocations of opposite sign may also be annihilated. However, the majority of the dislocations and the bulk of the strain energy are not removed by the usual recovery treatments. The relatively minor structural changes during recovery have a pronounced effect on residual stresses and on electrical properties, presumably because both of these phenomena are primarily affected by the small volume of severely disturbed lattice in the slip bands, Fig. 12-2.

The important characteristics of the recovery process are shown in Fig. 12-4. At a given temperature the rate is fastest initially and drops off at longer times. Thus the amount of recovery that occurs in a practical time increases with increasing temperature. In a given cold-worked metal the individual properties recover at different rates and attain various degrees of completion. The behavior of tungsten, shown in Fig. 12-5, is typical. Note that in this case, for example, annealing for one hour at 800°F produces a 75 percent relief of residual stresses, while the hardness is essentially unchanged by this heat treatment.

The principal application of recovery heat treatments is in stress-relieving cold-worked alloys to prevent stress-corrosion cracking or to minimize the distortion produced by residual stresses. Usually, some stress relief can be achieved without greatly affecting the mechanical properties, as the curves of Fig. 12-5 show in the case of tungsten. However, complete removal of residual stresses usually requires temperatures high in the recovery range. Such high-temperature treatment is commonly
Fig. 12-5. Approximate property variations produced by annealing cold-worked tungsten for one hour at temperatures below that necessary for complete recrystallization.

used for cast or welded steel parts. Recovery may affect the course of subsequent recrystallization of a cold-worked metal, since the tendency toward recrystallization is lowered when appreciable recovery has occurred.

**Recrystallization**

Although all the properties of a cold-worked metal are somewhat affected by recovery heat treatments, such important properties as yield strength and percent elongation can often be radically changed only by eliminating the distorted microstructure as a result of recrystallization. It will be recalled that many dislocations remain in a cold-worked metal that has been given a recovery heat treatment. This number is reduced to the value characteristic of strain-free (annealed) metal by the recrystallization process, which involves the motion of a high-angle boundary. However, before considering this topic it will be helpful to discuss the formation of low-angle boundaries, which often occurs as a transition between recovery and recrystallization.

**Subgrain structure.** A good example of the occurrence of low-angle boundaries within a metal grain is the formation of cells during creep Fig. 9-8(b). It will be recalled that neighboring cells differ slightly in orientation across the low-angle cell boundaries. The fragments of relatively perfect lattice that exist in a cold-worked metal (Fig. 12-2) are thought to be somewhat similar to cells, although the fragments themselves are more distorted and the slip-band (boundary) regions are severely
FIG. 12-6. Subgrain formation on heating a bent single crystal of iron-3% silicon alloy. (a) Orientation of the single crystal before being bent. (b) Dislocations on the slip planes produced by bending the crystal. (X200; reproduced at two-thirds size). (c) Alignment of dislocations produced by annealing at 950°C for 24 hours (X200; reproduced at two-thirds size).
deformed. The existence of fragments has been demonstrated by special x-ray techniques, but usually they cannot be observed under the microscope.

Under some conditions, when a cold-worked metal is heated a subgrain structure forms. This structure consists of many small regions of perfect lattice slightly misoriented with respect to one another and separated by low-angle grain boundaries. An example of this behavior is shown in Fig. 12-6 for an iron crystal containing silicon in solid solution. When the crystal was bent, it slipped on (011) planes in [111] directions (perpendicular to the (111) plane), Fig. 12-6(b). The slip lines in the cold-worked crystal are shown in the photomicrograph, and the corresponding pattern of dislocations on (011) planes is indicated schematically. It is known that a group of edge dislocations of one sign (positive dislocations in this case) have lower energy if they are aligned vertically. Figure 12-6(c) shows schematically how this alignment might occur at 90° to the slip planes, and the photomicrograph shows that corresponding subgrain boundaries are actually observed in a specimen annealed at a high temperature. Subgrain boundaries are quite mobile provided they represent a small disorientation between two neighboring regions, but their mobility decreases with increasing disorientation. Therefore the size of subgrains increases with increasing time and temperature but tends to approach a size limit.

The formation of subgrains in severely cold-worked material usually causes some loss in the strength that was obtained from work hardening. On the other hand, the presence of a high density of subgrain boundaries increases the strength of an initially soft material. An example of this effect is shown in Fig. 12-7 for pure nickel and for a nickel-titanium alloy. The various densities of subgrain boundaries were produced by giving the test specimens preliminary deformations of 1 to 6 percent and anneal-

---

* The process of forming this type of subgrain structure is often called polygonization, since in many cases the subgrains have the form of polygons, Figure 9-8(b).
ing them at 800°C for 1 hour. The boundaries produced in this way were effective impediments to the motion of dislocations and consequently raised the stress $S_0$ required to cause plastic flow during a subsequent tension test.

Primary recrystallization. For most metals this is the essential process that occurs when a cold-worked metal is heated. In very general terms it can be defined as the nucleation and growth of strain-free grains out of the matrix of cold-worked metal. However, it is important to note that primary recrystallization will be preceded by some degree of recovery and subgrain formation, processes that affect the nature of the cold-worked matrix. Also, the strain-free grains that result from primary recrystallization may undergo further change as a result of secondary recrystallization or grain growth. These two phenomena will be discussed in later sections.

In general the structure that forms during (primary) recrystallization is essentially the same as the structure that existed before cold-working. The commercial importance of (primary) recrystallization arises from the fact that the properties of an alloy after recrystallization are about the same as those it had before cold-working. For example, when an alloy is subjected to a cold-working operation such as deep drawing, it becomes harder and less ductile (Fig. 12-3), and it is therefore difficult to continue the forming operation. If the partially formed article is given a recrystallization anneal, the alloy is returned to its original condition of good ductility and easy deformation, and the article can then be given additional deep drawing. The opposite aspect of recrystallization is seen in efforts to prevent its occurrence. The strength of cold-worked copper (or aluminum) conductors, for example, may be disastrously reduced if appreciable recrystallization takes place under the time-temperature conditions of service.

Theory. Although a fundamental understanding of the recrystallization process has not yet been achieved, the controlling factors appear to be nucleation of strain-free grains and the growth of these nuclei to encompass the entire metal specimen. In some cases nuclei may consist of small undeformed regions of the initial grains, but usually nucleation occurs in the more drastically deformed portions of the grain. At slip planes, for example, a cluster of atoms in the highly strained lattice transforms spontaneously into a strain-free nucleus as a result of random thermal vibrations within the group. The rate of nucleation increases with increasing deformation and with increasing annealing temperature. Alloying elements in solid solution usually decrease the rate of nucleation.

The birth and growth of nuclei in the submicroscopic range are difficult to study. However, it is believed that there is a critical size below which a cluster of atoms cannot form a stable nucleus. Once the nucleus is formed,
growth proceeds by motion of the boundary between the stable, low-energy nucleus and the unstable, strained matrix. The nature of this phenomenon can be seen in the series of photomicrographs in Fig. 12-9. It is possible that the initial rate of growth, when the nucleus contains only a few score atoms, is much slower than the rate of growth that can be observed microscopically. In any event, there is an incubation period in which no visible recrystallization occurs, and this period may be as long as the time necessary for the entire course of visible recrystallization.

The rate of growth during recrystallization in the observable range is independent of time but increases with the degree of deformation and with the annealing temperature. The presence of both soluble and insoluble impurities usually decreases the rate of growth, and hence the rate of recrystallization. Growth ceases when all the cold-worked metal has been replaced by grains of the strain-free crystal structure. Then recrystallization is said to be complete.

The recrystallized grains usually are not randomly oriented but have their crystal axes lying near certain favored directions with respect to the cold-worked grains. For example, when severely cold-rolled copper is recrystallized the new grains have a preferred orientation such that the [100] direction is parallel to the direction in which rolling was done, and the (001) plane lies in the rolling plane. In this case the preferred orientation is different from that developed by cold-working. Since pronounced aligning of crystal directions can produce anisotropic behavior in polycrystalline metals, preferred orientations are ordinarily objectionable; the grain-oriented transformer steel described in Chapter 7 is a notable exception. It is rarely possible to obtain complete randomness of orientation in recrystallized metals, but the percentage of oriented grains can be reduced to a low value by various means. Small amounts of alloying elements may be effective for this purpose; about one percent tin essentially eliminates preferred orientation in copper. Also, a small amount of cold work and a low recrystallization temperature result in a minimum of preferred orientation.

Isothermal recrystallization. The most important aspect of recrystallization in structural materials is the loss of strength that accompanies appreciable disappearance of the cold-worked grains. While it is evident that a work-hardened alloy should not be subjected to conditions that will produce recrystallization in service, it is often difficult to establish the exact range of permissible temperatures and times. For example, although the term recrystallization temperature is useful for many purposes, it does not refer to a definite temperature below which recrystallization is impossible. Rather, the recrystallization temperature of a given alloy is the temperature at which the highly cold-worked alloy completely recrystallizes in about one hour. Such recrystallization temperatures are listed in Table 12-1.
Table 12-1
APPROXIMATE RECRYSTALLIZATION TEMPERATURES FOR SEVERAL METALS AND ALLOYS

<table>
<thead>
<tr>
<th>Material</th>
<th>Recrystallization temperature, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (99.999%)</td>
<td>250</td>
</tr>
<tr>
<td>Copper (OFHC)</td>
<td>400</td>
</tr>
<tr>
<td>Copper-5% zinc</td>
<td>600</td>
</tr>
<tr>
<td>Copper-5% aluminum</td>
<td>550</td>
</tr>
<tr>
<td>Copper-2% beryllium</td>
<td>700</td>
</tr>
<tr>
<td>Aluminum (99.999%)</td>
<td>175</td>
</tr>
<tr>
<td>Aluminum (99.0%+)</td>
<td>550</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>600</td>
</tr>
<tr>
<td>Nickel (99.99%)</td>
<td>700</td>
</tr>
<tr>
<td>Nickel (99.4%)</td>
<td>1100</td>
</tr>
<tr>
<td>Monel metal (Nickel + 30% copper)</td>
<td>1100</td>
</tr>
<tr>
<td>Iron (electrolytic)</td>
<td>750</td>
</tr>
<tr>
<td>Low-carbon steel</td>
<td>1000</td>
</tr>
<tr>
<td>Magnesium (99.99%)</td>
<td>150</td>
</tr>
<tr>
<td>Magnesium alloys</td>
<td>450</td>
</tr>
<tr>
<td>Zinc</td>
<td>50</td>
</tr>
<tr>
<td>Tin</td>
<td>25</td>
</tr>
<tr>
<td>Lead</td>
<td>25</td>
</tr>
</tbody>
</table>

for several metals and alloys. Very pure metals are seen to have low recrystallization temperatures compared with impure metals or alloys.

The wide use of the term recrystallization temperature reflects the fact that the recrystallization process is more sensitive to changes in temperature than to variations in time at constant temperature. The maximum temperature is usually fixed in engineering structures, but the time may reach extremely large values (scores of years). Therefore it is desirable to have a representation of recrystallization that takes time, as well as temperature, into account. The isothermal recrystallization curve shown in Fig. 12-8 meets this need.

The experimental points for constructing such a curve are obtained by placing ten or twenty specimens of the cold-worked alloy in a constant-
Fig. 12-8. A typical isothermal recrystallization curve.

Fig. 12-9. The course of isothermal recrystallization at 310°C in 99.95% aluminum that has been cold-worked 5%. (a) Heated for 50 hours, (b) 70 hours, (c) 80 hours, (d) 100 hours. (All photomicrographs X10; reproduced at three-fourths size.) (Courtesy W. A. Anderson.)
temperature bath or furnace. Specimens are removed periodically, and their percentages of recrystallization are determined by microscopic examination. Figure 12-9 shows the gradual structural changes that occur. The initial cold-worked alloy had a relatively fine grain size. This material forms the background in Fig. 12-9(a). By the time a specimen of the cold-worked alloy had been heated for 50 hours at 310°C, several of the recrystallized grains had grown large enough to be seen, Fig. 12-9(a). On further heating, the existing recrystallized grains continued to grow and additional recrystallized grains also appeared, Figs. 12-9(b) and 12-9(c). After about 100 hours at this temperature recrystallization was complete, Fig. 12-9(d). A plot of percent recrystallization versus the time of annealing forms the isothermal recrystallization curve. A characteristic feature of such a curve is the incubation period that precedes the first visible recrystallization.

It is evidently impractical to determine experimentally whether a given cold-worked alloy will recrystallize in a long period of engineering interest, e.g., twenty-five years. Fortunately, a convenient method of extrapolation is available for estimating the useful life of a cold-worked alloy at a given temperature. Figure 12-10(a) shows isothermal recrystallization curves obtained for pure copper at four different temperatures. A standard rel...
tion between the rate of a reaction and the temperature in degrees Kelvin is

\[
\text{Rate} = Ae^{-B/T},
\]  
(12-1)

where \( A \) and \( B \) are constants. Using

\[
\text{Rate} = \frac{1}{\text{time for 50\% recrystallization}},
\]  
(12-2)

as a measure of the reaction rate, it follows that a plot of the logarithm of the time for 50 percent recrystallization versus the reciprocal of the absolute temperature should be a straight line (see Problem 7). Figure 12-10(b) is such a plot of the data of Fig. 12-10(a). An extrapolation to twenty-five years made on this plot gives the surprising information that the cold-worked copper would be 50 percent recrystallized in this time even if it were refrigerated at 24°F.

If the constants \( A \) and \( B \) are known, Eqs. (12-1) and (12-2) can be used to calculate the time for recrystallization at any temperature. For example, the time (in minutes) for 50 percent recrystallization of cold-worked OFHC (oxygen-free high-conductivity) copper wire at 100°C (373°K) can be estimated with aid of the values \( A = 10^{12} \text{ min}^{-1} \) and \( B = 15,000 \) for this material. Equation (12-1) can then be written

\[
\text{Rate} = 10^{12}e^{-15,000/373},
\]  
(12-3)

\[
\text{Rate} = 10^{12}e^{-40.45} = 10^{12}10^{-17.45} = 10^{-5.45},
\]  
(12-4)

\[
\text{Rate} = 0.35 \times 10^{-5} \text{ min}^{-1}.
\]  

When Eq. (12-2) is used to express the rate, Eq. (12-4) can be put in the form

\[
\text{Time for 50\% recrystallization} = 2.9 \times 10^5 \text{ min}.
\]  
(12-5)

When this result is compared with the recrystallization temperature for OFHC copper (Table 12-1), it is seen that recrystallization is more than 1000-fold slower at 212°F (100°C) than at 400°F.

**Other variables.** A number of factors besides time and temperature influence the recrystallization process. The most important of these are

* These two constants can be calculated for a given cold-worked metal if the times for 50\% recrystallization at two temperatures are determined. Equation 12-1 can then be written for each of the two temperatures, and these two equations can be solved for \( A \) and \( B \).
RECOVERY, RECRYSTALLIZATION, AND GRAIN GROWTH [CHAP. 12]

FIG. 12-11. Effect of the degree of cold-working on the temperature necessary to cause recrystallization during heating for one hour. The position of the usual "recrystallization temperature" is indicated.

(1) alloying elements, (2) grain size, and (3) degree of cold work.*

Figure 12-11 shows typical effects of the degree of cold work on the temperature necessary to cause recrystallization. The rapid increase in temperature below about 20 percent cold work is notable. The capacity for recrystallization produced by a given degree of cold work is influenced by the grain size of the metal; a fine grain size causes recrystallization to occur in a shorter time or at a lower temperature. Various working processes, such as rolling, drawing, and pressing, also produce somewhat different effective amounts of deformation for a given percentage reduction in cross section. If cold-working is performed above room temperature, its effectiveness is reduced in proportion to the temperature. Similarly, a recovery treatment may reduce the tendency for recrystallization to occur during a subsequent high-temperature anneal.

The common means of increasing the useful temperature range of a cold-worked metal is by suitable alloying. Usually the addition of a small percentage of a soluble alloying element sharply raises the recrystallization temperature of the base metal. With further increase in alloy content, however, the recrystallization temperature usually attains a maximum.

* The percent cold work is usually expressed in terms of the reduction in height \( h \) (during cold rolling, for example), or the reduction area \( A \) in a process such as wire drawing. The corresponding formulas are

\[
\text{Percent cold work} = \left( \frac{h_0 - h_f}{h_0} \right) \times 100,
\]

\[
\text{Percent cold work} = \left( \frac{A_0 - A_f}{A_0} \right) \times 100,
\]

where \( h_0 \) and \( A_0 \) are the initial values and \( h_f \) and \( A_f \) are the values after cold-working.
FIG. 12-12. Typical property changes produced by heating a cold-worked metal for one hour at elevated temperatures.

value and may then decrease. Thus the optimum addition of magnesium to aluminum is one percent, and of zinc to copper is 5 percent. Although the various alloying elements tend to follow this general pattern in their influence on recrystallization, there is a wide variation in the effectiveness of specific addition metals. For example, beryllium and zirconium are outstanding in increasing the recrystallization temperature of aluminum, while molybdenum and tungsten are especially useful in steel.

It is important to remember that the property changes which occur as a result of heating a cold-worked metal or alloy may be the combined effects of recovery, recrystallization, and grain growth. Thus in Fig. 12-12 it is seen that ductility (expressed as reduction in area) increases sharply during recrystallization and finally decreases after pronounced grain growth occurs. On the other hand, the electrical resistance diminishes markedly during the recovery stage and somewhat further on subsequent recrystallization. The pattern of property change is dependent not only on the property being considered but also on the nature of the alloy and its history of mechanical and thermal treatment. In the case of hardness and strength the trends of these important design properties may be significantly different from the corresponding change in the percent recrystallization that has occurred. Thus there is sometimes good reason for determining the hardness or strength values directly during an anneal, rather than depending on deductions from the observed amount of recrystallization.
Secondary recrystallization. Under some conditions an alloy that has formed a fine-grained structure by primary recrystallization will experience pronounced grain growth if it is heated at a higher temperature. The mechanism involves the rapid migration of the boundaries of a few of the primary recrystallized grains, with the result that the majority of the primary grains are consumed and very large secondary grains are created. A stage in this process is shown for an iron-silicon alloy in Fig. 12-13. Since the specks in the photomicrograph are etch pits indicating the presence of dislocations, it is evident that in this alloy the secondary grains are more perfect than the initial recrystallized grains. However, the major driving force for secondary recrystallization is the reduction in grain-boundary energy that accompanies the drastic reduction in grain-boundary area. Other names for this phenomena are discontinuous grain growth and abnormal grain growth.

Grain Growth

When an ordinary, strain-free metal or alloy is heated at a sufficiently high temperature, the grain boundaries slowly migrate and produce a uniform increase in grain size. This process is known as normal grain growth, and it occurs far more slowly than the types of boundary migration considered above in connection with the annealing of cold-worked metals (namely, motion of subgrain boundaries, growth of primary recrystallized grains, and abnormal grain growth during secondary recrystallization).
The driving force for normal grain growth is the energy associated with grain boundaries. When the grain size increases, the total grain-boundary area decreases, and consequently the energy of the metal is lowered. An equation describing the kinetics of grain growth can be obtained by assuming that the instantaneous rate of growth $\frac{dD}{dt}$ is proportional to the grain-boundary energy per unit volume of the metal, which in turn is proportional to $\frac{1}{D}$, where $D$ is the grain diameter. This reasoning leads to the expression

$$\frac{dD}{dt} = K \frac{1}{D},$$

where $K$ is a constant. It is shown in Problem 9 that the integrated form of this equation is

$$D^2 - D_0^2 = Ct.$$  \hspace{1cm} (12-6)

Although Eq. (12-7) applies in only a few ideal cases, an analogous equation approximates the grain-growth behavior of single-phase alloys when the grain size is small compared with the dimensions of the specimen. This empirical equation is

$$D^{1/n} - D_0^{1/n} = Ct,$$  \hspace{1cm} (12-8)

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature, °F</th>
<th>$n$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (99.99%)</td>
<td>750</td>
<td>0.1</td>
<td>$8 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>930</td>
<td>0.2</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>1110</td>
<td>0.3</td>
<td>$6 \times 10^{-1}$</td>
</tr>
<tr>
<td>Cartridge brass 70% Cu, 30% Zn</td>
<td>930</td>
<td>0.2</td>
<td>$13 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>1110</td>
<td>0.2</td>
<td>$9 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>1290</td>
<td>0.2</td>
<td>$6 \times 10^{-7}$</td>
</tr>
<tr>
<td>Iron</td>
<td>930</td>
<td>0.1</td>
<td>$2 \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>1110</td>
<td>0.2</td>
<td>$6 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>1470</td>
<td>0.5</td>
<td>$4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Carbon steel (austenite) 0.8% C</td>
<td>1400</td>
<td>0.1</td>
<td>$6 \times 10^{-16}$</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>0.2</td>
<td>$2 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>1800</td>
<td>0.23</td>
<td>$2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
where $D$ is the grain diameter in millimeters that exists after heating for $t$ minutes at constant temperature, $D_0$ is the initial grain diameter, and $n$ and $C$ are independent of time but vary with factors such as composition and temperature. $C$ increases steadily with temperature, but the value of $n$ appears to approach 0.5 as an upper limit with increasing temperature. Approximate values of $n$ and $C$ are given in Table 12-2 for several metals and single-phase alloys. It should be noted that the grain growth occurring with increasing time at constant temperature is small compared with that occurring with increasing temperature at constant time (usually one hour at temperature). Figure 12-14 shows the grain-growth behavior of two steels as the austenitizing temperature is increased. The grains of the coarse-grained steel grow in the manner characteristic of a single-phase alloy.

The restricted grain growth at low heating temperatures shown by fine-grained steel is typical of the behavior of alloys that contain a finely dispersed second phase. In steels, nonmetallic inclusions formed during the deoxidation of the liquid steel tend to restrain grain growth. Usually the larger the number of second-phase particles, the smaller the grain size in metals containing a dispersed phase. Above a certain high temperature, however, grain coarsening occurs, in which a few large grains partially or completely replace the fine grains that exist over a wide range of lower temperatures. A second possible cause of restricted grain growth is the presence of strong preferred orientation of the initial set of grains. This restrictive influence, too, is overcome at high temperatures, and grain coarsening occurs.

**Final Grain Size**

The final grain size of a cast alloy is determined during the solidification process, and usually it cannot be changed by heat treatment, since grain growth is essentially lacking in such alloys. Almost all wrought alloys, on the other hand, undergo recrystallization one or more times during their fabrication. If a specified grain size is desired, it must be obtained by suitable control of the recrystallization process and by prevention of excessive grain growth.
FIG. 12-15. Effect of grain size on the flow stress and ductility (% elongation) of cartridge-brass tested in tension.

Brass intended for cold-working operations is an example of commercial grain-size control. Figure 12-15 shows that the ease of working of cartridge brass (70% Cu, 30% Zn) increases with increasing grain size. Not only is the ductility improved but the flow stress is lowered as well. On the other hand, there is a greater problem with surface appearance as the grain size increases, since the nonuniformity of deformation from grain to grain becomes plainly visible. Figure 12-16 shows the "orange peel" surface that occurs on coarse-grained metals that are subjected to severe deformation. The choice of grain size in this case is therefore a compromise, and Table 12-3 shows the values that are recommended for various applications.

The desired grain size in brass sheet for cold-forming operations is produced during its manufacture by annealing the cold-rolled sheet. Since the annealing temperature is ordinarily above the minimum temperature required to cause recrystallization, the grain size is determined both by the recrystallization process and by subsequent grain growth. The grain size

<table>
<thead>
<tr>
<th>Grain diameter, mm</th>
<th>Type of cold-forming operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>Light forming</td>
</tr>
<tr>
<td>0.025</td>
<td>Shallow drawing</td>
</tr>
<tr>
<td>0.035</td>
<td>Average drawing</td>
</tr>
<tr>
<td>0.050</td>
<td>Deep drawing</td>
</tr>
<tr>
<td>0.100</td>
<td>Severe drawing on thick sheet</td>
</tr>
</tbody>
</table>

*Data from Metals Handbook, 1948.
Fig. 12-16. The effect of grain size on the surface appearance of cold-drawn brass sheet. (Courtesy H. L. Burghoff, Chase Brass and Copper Company.)
heat treatments. This critical deformation, approximately 5 percent, may occur in parts subjected to deformation, such as bending, in which the degree of cold work varies from zero to a maximum value.

* This is the basis of the strain-anneal method for producing single crystals.

References


PROBLEMS

1. The electrical conductivity of a pure metal is decreased drastically by the addition of an alloying element that forms a solid solution, but is decreased only slightly by cold-working. Show how this difference in behavior might be explained in terms of the difference in relaxation times, \( r \) (Eq. 7-5), in the two structures. Since a low value of \( r \) is attributed to interference with motion of the electron waves, use sketches of the two structures to show the importance of the regions of perfect lattice in cold-worked metal.

2. The pattern of residual stresses in a cold-rolled plate is similar to that shown in Fig. 8-11(b). It is common experience that the plate warps if a layer of metal is chined from one surface. (a) Predict the direction in which the plate would bow. Note that the metal removed was under tension. (b) Explain whether it is possible to eliminate the cause of warping without sacrificing the strengthening effect of the cold work.

3. Criticize this statement: "Recovery of cold-worked tungsten occurs at 800°F."

4. OFHC copper that has had its yield strength increased by a factor of four through cold-working is proposed for use in an electrical device operating at 300°F. A safety factor of two is to be employed in determining the maximum allowable stress. (a) Using values of \( A = 10^{12} \text{ min}^{-1} \) and \( B = 15,000 \) in Eq. (12-1), calculate the approximate useful life of the electrical device. (b) Why should recovery effects be considered? (c) Why is it unnecessary to consider the effects of grain growth?

5. The presence of an alloying element in solid solution usually decreases the rate of nucleation in the recrystallization process. Recalling that both nucleation and growth occur in recrystallization, explain why, in spite of this effect on rate of nucleation, the grain size after recrystallization may be decreased by the addition of such an alloying element.

6. Give the advantages of plotting recrystallization data (a) at constant temperature, and (b) at constant time.

7. Show how Eqs. (12-1) and (12-2) determine what quantities should be plotted to obtain the straight-line extrapolation used in Fig. 12-10(b).

8. List a number of means that might be used to raise the temperature at which a cold-worked copper article, which must have good electrical conductivity, will recrystallize in five years.

9. It can be shown that Eq. (12-7) is obtained when Eq. (12-6) is applied to the problem of the growth of a grain whose diameter is \( D_0 \) at time \( t = 0 \). (a) Algebraically rearrange Eq. (12-6) so that \( D \) and \( dD \) are on one side of the equation and \( dt \) is on the other side. (b) Integrate both sides of this equation over the interval between zero time and some arbitrary time \( t \). Note that the corresponding limits on the grain diameter are \( D_0 \) and \( D \). (c) Combine the constants into a single constant \( C \).

10. As a useful approximation it is often assumed that no grain growth occurs in a steel heated at 1400°F, but that grain growth does occur at temperatures near 1600°F. Taking an initial grain size of 0.05 mm, calculate the grain growth that would occur on heating a 0.8% carbon steel one hour at each of these temperatures.
CHAPTER 13

AGE HARDENING

"... I can speak only of the effect of the hardening process on aluminum alloys ... without being able to give an explanation of its nature."

ALFRED WILM (1911)

INTRODUCTION

In the many years since Wilm discovered a new hardening process for aluminum alloys, enough has been learned about the nature of the phenomenon to permit its application to many metals. Age hardening is now one of the outstanding methods of strengthening commercial alloys. Although a complete understanding of the hardening mechanism has not yet been achieved, considerable progress has been made toward this goal. It will be recalled that metals are weak because of the motion of dislocations in the crystal structure and that strengthening is produced when this motion is impeded. In commercial age-hardening alloys it is likely that a number of mechanisms contribute to the over-all effect on dislocation motion. Therefore, before discussing the concept of "lattice-coherency" that is characteristic of age-hardening alloys, it will be helpful to review briefly the general topic of hardening of metals and alloys.

General hardening processes. We begin with a consideration of a pure metal, the simplest case. In an annealed metal the mobility of dislocations can be significantly affected by reducing the volume available for continuous slip, for example by decreasing the grain size. Figure 12-15 shows an instance in which this method is effective in a commercial alloy, but usually the effect of grain size is small. Subgrain boundaries are also effective in limiting the volume available for easy slip, as shown by Fig. 12-7. The greatest strengthening of pure metals is obtained by cold-working, Fig. 12-3, and it will be recalled that in this case a complex pattern of dislocations is produced that makes further motion extremely difficult.

The hardening procedures for pure metals can also be used for alloys, and in this case several other methods of strengthening may also be available. These methods are conveniently divided into two classes: those based on solid-state reactions found in a relatively small number of
Fig. 13-1. The formation of a Cottrell atmosphere of solute atoms around a dislocation. The two solute atoms shown are merely representative of the large number that may constitute the atmosphere. (a) Large solute atoms in random positions create strain energy. (b) Movement of solute atoms to positions below dislocation lowers the energy.

alloy systems, and those based on alloy hardening (solid-solution formation or the presence of a second phase), which is found in all alloys. The more general alloy hardening will be considered first.

An alloying element that goes into solid solution always hardens the solvent metal. In dilute solutions the amount of hardening is roughly proportional to the concentration of the alloying element, and if more than one element is present, the total hardening is approximately the sum of the characteristic effects of each element. The hardening produced by a given alloying element appears to depend on the differences in size and electronic structure between it and the solvent metal. As explained below, dislocations are apparently not seriously impeded by solute atoms that are merely distributed at random in the solvent. However, if the solute atoms collect preferentially around the dislocations, then the force required to move a dislocation may be greatly increased. The reason for this behavior is shown in Fig. 13-1 for a solute atom that is larger than the matrix atom. Since the matrix is in tension in the region below the edge dislocation, the energy of the system is lowered when the solute atoms move from random positions in the lattice to positions in this region. The dislocation is then said to be locked by its solute "atmosphere." Other suggested mechanisms of solid-solution hardening involve preferential segregation of solute atoms in stacking faults or in ordered arrays, both of which increase the difficulty of dislocation movement.
Another type of alloy hardening occurs when a second phase is present. Although a dislocation can pass through an array of isolated solute atoms, it cannot do this in the case of a second-phase particle. Rather, the dislocation must be forced between adjacent particles as shown schematically in Fig. 13-2, leaving a dislocation loop around each particle. According to this picture the stress required would decrease as the spacing $d$ between the particles increases. This explanation will be applied in a later section to account for the changes in strength during the later stages of precipitation hardening.

Solid-state reactions. Alloy hardening and cold-working are applied widely, but in certain alloy systems it is possible to replace or augment them by special hardening reactions that occur in the solid state. These solid-state reactions are especially significant for the following reasons: they increase hardness far above the level possible by alloy hardening alone, they do not require that the part be plastically deformed, and they allow the hardening to be done at a convenient point in the fabrication process. However, there are a number of restrictions on this type of hardening:

1. Not every alloy system can undergo a given solid-state reaction. Eutectoid decompositions, for example, are not commonly found in phase diagrams.
2. The occurrence of a solid-state reaction under equilibrium conditions does not lead to appreciable hardening; to cause hardening it is necessary to form a nonequilibrium structure (martensite in steels, for example).
3. The degree of hardening produced by a given solid-state reaction varies from system to system, and it may be negligibly small in some instances. The occurrence of a given reaction must therefore be considered a necessary but not a sufficient condition for hardening.

The following are some of the solid-state reactions capable of producing useful hardness increases:
(a) eutectoid decomposition
(b) precipitation from solid solution
(c) ordering of a random (disordered) solid solution
(d) diffusion reaction (e.g., internal oxidation)

Schematic illustrations of the necessary form of phase relationships for these reactions are shown in Fig. 13-3. Conditions such as those represented in Fig. 13-3(a), a typical eutectoid-type diagram, are required to produce eutectoid decomposition. Precipitation can occur if the boundary line (solvus line) separating a one-phase and a two-phase region slopes in the manner sketched in Fig. 13-3(b). For ordering to be possible, a reaction of the type shown in Fig. 13-3(c) must form a part of the solid-state behavior of the alloy system in question. The requirements for diffusion reaction are indicated in Fig. 13-3(d). It is seen that the composition of the hardenable alloy (metal B in metal A) must shift from a one-phase region to a two-phase region as a result of the diffusion of a third component (metal C) into the initial alloy. The two age-hardening processes and diffusion-reaction hardening are considered in this chapter. Eutectoid decomposition, on which the hardening of steel is based, will be treated in

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**Fig. 13-3.** The form of equilibrium diagram necessary for each of four solid-state reactions. (a) Eutectoid decomposition. (b) Precipitation from solid solution. (c) Ordering of a random solid solution. (d) Diffusion reaction.
the following chapter. It should be mentioned that other less important hardening reactions are known to exist, such as the hardening of certain cold-worked metals during recovery, and still other reactions perhaps remain to be discovered.

PRECIPITATION HARDENING

The necessary condition for precipitation from solid solution is merely the existence of a sloping solvus line, as shown in Fig. 13-3(b). Therefore precipitation occurs to some degree in almost all alloy systems and to a marked extent in hundreds of known cases. There is no doubt that virtually any metal can be made to precipitation harden by the addition of a properly chosen alloying element, and still further hardening should be possible in ternary or higher component alloys. Examples of this hardening process have already been given in discussing magnesium and copper-beryllium alloys, and additional commercial applications are listed in a later section.

Heat treatment. The entire process of producing a precipitation-hardened alloy may be divided into three parts: (1) choosing the composition, (2) solution heat-treating, and (3) precipitation heat-treating. The development of commercial precipitation-hardening alloy compositions is a long, difficult task, but it is possible to state some of the principles underlying such development. The equilibrium diagram of Fig. 13-4 is typical of a system that may show hardening as a result of precipitation of the beta phase from the supersaturated alpha solid solution. While the

![Equilibrium diagram](image-url)

**Fig. 13-4.** Equilibrium diagram on which are indicated compositions of a wrought and a cast alloy suitable for precipitation hardness.
maximum hardening effect is produced in this case at 6 percent metal B, the limit of solubility of metal B in metal A, some hardening can occur in the entire range of compositions over which the alpha-plus-beta phase field extends at low temperatures. In practice, compositions other than that capable of maximum hardening are used. The casting properties of cast alloys are often improved by the presence of appreciable eutectic liquid during solidification. Therefore a composition such as 9 percent metal B may be used. The composition of wrought alloys may be held to about 4 percent metal B to allow the alpha phase to be obtained for hot-working. In many cases the maximum working temperature is that of the binary eutectic or of a still lower-melting ternary eutectic in complex alloys.

A similar heat treatment is used for both cast and wrought alloys, except that longer times or higher temperatures must be used for the more slowly reacting cast materials. The purpose of the first step, solution treatment, is to dissolve a maximum amount of the second phase in the alpha solid solution and then to retain this solution down to room temperature. This is accomplished by (1) heating the alloy to a high temperature, but below the temperature at which excessive grain growth or melting of one of the constituents would occur, (2) holding for a fraction of an hour to almost a day to allow solution to take place, and (3) quenching in water to obtain the supersaturated solid solution at room temperature. The hardness after solution treatment is relatively low, Fig. 13-5, but it is higher than that of the slowly cooled, annealed material.

The full hardness of these alloys is developed during the precipitation treatment, in which the supersaturated solution undergoes changes that lead eventually to the formation of the second phase. In some cases the precipitation may occur in a reasonable time at room temperature, and the alloy is then said to be naturally aging. Usually it is necessary to age the alloy artificially by holding it in a temperature range such as that shown in Fig. 13-4. The exact temperature used for the precipitation heat treatment is determined by two factors: (1) the time for appreciable reaction and (2) the property of principal interest. The time factor must be of reasonable length for industrial heat treatment. (The higher the temperature, the shorter the time.) In regard to the second factor it should be understood that different properties change at different rates during precipitation. For example, the strength properties tend to reach higher maximum values at lower precipitation temperatures. The course of aging at two different temperatures is shown in Fig. 13-5. Properties such as hardness attain a maximum value during precipitation at a given temperature and then gradually decrease as a result of overaging. This eventual softening is a natural consequence of the approach of the alloy to the equilibrium condition with increasing time at temperature. In
fact, a greatly overaged alloy would be essentially identical with an \textit{annealed} alloy, i.e., one in which the equilibrium structure is produced by slow cooling from the solution-treating temperature.

In addition to composition and heat-treating conditions, the properties obtained in certain alloys are greatly affected by cold-working after solution treatment. In some instances cold-working interferes with the development of maximum property values during the following precipitation treatment, but frequently the important design factor, yield strength, can be significantly increased by this means.

\textbf{Theory}. An adequate theory of precipitation hardening should be able to explain such phenomena as the effect of plastic deformation on the course of hardening, the fact that not all systems capable of precipitation are capable of hardening, and the nature of overaging. The \textit{coherent lattice theory} is at present the most useful view of the precipitation hardening process. According to this theory the first step in precipitation is the congregation of solute atoms in the matrix lattice as a result of statistical fluctuations in the solid solution. The regions rich in solute are called clusters and correspond to the embryos of nucleation theory (see Chapter 5). In the next step in the process, solute atoms diffuse to the clusters from the surrounding matrix and convert some of them into nuclei of a new phase. During the early stages of precipitation the equilibrium phase does not form directly, but an intermediate crystal structure related to it grows in close contact with the solid solution. Figure 13-6(b) is a schematic picture of this \textit{transition lattice} and shows the distortion of the solid solution that exists so long as there tends to be atom matching (coherency) between the two structures. The initial particles usually are not spherical but are platelike or rodlike in shape. When their dimensions are small these particles produce special x-ray effects, such as \textit{Guinier-Preston streaks}, rather than the usual diffraction pattern.
Even though conditions may not be favorable for rapid development of the equilibrium phase, after a sufficient time this more stable phase eventually forms. Usually it nucleates separately from the transition lattice, and during the subsequent growth process it competes with this less stable lattice for solute atoms, eventually causing it to redissolve. In a few alloys the transition lattice transforms directly to the equilibrium precipitate. Also, in many precipitation-hardenning systems the intermediate crystal structure fails to develop far enough to be called a transition lattice before it is replaced by the equilibrium precipitate.

Although the equilibrium precipitate is oriented in a definite position...
Fig. 13-7. Explanation of the effect of lattice coherency and particle size on the spacing $d$ of Fig. 13-2. (After Geisler.) (a) The effective size of coherent particles is increased by the surrounding volume of strained matrix. (b) Comparable particles of equilibrium precipitate have a smaller effective size; therefore $d$ is larger. (c) When particles agglomerate during overaging the spacing $d$ becomes still larger.

Fig. 13-8. Discontinuous precipitation at grain boundaries in a copper-2% beryllium alloy (X75). (W. D. Robertson and R. S. Bray, "Precipitation from Solid Solution," American Society for Metals, 1958.)
with respect to the solid solution in which it forms, there is not the atom-to-atom registry or coherency between these two lattices that characterizes the intermediate crystal structures. An equilibrium precipitate particle is shown schematically in Fig. 13-6(c). The dislocation theory of the hardening effect of a second phase, Fig. 13-2, can be used to explain why the equilibrium precipitate is less effective in strengthening the alloy than is a coherent region of similar size. Because of the surrounding volume of strained matrix, the coherent particle has a much larger effective size and Fig. 13-7(a) shows that the spacing \( d \) is reduced compared with that for the equilibrium precipitate. It will be recalled that a small \( d \) is associated with high strength. During further aging the size of the equilibrium precipitate particles increases and their number decreases, as shown in Fig. 13-7(c). The interparticle spacing then increases still further and causes a progressive decrease in hardness during overaging.

In addition to the uniform, general precipitation described above, some systems experience discontinuous precipitation. This process usually occurs at grain boundaries and consists in the growth of lamellae of the second phase interspersed with the depleted matrix. Figure 13-8 shows this phenomenon in a copper-beryllium alloy. Since the properties obtained from this type of precipitation are poorer than those obtained from general precipitation, the heat treatment or composition is often adjusted to minimize discontinuous precipitation. Small additions of nickel or cobalt are used in copper-beryllium alloys for this purpose.

**Applications.** Precipitation hardening is the most important method of strengthening nonferrous metals by solid-state reaction. It is especially useful for aluminum, the principal metal of this class, and both cast and wrought aluminum alloys are precipitation hardened.

Since detailed information on the wide variety of aluminum alloys available commercially is given in the *Metals Handbook*, only a brief survey of representative alloys will be presented here. The alloy designations used for the wrought alloys in Table 13-1 (p. 452) developed from an earlier system in which only one to three numbers were used. For example, alloy 5052 was previously 528, where the 8 identified it as a wrought alloy. The first number in the present designation specifies the alloy group according to the following system:

<table>
<thead>
<tr>
<th>Alloy number</th>
<th>Major alloying element</th>
</tr>
</thead>
<tbody>
<tr>
<td>1xxx</td>
<td>Commercially pure aluminum (99+ % Al)</td>
</tr>
<tr>
<td>2xxx</td>
<td>Copper</td>
</tr>
<tr>
<td>3xxx</td>
<td>Manganese</td>
</tr>
<tr>
<td>4xxx</td>
<td>Silicon</td>
</tr>
<tr>
<td>5xxx</td>
<td>Magnesium</td>
</tr>
</tbody>
</table>
Table 13-1 shows the range in mechanical properties of each alloy from the soft to the hard condition. The condition or temper of an alloy can be indicated by adding a symbol to the alloy designation. The principal part of this symbol is a letter having the following significance:

<table>
<thead>
<tr>
<th>Letter</th>
<th>Condition of alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>As fabricated</td>
</tr>
<tr>
<td>O</td>
<td>In soft condition as a result of annealing (recrystallizing)</td>
</tr>
<tr>
<td>H</td>
<td>Strain hardened by a cold-working process</td>
</tr>
<tr>
<td>T</td>
<td>Heat treated</td>
</tr>
</tbody>
</table>

The letters H and T are usually followed by numbers indicating in more detail the treatment that the alloy received. For example, H1 designates an alloy that has been strain hardened only, H2 designates one that has been strain hardened and partially annealed, and H3 designates one that has been strain hardened and stabilized by suitable annealing. A second number, 2, 4, 6, 8, or 9, is used to indicate increasing amounts of strain hardening. For example, the second alloy in Table 13-1 is designated 5052-O in its soft condition, while its hardest commercial temper is 5052-H18.

The various tempers produced by heat treatment are indicated by T combined with the following numbers:

| T2 | Annealed (applies only to castings, annealed to improve ductility for example) |
| T3 | Solution heat-treated and then cold-worked               |
| T4 | Solution heat-treated and naturally aged                  |
| T5 | Artificially aged only                                   |
| T6 | Solution heat-treated and artificially aged               |
| T7 | Solution heat-treated and stabilized (by an overaging heat treatment) |
| T8 | Solution heat-treated, cold-worked, and then artificially aged |

For example, the fifth alloy in Table 13-1 is designated 7075-O in its soft condition, which is produced by annealing for a few hours at 775°F. The hard temper, 7075-T6, is produced by solution heat-treating at 870°F.
**Table 13-1**

**Some Characteristics of Several Types of Aluminum Alloys**

<table>
<thead>
<tr>
<th>Alloy designation</th>
<th>Principal alloying elements</th>
<th>Hardening process*</th>
<th>Range of properties (soft to hard conditions)</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tensile strength, lb/in²</td>
<td>Yield strength, lb/in²</td>
</tr>
<tr>
<td>Wrought alloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>Commercial purity 2.5% Mg</td>
<td>Cold-working</td>
<td>13,000–24,000</td>
<td>5,000–22,000</td>
</tr>
<tr>
<td>5052</td>
<td></td>
<td>Cold-working</td>
<td>28,000–42,000</td>
<td>13,000–37,000</td>
</tr>
<tr>
<td>2024</td>
<td>4.5% Cu, 1.5% Mg (with protective sheet of pure aluminum)</td>
<td>Precipitation</td>
<td>27,000–48,000</td>
<td>11,000–47,000</td>
</tr>
<tr>
<td>6061</td>
<td>1.5% MgSi</td>
<td>Precipitation</td>
<td>18,000–45,000</td>
<td>8,000–40,000</td>
</tr>
<tr>
<td>7075</td>
<td>5.0% Zn, 2.0% Mg, 1.6% Cu</td>
<td>Precipitation</td>
<td>33,000–83,000</td>
<td>15,000–73,000</td>
</tr>
<tr>
<td>Cast alloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>195</td>
<td>4.5% Cu</td>
<td>Precipitation</td>
<td>22,000–41,000</td>
<td>16,000–32,000</td>
</tr>
<tr>
<td>319</td>
<td>3.5% Cu, 6.3% Si</td>
<td>Precipitation</td>
<td>27,000–36,000</td>
<td>18,000–20,000</td>
</tr>
<tr>
<td>356</td>
<td>7.0% Si, 0.3% Mg</td>
<td>Precipitation</td>
<td>~38,000</td>
<td>~27,000</td>
</tr>
</tbody>
</table>

* In addition to alloy hardening.
and aging (precipitation heat-treating) at 250°F for about 25 hours. Figure 13-9 shows the property changes that occur during this precipitation treatment. Since alloying and the precipitation heat treatment decrease the corrosion resistance of aluminum, certain of the high-strength alloys are protected by a layer of pure aluminum firmly bonded to the surface by a hot-rolling process. Alclad 2024 alloy is an example of this type of product.

The heat treatment of aluminum alloys illustrates the relation between phase diagrams and the structure of alloys. For example, the structure of alloy 195 in the as-cast condition, Fig. 13-10(b), shows coarse particles of the \( \theta \)-phase, \( \text{CuAl}_2 \), that formed as a divorced eutectic structure during solidification. The matrix is a solid solution, in agreement with the phase diagram, Fig. 13-10(a). However, there is another phase in this structure, the dark \( \text{(Al, Fe, Si)} \) constituent that is formed by the iron and silicon impurities in the alloy. Solution heat treatment dissolves both the \( \theta \)-phase and the impurity phase, leaving only the supersaturated solid solution when the alloy is quenched, Fig. 13-10(c). Although the subsequent aging treatment causes structural changes that double the yield strength of this alloy, the changes are not visible in the microstructure, Fig. 13-10(d).

With the electron microscope it is possible to see additional structural details in an alloy similar to 6061, but of higher than commercial purity. During aging at room temperature this alloy experiences substantial hardening as the \( \text{Mg}_2\text{Si} \) phase attempts to precipitate from the solid solution. A subgrain structure is found to exist in this alloy both in the solution-treated condition and after room-temperature (natural) aging, Fig. 13-11(a), although no precipitate is visible. Only if the alloy is greatly overaged and softened, Fig. 13-11(b), can precipitate particles be seen.

Since the majority of commercial aluminum alloys contain at least two
The microstructure of aluminum alloy 195 (4.5% Cu, 0.8% Si, 0.5% Fe) after various heat treatments. (Courtesy Alcoa Research Laboratories.) (a) A portion of the aluminum-copper phase diagram showing the position of alloy 195. (b) As-cast alloy with particles of $\theta$ and $\alpha$ (Al, Fe, Si) in dendrites of the $\alpha$ solid solution. (c) The alloy after solution heat treatment at 900°F for 12 hours; only the solid solution remains. (d) After aging for 4 hours at 310°F no change is seen in the microstructure. (Photomicrographs X250; reproduced at two-thirds size.)
alloying elements, it is often necessary to use ternary equilibrium diagrams in describing the phase relations. Casting alloy 319 (3.5% Cu, 6.3% Si) is a convenient example for illustrating this point, since the portion of the ternary diagram involved is a relatively simple ternary eutectic, Fig. 13-12(a). The ternary eutectic (lowest-melting) composition can be seen quite clearly in the liquidus surface, Fig. 13-12(b), which is shown for a somewhat wider range of compositions than in the ternary diagram.

The solution heat-treatment of alloy 319 is carried out at 940°F. According to the isothermal section at this temperature, Fig. 13-12(c), the alloy should then consist only of the α-matrix plus particles of silicon. The actual microstructure, Fig. 13-12(d), is somewhat more complex, since it also contains two types of (Al, Fe, Si) constituent because of the iron impurity in the alloy. Hardening of this alloy occurs when it is subjected to aging, usually at 310°F. The isothermal section for this temperature, Fig. 13-12(e), shows that an additional phase, θ (CuAl2), exists under equilibrium conditions. Therefore the observed hardening is produced during the processes leading to the precipitation of this phase. The
Fig. 13-12. The equilibrium phase relations in aluminum alloy 319. (a) Space model of the aluminum corner of the Al-Cu-Si ternary diagram. The position of alloy 319 is shown. (b) Liquidus surface of a larger portion of the Al-Cu-Si diagram. (After Phillips.)
APPLICATIONS

Fig. 13-12. (Cont.) (c) Isothermal section through the diagram in (a) at 940°F, the solution-treating temperature for alloy 319. (d) Photomicrograph of alloy 319 after solution treatment at 940°F. (e) Isothermal section through (a) at 310°F, the aging temperature for alloy 319. (f) Photomicrograph of alloy 319 after slow cooling to 310°F showing the occurrence of precipitation. (Photomicrographs X250; reproduced at two-thirds size. Courtesy Alcoa Research Laboratories.)
### Table 13-2

**Some Characteristics of Several Nickel Alloys**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Principal alloying elements</th>
<th>Tensile strength, lb/in²</th>
<th>Yield strength, lb/in²</th>
<th>Elongation in 2 inches, %</th>
<th>Endurance strength (10⁸ cycles), lb/in²</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;A&quot; nickel, hot-rolled</td>
<td>none</td>
<td>65,000</td>
<td>30,000</td>
<td>50</td>
<td>30,000</td>
<td>Chemical industry, nickel plating</td>
</tr>
<tr>
<td>Duranickel, cold-drawn and precipitation hardened</td>
<td>4.4% aluminum, 0.4% titanium</td>
<td>190,000</td>
<td>150,000</td>
<td>20</td>
<td>60,000</td>
<td>Springs, plastics, extrusion equipment</td>
</tr>
<tr>
<td>Monel, hot-rolled</td>
<td>30% copper</td>
<td>90,000</td>
<td>55,000</td>
<td>35</td>
<td>42,000</td>
<td>Oil refinery parts</td>
</tr>
<tr>
<td>&quot;K&quot; Monel, cold-drawn and precipitation hardened</td>
<td>26% copper, 3% aluminum</td>
<td>180,000</td>
<td>160,000</td>
<td>5</td>
<td>46,000</td>
<td>Pump rods, valve stems</td>
</tr>
<tr>
<td>Inconel, hot-rolled</td>
<td>14% chromium, 6% iron</td>
<td>120,000</td>
<td>65,000</td>
<td>35</td>
<td>45,000</td>
<td>Gas turbine parts</td>
</tr>
<tr>
<td>Inconel &quot;X&quot;, hot-rolled and aged at 1300°F</td>
<td>15% chromium, 7% iron, 2.5% titanium</td>
<td>180,000</td>
<td>130,000</td>
<td>25</td>
<td>60,000</td>
<td>Springs and bolts subjected to corrosion</td>
</tr>
</tbody>
</table>
precipitated $\delta$-phase can be seen in a slowly cooled alloy, Fig. 13-12(f), although as in the 195 alloy it cannot be detected in photomicrographs of alloys aged to maximum hardness.

Nickel is another metal whose alloys are hardened principally by precipitation. Nickel is much like iron in its mechanical properties, but its corrosion properties are so much better than those of iron that it is used for many purposes despite the fact that it costs about ten times as much. Typical nickel alloys are surveyed in Table 13-2. Other nickel alloys with special electrical and magnetic properties have been considered in previous chapters. These included Alnico V and Canife, which are hardened by precipitation.

Precipitation hardening in steels is of minor interest compared with eutectoid decomposition hardening, but there are several aspects of precipitation in iron-base alloys that deserve mention. One of these is the decreased ductility of low-carbon steels resulting from the precipitation of carbon or nitrogen during quench aging or strain aging. Quench aging is the usual type of precipitation hardening, while strain aging is precipitation resulting from a cold-working operation. Both these aging effects are undesirable in mild steel, and various means, such as fixing of the carbon and nitrogen, are used to minimize them.

The following three examples of beneficial precipitation hardening in steel are of considerable industrial importance. Steels containing about one percent copper can have their yield strengths increased 25,000 lb/in$^2$ by a precipitation treatment, with only a moderate decrease in ductility. An additional advantage of these copper-bearing steels is their significantly greater resistance to atmospheric corrosion. The precipitation hardening of tool steel and stainless steel by use of aluminum is a second example. Prior to this development the popular 18 chromium-8 nickel type stainless steels could be hardened only by cold-working. The third example, one of the least understood instances of this reaction in steels, is the secondary hardening of high-speed tool steel, which has been attributed to the precipitation of a complex carbide.

**ORDER HARDENING**

The term age hardening is sometimes used as a synonym for precipitation hardening. However, this term is often needed for another, more general purpose, because order hardening (and perhaps other hardening reactions) may also occur as a result of an aging process. Therefore when a multi-component alloy hardens on being subjected to such a heat treatment, it may be impossible to determine the type of reaction that caused it to harden if its complex equilibrium diagram is unknown. However, it is possible and customary to refer to the unknown process by the general
name of age hardening. In this section a second age-hardening process, order hardening, will be discussed.

Theory. Order hardening is only a part of the larger field of order-disorder transformations, the equilibrium relations of which were considered in Chapter 6. When the atoms of a disordered solid solution arrange themselves in an orderly manner at a lower temperature, two possible structures may be produced. The first may be called an isostructural ordered phase (Fig. 13-13b); it is marked by the fact that the relative atom positions are almost the same as in the disordered phase. Little hardening can be produced by the formation of this type of ordered structure. A neostructural ordered phase (Fig. 13-13c), on the other hand, has a crystal structure that is significantly different from that of the disordered phase from which it forms. This has been indicated schematically by showing the neostructural ordered phase to have a unit cell differing in size and shape from the unit cell of the random solid solution from which it forms. As a result, lattice straining occurs during the formation of neostructural ordered phases, with an attendant increase in the hardness and strength of the alloy.

In analogy with overaging in precipitation hardening, the existence of a completely ordered structure causes the alloy to be soft. For this reason a heat treatment like that used in precipitation hardening is also used for order hardening. Figure 13-14 indicates the usual steps for successful order hardening, namely:

![Fig. 13-13. The unit cells of typical isostructural and neostructural ordered phases. (a) Random solid solution. (b) Isostructural ordered phase, A₃B. (c) Neostructural ordered phase, AB.](image)
1. choosing a composition within the range of a neostructural ordered phase;

2. obtaining the disordered solid solution at room temperature by (a) heating the alloy at a temperature within the range shown for the disordering heat treatment, (b) rapidly cooling from this temperature;

3. causing regions of ordered structure to form in the solid solution by holding the alloy at a temperature within the range indicated for the ordering heat treatment in Fig. 13-14.

During this final heat treatment, large numbers of nuclei of the ordered phase form and then proceed to grow at the expense of the disordered solid solution. The resulting hardening continues until some maximum value is reached, beyond which overaging (softening) occurs.

Ordering heat treatments at relatively high or low temperatures produce changes in hardness similar to those shown for precipitation hardening in Fig. 13-5. The ductility is decreased to about one-third of the value characteristic of the disordered alloy, but usually the remaining ductility is sufficient for engineering purposes. In comparison, about the same decrease in ductility is caused by precipitation hardening, and a somewhat greater decrease is produced by drastic cold-working, while solid-solution hardening has little effect on ductility. An important property change produced by ordering, even in the absence of hardening, is a great
reduction in electrical resistance. For example, in the gold-copper system the ordered phases have only about one-third the resistance of the corresponding disordered solid solutions and are almost equal to copper in conductivity. Figure 13-15 shows the changes in hardness and electrical resistance that occur during the ordering of the CoPt composition in the cobalt-platinum system. The magnetic hardness of this alloy parallels its mechanical hardness, and suitably aged alloys are superlative permanent magnets.

**Applications.** The principal applications of order hardening at present are in various uses of precious metals, such as jewelry, dental alloys, and electrical contacts. Generally, complex alloys in which several hardening processes may operate are used, but 18-carat gold is an example of simple order hardening by the formation of the AuCu neostructural ordered phase. Vicalloy (35% iron, 52% cobalt, 13% vanadium) is a permanent-magnet alloy that hardens by means of an ordering reaction. Ordering, as well as precipitation, may play a role in the strengthening of complex, high-temperature alloys such as S-816, Table 9-6. Solution treatment followed by aging near 1500°F improves the properties of many of these alloys for use at slightly lower temperatures.

**Diffusion-Reaction Hardening**

In contrast to precipitation hardening and order hardening, which require special heat treatments for their development, *diffusion-reaction hardening* is produced by changing the composition of the alloy. Thus, if metal $A$ dissolves metal $B$ but has limited solubility for the compound $B_xA_y$, it is sometimes possible to obtain considerable hardening by diffusing
metal C into the solid solution, thereby tending to precipitate $B_2C_x$. This process can be visualized with the aid of Fig. 13-3(d). The hardenable alloy is initially the alpha solid solution (metal B dissolved in metal A). As metal C diffuses into this solid solution, the overall composition gradually shifts into the alpha-plus-beta region of the diagram, and the beta phase ($B_2C_x$) tends to precipitate. Presumably, hardening is the result of lattice coherency which exists in the early stages of the precipitation of $B_2C_x$ in the solid solution. Only the surface layer is hardened by this process, since only a small depth is normally reached by the diffusing element.

The nitriding process for the surface hardening of steels, briefly described in Table 9-7, is an example of industrial use of diffusion-reaction hardening. The elements aluminum, chromium, and vanadium have a strong tendency to form nitrides. Therefore, when nitrogen diffuses into a steel containing one or more of these elements, particles of the nitride phases form within the steel. The extreme surface hardness that results from the nitriding treatment is attributable to the state of fine dispersion of the nitride particles rather than to the inherent hardness of large nitride grains. Softening that occurs when a nitrided steel is subjected to prolonged heating above 1000°F may be caused by loss of lattice coherency as the nitride particles become larger.

Internal oxidation, considered as a type of corrosion in Chapter 10, is an additional example of this type of hardening. The oxide forms below the surface of the alloy, and in certain cases appreciable hardening results from this internal oxidation. A silver alloy containing 0.3 percent magnesium, for example, increases its Vickers hardness from 40 to 170 on being heated in air for two hours at 800°C. About the same increase can be obtained in a copper-0.3 percent beryllium alloy. A special advantage of this type of hardening is the low electrical resistance that can be obtained. A serious disadvantage is the intergranular brittleness developed in some polycrystalline alloys. The improvement in tensile strength is only moderate, but creep strength and recrystallization temperature are greatly improved, suggesting possible applications in electrical and electronic devices.

References

PROBLEMS

1. List the hardening processes that can be used with (a) pure metals, (b) alloys.

2. What are (a) the advantages and (b) the restrictions in employing solid-state reactions to strengthen alloys?

3. What condition is necessary to render an alloy system capable of precipitation hardening?

4. Criticize the statement, "A precipitation hardening alloy can be annealed by water quenching from a suitable high temperature."

5. Use the copper-beryllium equilibrium diagram, Fig. 13-16, to choose a suitable composition for a wrought, hardenable alloy in this system. (a) What type of solid-state reaction is the basis of hardening in this case? [Note that eutectoid decomposition hardening is not feasible in this system because of the brittleness of alloys in the corresponding range of compositions.] (b) Approximately what composition is suitable for a wrought alloy? (c) Describe the procedure for the solution heat treatment of this alloy. (d) Estimate the heat-treating temperature and time that would be suitable for the precipitation heat treatment in this case.

6. Assuming that the precipitation reaction is controlled by diffusion, use the data given in Chapter 11 to estimate the time to reach maximum hardness at 100°C in an aluminum-4% copper alloy if the time at 150°C is 10 hours.

7. Explain how the formation of a neostructural ordered phase within a solid solution might set up strains similar to those produced by lattice coherency in precipitation hardening.

8. (a) Explain the process of internal oxidation by a suitable sketch. (b) What relation must exist between the diffusion constants of oxygen and of the solute metal in the solvent? Why? (c) Show by a sketch similar to Fig. 13-6 how lattice straining might occur during internal oxidation.

![Figure 13-16](attachment:image.png)
CHAPTER 14

HEAT TREATMENT OF STEEL

"When the pores of the steel have been well dilated and softened by the strong fire, and the heat has been driven out of them by the violence of the coldness of the water, these pores shrink, and the steel is converted into a hard material which, because of the hardness, is brittle."

RINGUCCIO (1540)

INTRODUCTION

For thousands of years the hardening of steel has been a principal subject in metallurgy. There have always been explanations of why the hardening occurs, but only during the past twenty years has theory radically affected practical heat-treating operations. The present theory is by no means complete, and the basic causes of hardening and embrittlement remain unknown. In this chapter is given, therefore, a broad picture of steel heat-treating that will permit the addition of the important details that are certain to become available during the coming years.

Steel heat treatments are made possible by the eutectoid reaction in the iron-carbon system. It will be recalled from Chapter 6 that the equilibrium reaction involves the decomposition, on cooling, of one solid phase into two other solid phases. Thus austenite in steel decomposes into a mixture of ferrite and cementite. Before considering the details of how the eutectoid reaction in steel can be controlled to produce a variety of useful properties, it is important to note that other alloy systems having this reaction behave in a manner similar to steels. In Chapter 6 aluminum-bronze was given as an example of a nonferrous alloy that can be hardened appreciably by eutectoid decomposition. This alloy is considered again in Problem 2 at the end of this chapter. The iron-hydrogen system is remarkably like the iron-carbon system in its eutectoid-reaction pattern, and it is unusual in developing hardness values comparable to those found in steels. No other alloy system approaches the iron-carbon system in industrial importance, however, and a principal reason for studying the related eutectoid reactions is to learn more about steel heat treatments.
Fig. 14-1. The approximate hardness of carbon steels after three different heat treatments, and the corresponding microstructure in a 0.8%C steel. (After Hain. Photomicrographs X2500; reproduced at two-thirds size. Courtesy United States Steel Research Laboratory.)
Equilibrium Conditions

The microstructures produced by slowly cooling iron-carbon alloys from the austenite region were considered in Chapter 6. It is usually assumed that this heat treatment (annealing) produces the equilibrium structure and a correspondingly low hardness. In fact, Fig. 14-1 shows that a sharp distinction exists between the hardness of a steel in the annealed condition and in the hardened (martensitic) condition. Annealed steels, however, are not in true equilibrium, since a spheroidized structure is produced by a longer heat treatment. Furthermore, even spheroidized steels are not completely at equilibrium; the carbide particles tend to grow larger and to graphitize, that is, to decompose into graphite and ferrite in accordance with Eq. (6-12). Even at temperatures near 1000°F, most steels graphitize only in the course of many years, but in some cases, such as steam-turbine piping, the conditions necessary for this reaction exist. Disastrous failures have occurred in such piping because of graphitization. (The addition of chromium appears to inhibit the formation of graphite under the conditions in question.)

Thus a rigorous definition of the equilibrium structures of steel should be made in terms of graphite and ferrite. It is more convenient, however, to define equilibrium heat treatments as those for which the usual ( metastable) equilibrium diagram, Fig. 14-3, can be used with reasonable success. These equilibrium heat treatments include austenitizing, annealing, normalizing, and spheroidizing. Diagrams other than the equilibrium diagram must be used in considering hardening heat treatments that require rapid cooling to obtain a nonequilibrium structure.

Austenitizing. The face-centered cubic form of iron, austenite, that exists at high temperatures is capable of dissolving as much as 2 percent carbon. When the austenite decomposes on cooling, only a small fraction of its carbon content can dissolve in the body-centered cubic iron (ferrite) that exists at low temperatures, and the bulk of the carbon appears in another form, Fe₃C for example. The exact nature of austenite decomposition varies with the type of steel heat treatment, but almost all heat treatments require that austenite be produced as a first step in heat-treating operations. The equilibrium diagram of Fig. 14-3 shows the lowest temperatures at which 100 percent austenite can be obtained. This temperature varies with carbon content; with increasing carbon content it decreases along the A₃ line to a minimum value A₁ at the eutectoid composition (0.8 percent carbon) and then increases along the A_cm line. However, these lowest temperatures are not used in practical heat treatments because of the slow reaction rates they produce. Figure 14-2 shows several important aspects of the austenitizing of eutectoid steels.
Time required for the isothermal formation of austenite in a normalized eutectoid steel at various austenitizing temperatures. (After Roberts and Mehl.)

As a function of time and temperature, the temperature must be somewhat above the equilibrium temperature $A_1$ to produce austenitization in a reasonable time. The first stage in the production of homogeneous austenite is the nucleation and growth of austenite from pearlite. However, after complete disappearance of the pearlite some carbide particles remain in the austenite, and even after the carbides have dissolved, their trace remains for some time in the form of inhomogeneities of carbon concentration in the austenite.

Every stage in the formation of homogeneous austenite is accelerated
by (1) increasing the temperature, and (2) increasing the fineness of the initial carbide particles. Both these factors are taken into account in commercial heat-treating operations, but temperature is the more important. The temperature used for hypoeutectoid and eutectoid steels is about 100°F above the minimum temperature for 100 percent austenite, and the corresponding time is one hour per inch of cross section of the bar being heated.* Much of this time is used in raising the bar to the temperature range in which austenitization occurs. Among the reasons for keeping the austenitizing temperature as low as possible is the increased tendency toward (1) cracking and distortion, (2) oxidation and decarburization, and (3) grain growth, as the temperature is raised. Also, higher temperatures and longer heat-treating add to the cost of the process.

At the high carbon contents of hypereutectoid steels the temperature needed for obtaining 100 percent austenite is frequently quite high. Fortunately, austenite suitable for hardening in such cases is obtained at about 1425°F. The small amount of equilibrium carbide dispersed in the austenite has little effect on the final mechanical properties, and it may actually improve wear resistance. Of course if the carbide forms an embrittling network at the grain boundaries, it is necessary to eliminate this undesirable structure by a preliminary heating above the Ac₃ line followed by moderately fast cooling. Very low-carbon steels, too, must be heated to high temperatures to austenitize them completely, but steels containing less than about 0.2 percent carbon respond poorly to hardening heat treatment and are seldom heated for this purpose.

Even the relatively low austenitizing temperatures that are adequate for steels near 0.8 percent carbon may still be too high if cracking and distortion are serious problems. Although it is impractical to lower the austenitizing temperature with respect to the temperature necessary for 100 percent austenite, it is possible to lower this equilibrium temperature by adding such suitable alloying elements as manganese and nickel. These elements not only lower the A₁ temperature but also further decrease the austenitizing temperature of hypoeutectoid steels by shifting the eutectoid point to a lower carbon content. It should be noted that other alloying elements tend to raise the A₁ temperature. Also, almost all alloying elements decrease the rate at which austenite is formed, and some of the alloy carbides are especially difficult to dissolve. Such undissolved carbides may be useful in preventing grain growth at high austenitizing temperatures.

*This general rule for heating time is a conservative estimate. An excellent, detailed discussion of this point is given in Tool Steel Simplified, Revised Edition, by F. R. Palmer and G. V. Loomis (pp. 472-499), published by Carpenter Steel Company, Reading, Pennsylvania, in 1948.
Consideration of the austenitizing process suggests another means of decreasing distortion during subsequent quenching operations. After the austenite has been formed at a higher temperature, the steel may be cooled about 100°F to just above the critical temperature ($A_3$, $A_1$, or $A_{cm}$). The austenite is stable in this region and may be quenched more safely from the lower temperature.

**Annealing.** The word annealing has the general meaning of *holding at a high temperature* and is therefore used to describe scores of heat treatments. However, in steel heat-treating it usually refers to furnace cooling from the austenitizing range shown in Fig. 14-3. This treatment is used primarily to soften certain steels to the point of optimum machinability, but it may also be used for grain refinement or chemical homogenization. It might be well to review at this point the treatment of phase analyses of the annealing of steels of various carbon contents, discussed in Chapter 6 (especially Fig. 6-25). (See Problem 1 of the present chapter.) It will be recalled that peritectoid reactions produce primary ferrite or cementite during equilibrium cooling of hypoeutectoid or hypereutectoid steels. These reactions tend to occur also during faster cooling, although in decreased amount. For simplicity this chapter is limited to eutectoid steels in which the peritectoid reactions are absent.

**Normalizing.** The name of this heat treatment was perhaps suggested by the fact that steels are air cooled from the usual manufacturing operations, like hot rolling and forging, carried out on steels in the austenite range. Therefore to put a steel in the normal condition it is air cooled from the range of austenitizing temperatures shown in Fig. 14-3. The properties of such normalized steels depend on the chemical composition and on the cooling rate; the latter in turn is determined by the size of the bar being considered. Although these two factors can produce considerable variation in the hardness of normalized steels, usually the microstructure contains relatively fine pearlite, and a phase analysis based on equilibrium cooling is not greatly in error for low- and medium-carbon steels. The principal uses of normalizing are to refine the structure of steel castings and of overheated steels and to eliminate the carbide network at the grain boundaries of hypereutectoid steels. These structural changes improve the engineering properties of the alloys.

**Spheroidizing.** The spheroidized structure shown in Fig. 14-1 produces a steel with minimum hardness and maximum ductility. At high carbon or alloy contents this structure is needed for optimum machinability and for the prevention of cracking during cold-forming operations. A number of heat treatments can be used to produce a spheroidized structure, but
all of them are relatively long and costly. Since a fine initial carbide size accelerates spheroidization, normalized steels are often chosen as the material to be processed. Spheroidization of the fine pearlite takes place when the steel is heated to just below the $A_1$ temperature and held there for about ten hours. Other methods involve holding the steel alternately just above and just below the $A_1$ temperature, or employ a high-temperature isothermal transformation of the austenite.

**NONEQUILIBRIUM AUSTENITE DECOMPOSITION**

Many heat treatments of steel involve reaction conditions so far removed from equilibrium that equilibrium diagrams are of only limited use. Their usefulness is restricted to fixing the austenitizing temperature and predicting the phases that are eventually obtained at a given composition and temperature. The principal source of information on the actual process of austenite decomposition under nonequilibrium conditions is the TTT diagram, which relates the transformation of the austenite to the time and temperature conditions to which it is subjected. Other names for this diagram are the S-curve and the C-curve.

**TTT diagram.** The TTT diagram describes the decomposition of austenite in a given steel. Therefore, for each steel composition there is a different diagram. Furthermore, such factors as the grain size of the austenite and the presence of inclusions or other inhomogeneities can change the diagram for a given steel composition, although these complications are frequently neglected. An understanding of TTT diagrams is best obtained by considering the procedure used in constructing a typical diagram.

Figure 14-4(a) indicates the method used to determine an isothermal reaction curve at a single temperature for a given steel. A number of small specimens are austenitized at a suitable temperature and are quickly transferred to a bath held at the desired reaction temperature below $A_1$. Their small size allows them to cool to the reaction temperature in a fraction of a second. After a given specimen has been allowed to react isothermally for a certain time, it is quenched in water. This stops the reaction by causing the remaining austenite to change almost instantly to martensite. When the specimen is examined under the microscope, it is usually easy to distinguish the portion of the austenite that reacted isothermally from the portion that changed to martensite on cooling. Figure 14-4(b) shows how the data on times of reaction and the corresponding amounts of austenite transformation can be plotted to give an isothermal reaction curve.

It is possible to summarize the data from a series of isothermal re-
Fig. 14-4. The method of obtaining an isothermal reaction curve at 1300°F for a eutectoid steel. (a) The steps in obtaining specimens. (b) Reaction curve determined by a metallographic examination of specimens treated as in (a). (Photomicrographs ×1000, reproduced at one-half size. Courtesy United States Steel Research Laboratory.)
action curves obtained over the whole temperature range of austenite instability for a given steel. The result is the TTT diagram for that steel. The diagram for eutectoid carbon steel is shown in Fig. 14-5, and the points determined by the isothermal reaction curve of Fig. 14-4(b) are indicated. The diagram shows the austenite decomposing in two radically different ways. At high temperatures the reaction products form with increasing time at constant temperature. Martensite, on the other hand, forms only with decreasing temperature and has almost no tendency to continue forming at constant temperature. These two modes of austenite decomposition will be considered next.

Before continuing with a detailed discussion of the constituents that may appear in steels, it will be helpful to summarize our discussion of austenite decomposition and to anticipate its relation to the tempering of martensite. Table 14-1 is useful for this purpose. It is shown here that, depending on the temperature, austenite may decompose into spheroidite, pearlite, bainite, or martensite. Of course it is also possible to produce mixtures of two or more of these constituents. The changes produced in martensite by an additional heat treatment, tempering, are of great
### Table 14-1

#### Relations among the Various Constituents Appearing in Steels

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Austenite</strong></td>
<td>Face-centered cubic iron phase containing carbon in interstitial solid solution and other alloying elements, such as manganese, nickel, chromium, etc., in substitutional solid solution. Photomicrograph shown in Fig. 5-21(b).</td>
</tr>
<tr>
<td><strong>Spheroidite</strong></td>
<td>Microconstituent composed of large spheroids of carbide phase in a matrix of ferrite phase. Photomicrograph shown in Fig. 14-1.</td>
</tr>
<tr>
<td><strong>Ferrite</strong></td>
<td>Body-centered cubic iron phase with very limited solubility for carbon. Like austenite, this phase may have other alloying elements in substitutional solid solution. Photomicrograph shown in Fig. 5-32(a).</td>
</tr>
<tr>
<td><strong>Pearlite</strong></td>
<td>Microconstituent composed of alternate plates of carbide phase and of ferrite phase. Photomicrograph of pearlite in an annealed 0.8% carbon steel shown in Fig. 14-1.</td>
</tr>
<tr>
<td><strong>Martensite</strong></td>
<td>Microconstituent composed of carbide phase in a ferritic matrix (see discussion in later section). Photomicrographs are shown in Fig. 14-19.</td>
</tr>
<tr>
<td><strong>Tempered martensite</strong></td>
<td>Microconstituent composed of carbide phase in a ferrite matrix (see discussion in a later section). Photomicrographs of tempered martensite are shown in Fig. 14-19.</td>
</tr>
<tr>
<td><strong>Primary troostite</strong></td>
<td>Older nomenclature for fine pearlite that could not be resolved by the light microscope. This type of pearlite appears in a portion of Fig. 14-6(a).</td>
</tr>
<tr>
<td><strong>Bainite</strong></td>
<td>Microconstituent composed of carbide phase and ferrite phase. Two different types of these phases are shown in Fig. 14-6.</td>
</tr>
<tr>
<td><strong>Martensite</strong></td>
<td>Body-centered tetragonal iron phase produced by entrapping carbon atoms (see discussion in later section). Photomicrograph of martensite in a harden 0.8% carbon steel shown in Fig. 14-1.</td>
</tr>
<tr>
<td><strong>Tempered martensite</strong></td>
<td>Microconstituent composed of carbide phase in a ferrite matrix (see discussion in a later section). Photomicrographs are shown in Fig. 14-19.</td>
</tr>
<tr>
<td><strong>Secondary troostite</strong></td>
<td>Older nomenclature for a tempered martensite that could not be resolved by the light microscope. Photomicrograph of this structure is shown in Fig. 14-19(a).</td>
</tr>
<tr>
<td><strong>Sorbite</strong></td>
<td>Older nomenclature for a tempered martensite that could be resolved with difficulty by the light microscope. Photomicrograph of this structure is shown in Fig. 14-19(b).</td>
</tr>
</tbody>
</table>

* The terms that appear inside boxes are older, equivalent nomenclatures that may be encountered in the literature but that do not constitute an essential part of the present discussion.
PEARLITE AND BAINITE

interest and are shown as a second series of decomposition products. The principal product is tempered martensite. Since spheroidite is the equilibrium ferrite-carbide aggregate, it is not surprising that it can be obtained either directly from austenite or as a product of tempering martensite. The significance of the older terms troostite and morbite is also indicated in this table.

Pearlite and bainite. Under the conditions used in determining a TTT diagram, both pearlite and bainite form isothermally from austenite; that is, they form with increasing time at constant temperature. As Fig. 14-5 shows, pearlite is the decomposition product of austenite at temperatures between $A_1$ and about the “nose” (or “knee”) of the TTT diagram. When austenite is cooled to a temperature within this range, there is an initial period in which no evidence of pearlite formation can be detected. This behavior is similar to the incubation period in the recrystallization of cold-worked metals. Eventually, decomposition of the austenite begins with the formation of a region of cementite that acts as the nucleus for a nodule of pearlite. This nucleation occurs preferentially at the grain boundaries of the austenite or at an inhomogeneity such as an inclusion. Growth of the pearlite nodule proceeds with the formation of alternate plates of ferrite and cementite and with the simultaneous edgewise growth

![Pearlite and Bainite Images](image_url)
of these plates [Fig. 14-4(b)]. The time necessary for pearlite formation decreases continuously with decreasing temperature, and the thickness of the ferrite and cementite plates also decreases, with a consequent increase in hardness. The increase in hardness with decrease in the temperature of austenite decomposition is also characteristic of bainite formation.

In a temperature range near the nose of the TTT diagram both pearlite and bainite tend to form, as seen in Fig. 14-4(a). However, at temperatures below this range and above the \( M_s \) point (where martensite starts to form) bainite is the only product of isothermal decomposition of austenite. The aspect of bainite changes with the temperature at which it forms. Figure 14-6 shows the 'feathery' bainite obtained in the upper part of the temperature range and the 'ar icular' (needlelike) bainite produced by lower reaction temperatures. The process of bainite formation is different at different temperatures, but in general bainite is a ferrite-cementite aggregate that forms by growing from a ferrite nucleus. The TTT diagrams of some alloy steels show two noses, one of which is associated with pearlite formation and the other with bainite formation. In these cases it may be possible for bainite to form during a quenching operation, but in carbon steels isothermal reaction is necessary to produce the characteristic bainitic structure.

Martensite. Although the austenite in a eutectoid steel is unstable at all temperatures below \( A_1 \), it has been seen that the face-centered cubic austenite does not change immediately to body-centered cubic ferrite (plus cementite) on being cooled to temperatures only moderately below \( A_1 \). At these temperatures the decomposition occurs by nucleation and growth of the equilibrium phases, and the diffusion process involved takes a relatively long time. At a sufficiently low temperature, however, the driving force that tends to cause the transformation from face-centered cubic to body-centered cubic iron becomes so strong that the change occurs without the diffusion of carbon. Since the amount of carbon present is 100 times more than can be held in solid solution, the body-centered cubic lattice is actually distorted into a tetragonal structure to which the name martensite is given. The great hardness of martensite is believed to be a result of the severe lattice strain produced by the trapped carbon atoms.

The upper temperature at which martensite begins to form is called the \( M_s \) point. At this temperature only about one percent martensite has formed during cooling of the austenite. As austenite is cooled to lower and lower temperatures the amount of martensite increases, until at the \( M_f \) point the steel is essentially all martensite (99 percent) after rapid cooling. If austenite is rapidly cooled to a temperature between
$M_s$ and $M_f$, the austenite that has not changed to martensite during cooling transforms isothermally to bainite during prolonged holding at the reaction temperature. Carbon and most other alloying elements decrease both the $M_s$ and $M_f$ temperatures, so that in certain steels even the $M_s$ point is below room temperature. Certain properties of alloy steels with an $M_f$ point below room temperature can be improved by the use of a refrigeration treatment that causes additional martensite to form. Although it has been shown that the austenite-to-martensite reaction requires a finite time, martensite formation in commercial steels is practically instantaneous.

**Continuous cooling diagram.** Commercial heat-treating operations on large pieces of steel involve cooling from the austenitizing temperature at rates that are low compared with those used in obtaining TTT curves.

![Continuous Cooling Diagram](image-url)

**Fig. 14-7.** An approximate CCT (continuous cooling transformation) diagram for eutectoid carbon steel.
We should not assume, therefore, that a given piece of steel can be cooled instantly to any temperature (to produce martensite, for example). It would be useful to have a diagram showing the changes that occur in a given steel during cooling at the various rates produced by commercial quenching operations. The complications in the actual cooling of metals make the construction of such a diagram extremely difficult, but an approximation to it is the diagram showing the transformation of austenite at the rates of cooling in various positions in a Jominy bar (see Fig. 14-15). By analogy with the more common TTT diagram, this diagram may be termed a CCT (continuous cooling transformation) diagram.

Although few accurate CCT diagrams are available, Fig. 14-7 is an approximation to the one for a eutectoid carbon steel. Figure 14-5 is the corresponding TTT diagram. The most important cooling rates on the CCT diagram are those that result in 50 percent and in 50 percent martensite. The first of these, the critical cooling rate, determines the position of the nose of this diagram, the time for which is about twice the time for the nose of the TTT diagram. The cooling rate that produces 50 percent martensite is very significant in practical heat-treating, since full hardening is usually defined in terms of 50 percent martensite at the center of the bar. No bainite forms in a eutectoid carbon steel during continuous cooling, and even in alloy steels the bainite reaction may be slowed down one thousandfold as a result of changes that take place in the earlier stages of continuous cooling.

**Hardening Heat Treatments**

The basic requirements for hardening a steel by means of the eutectoid-decomposition reaction can be summarized as follows:

1. **Adequate carbon content.** In view of the nature of martensite hardness, it is clear that some carbon must be present to produce hardening of a steel. Figure 14-1 shows that the maximum hardness increases with increasing carbon content, but since the ductility decreases rapidly, the carbon content is held near 0.45 percent in many engineering steels. For wear resistance the carbon content may be increased to over 1.0 percent, for example in tool and die steels.

2. **Nonequilibrium austenite decomposition.** Inasmuch as austenite decomposition under equilibrium conditions may produce coarse pearlite that is relatively soft, various degrees of hardening are represented by fine pearlite, bainite, and martensite. Although the term steel hardening usually refers to the production of martensite, the other two reaction products are frequently desired. The rate at which austenite must be cooled to produce a given nonequilibrium reaction product is widely variable, but quenching is always used.
Tempering is discussed on page 489, but it can be noted here that tempering is not used to harden a steel. The purpose of tempering is to restore a portion of the ductility that is lost by hardening, and often an appreciable softening is produced by the tempering heat treatment. It is also notable that alloying elements are not necessary for steel hardening and do not significantly increase the hardness of martensite obtainable in a steel of given carbon content. On the other hand, carbon is an essential component if an alloy of iron, possibly with one or more alloying elements, is to be capable of hardening by eutectoid decomposition.

Quenching. The rate at which a given portion of a steel bar cools from the austenitizing temperature depends on two factors: (1) the temperature to which the surface of the bar is cooled by the quenching medium, and (2) the rate of heat flow in the steel bar itself. This rate is relatively low, so that the center of a large bar of steel would cool slowly even if the surface of the bar could be cooled instantly to room temperature. Although heat flow is evidently important in steel hardening, it is subject to little variation and will not be considered further.

If the only object in commercial quenching of steel were to lower the surface temperature of the bar as rapidly as possible, a water solution would be a suitable cooling medium. It will be seen later that cooling in water often approximates the ideal quench, instantly lowering the surface temperature of the bar to room temperature; but an additional requirement in quenching is that cracking and excessive distortion must be prevented. Since the large temperature gradients that cause distortion are an inevitable consequence of using a drastic quenching medium, it is often necessary to use such milder cooling media as oil or an air blast. Figure 14-8 shows the smaller temperature difference between the surface and center of a steel bar quenched in oil compared with one quenched in water.

Analysis of the reactions in steel during cooling is complicated by nonuniformity in the quenching process. During the cooling of steel in a liquid medium from the austenitizing temperature, three overlapping stages of quenching occur, Fig. 14-9. The first stage is marked by the presence of a vapor film around the red-hot metal. This low-conductivity film causes slow cooling in the temperature range in which rapid cooling is necessary to avoid pearlite formation. Therefore, for effective quenching this first stage is practically eliminated by such means as agitation of the quenching liquid.
the quenching medium or addition to it of suitable chemicals. Sodium chloride and sodium hydroxide are useful additives for water quenching. During the second stage of cooling, both vapor and liquid are in contact with the hot metal, and vapor bubbles effectively transfer heat from the metal surface to the body of the quenching medium. Third-stage cooling begins when the surface of the metal cools below the boiling point of the liquid. In this stage the liquid is in complete contact with the bar and heat is transferred by the relatively slow processes of conduction and convection.

Since the cooling of steel during quenching is a complicated function of both time and position in the bar, it has been convenient to use experimentally determined cooling curves for many purposes. The Jominy hardenability test is a source of such curves. This test uses water quenching, but cooling data for other quenching media are obtained conveniently by the use of heat-flow laws.
Hardenability. In practice the success of a quenching operation is determined not in terms of stages of quenching but by the production of the desired nonequilibrium decomposition product of austenite, usually martensite. A second factor, hardenability, plays an important role in such successful hardening. In the absence of adequate hardenability the most drastic quench is incapable of producing martensite in a steel bar of a given size. A convenient method of separating the effects of quenching and of hardenability on martensite formation involves the use of $H^*$ values for various types of quenching. The ideal quench, which would instantly cool the surface of a hot bar to room temperature, has an $H$ value of infinity ($\infty$). Actual quenching mediums have $H$ values from 10 to 0.02, and their effectiveness compared with the ideal quench can be determined. The $H$ values of several quenching mediums are given in Table 14-2.

**Table 14-2**

<table>
<thead>
<tr>
<th>Type of quench</th>
<th>$H$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>$\infty$</td>
</tr>
<tr>
<td>Agitated brine</td>
<td>5</td>
</tr>
<tr>
<td>Still water</td>
<td>1</td>
</tr>
<tr>
<td>Still oil</td>
<td>0.3</td>
</tr>
<tr>
<td>Cold gas</td>
<td>0.1</td>
</tr>
<tr>
<td>Still air</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*H* represents the cooling power of the quenching medium; it does not stand for hardenability.

**Ideal critical diameter.** The definition of hardenability is conveniently given in terms of a specific measure of hardenability, i.e., the *ideal critical diameter* $D_i$. This hardenability value for a given steel is the diameter in inches of a cylindrical bar that will form 50 percent martensite at the center during an ideal quench. (The 50 percent martensite value is arbitrarily chosen for convenience in measuring.) The significance of this hardenability value is that a bar of this steel with a diameter larger than the ideal critical diameter cannot be hardened all the way through its cross section even by an infinitely rapid quench. Thus hardenability is an index of the depth to which martensite can be formed in a given steel as the result of a given hardening treatment. Hardenability is not an indication of the hardness of a steel. The hardness of martensite is determined by carbon content, and a high-carbon steel may have a relatively low hardenability.
The ideal critical diameter can be determined experimentally, but it can also be calculated from the chemical composition of the steel. For the latter purpose two types of factor are required: a base diameter $D_c$ that depends on carbon content and grain size,* Fig. 14-10, and multiplying factors $F$ for each of the alloying elements, Fig. 14-11. The ideal critical diameter is the product of $D_c$ and all the multiplying factors for the alloying elements in the given steel. Thus the ideal critical diameter of a steel with a No. 8 grain size and containing 0.5% C, 0.6% Mn, 1% Cr, and 2% Ni is

$$D_I = D_c \times F_{\text{Mn}} \times F_{\text{Cr}} \times F_{\text{Ni}},$$

$$D_I = 0.22 \times 3.00 \times 3.17 \times 1.77 \quad (14-1)$$

$$= 3.70 \text{ inches}.$$ 

Since the ideal critical diameter represents the size bar that could be fully hardened (50 percent martensite at the center) by an ideal quench, it is evident that only smaller bars of this steel can be fully hardened by such actual quenching mediums as oil or water. Figure 14-12 shows the relation between ideal critical diameter and the critical diameter $D_0$.

* The meaning of the A.S.T.M. grain size numbers is shown by the ordinates of Fig. 12-14.
† The critical diameter corresponding to an actual quenching medium has also been denoted by $D_0$ in the literature.
3.80
3.40
3.00
2.60
2.20
1.80
1.40
1.00

Mn
Cr
Ni
Si

HARDENABILITY

FIG. 14-11. Multiplying factors $F$ for several of the common alloying elements. (Boyd and Field.)

Fig. 14-12. The relation between ideal critical diameter and critical diameter $D_R$ that can be fully hardened using a quenching medium with a given cooling power $H$.

that can be fully hardened by means of a quenching medium with a given $H$ value. From this chart it can be determined that for a steel with $D_R = 3.70$ inches, $D_{1.0} = 2.80$ inches and $D_{0.3} = 1.75$ inches. That is, a 2.80-inch bar of this steel can be fully hardened by water quenching, and a 1.75-inch bar by oil quenching.

An additional correction of the ideal critical diameter must be made when the part to be hardened cannot be considered equivalent to a long
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Fig. 14-13. The relation between ideal critical diameter and the critical thickness $T_n$ of a plate that can be fully hardened using a quenching medium with a given cooling power $H$.

Fig. 14-14. The steps in obtaining a Jominy curve. (a) Procedure for end-quenching a Jominy bar after transfer to the quenching jig from the austenitizing furnace. (b) Jominy curve obtained by plotting the hardness values measured along the length of the quenched bar.
Hardenability

Cooling Rate at 1300°F, °F/sec

<table>
<thead>
<tr>
<th>Distance from End of Jominy Bar, inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>190</td>
</tr>
</tbody>
</table>

**Fig. 14-15.** The correspondence between cooling rates at the center of ideal rounds and at various distances from the quenched end of a Jominy bar.

cylinder. Figure 14-13 shows the relation between ideal critical diameter and the critical thickness of a plate that can be hardened by a given quench. For complex shapes it is usually possible to make a fairly close estimate of the corresponding ideal critical diameter by comparison with the data for cylinders and plates.

**Jominy test.** Hardenability is a property of steel, and a given heat of steel has a definite hardenability, which may be expressed in terms of ideal critical diameter. However, other measures of hardenability such as that given by a Jominy test, may also be used. This test is standardized and can be performed easily by both users and manufacturers of steel. Figure 14-14(a) shows the procedure for end-quenching the standard Jominy bar after it has been given a suitable austenitizing treatment. This type of quenching produces in the bar a wide range of cooling rates that decrease from a maximum at the quenched end. Figure 14-15 gives the cooling rate at various distances from the quenched end and also shows the corresponding size of ideal round that has the same cooling rate at its center. Hardness tests along the length of the end-quenched bar are plotted to obtain a Jominy curve, Fig. 14-14(b).

Typical Jominy curves for a number of AISI (American Iron and Steel Institute) steels, Table 14-3, are shown in Fig. 14-16(a). A Jominy curve is strictly valid only for a given heat of the specified steel, since the permitted range in chemical composition allows an appreciable range in hardenability. Figure 14-16(b) shows the hardenability band within which the hardenability curves for all heats of AISI 4145H steel will lie.

The wide possible variation in hardenability among bars of steel of the same AISI grade must be considered in choosing a steel to meet a hardenability requirement. In mass production heat treatments it is generally
### Table 14-3

**Brief Descriptions of Some AISI Steels**

<table>
<thead>
<tr>
<th>AISI number</th>
<th>Average alloy content*</th>
<th>Average hardenability of 0.45% carbon steel; ideal critical diameter in inches</th>
<th>Approximate cost relative to carbon steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>10xx</td>
<td>none</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>13xx</td>
<td>1.8-2.0% Mn</td>
<td>3.3</td>
<td>1.2</td>
</tr>
<tr>
<td>20xx</td>
<td>3.5% Ni</td>
<td>3.4</td>
<td>1.8</td>
</tr>
<tr>
<td>31xx</td>
<td>0.7-0.8% Cr, 1.3% Ni</td>
<td>4.7</td>
<td>1.4</td>
</tr>
<tr>
<td>41xx</td>
<td>0.5-1.0% Cr, 0.2-0.3% Mo</td>
<td>6.3</td>
<td>1.4</td>
</tr>
<tr>
<td>43xx</td>
<td>0.5-0.8% Cr, 1.8% Ni, 0.3% Mo</td>
<td>7.5 (0.40% C)</td>
<td>1.7</td>
</tr>
<tr>
<td>51xx</td>
<td>0.8-1.1% Cr</td>
<td>3.3</td>
<td>1.3</td>
</tr>
<tr>
<td>61xx</td>
<td>0.8-1.0% Cr, 0.1-0.2% V</td>
<td>3.7</td>
<td>1.6</td>
</tr>
<tr>
<td>86xx</td>
<td>0.6% Ni, 0.5-0.7% Cr, 0.2% Mo</td>
<td>4.0</td>
<td>1.4</td>
</tr>
<tr>
<td>87xx</td>
<td>0.6% Ni, 0.5% Cr, 0.3% Mo</td>
<td>4.4</td>
<td>1.4</td>
</tr>
<tr>
<td>92xx</td>
<td>1.4-2.0% Si, 0.6-0.9% Mn, 0-0.7% Cr</td>
<td>2.7 (0.55% C)</td>
<td>1.4</td>
</tr>
<tr>
<td>94xx</td>
<td>1.1-1.2% Mn, 0.5% Ni, 0.4% Cr, 0.1% Mo</td>
<td>4.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*All the steels contain less than 1.0% Mn, 0.05% P, 0.05% S, 0.35% Si, and residual amounts of other alloying elements unless otherwise noted.

Uneconomical to choose a steel of such high hardenability that even bars with the minimum hardenability would be satisfactory, since this would require a more expensive steel. However, to avoid excessive rejections because of inadequate hardening, a suitable steel must possess a reasonably high average hardenability.

The decomposition of austenite in a portion of a quenched bar is governed by the cooling rate at that place in the bar. Correlation of the cooling rates at various depths below the surface of an actual steel part with the corresponding cooling rates in a Jominy test makes it possible to predict the hardness distribution that would be produced by a given quenching medium. Often the hardness (and strength) must be above a specified value throughout a given steel part. Since the center hardness is the minimum value in a steel bar, attention can often be restricted to this point in the bar. The Jominy method allows consideration of center hardnesses different from the hardness corresponding to 50 percent martensite used in defining ideal diameter. However, in practice the "half-
INTERRUPTED QUENCHING

Interrupted quenching. The rapid cooling to room temperature ordinarily used to cause martensite formation has the disadvantage of setting up severe stresses in the steel. These stresses are the combined effect of contraction during cooling and expansion caused by the martensite reaction, and they can easily cause cracking or distortion of heat-treated parts. The very slow cooling rate produced by cooling steel in still air from the austenitizing temperature decreases quenching stresses to a minimum, but steels with sufficient hardenability to form martensite on air cooling are expensive. Such air-hardening steels are chosen for complex dies for which preliminary machining costs are high; in these cases it is economical to protect the investment in machining operations by the use of a steel that can be hardened with a minimum danger of distortion or cracking. Almost equal freedom from quenching stresses can be obtained in steels of moderate hardenability by an interrupted quenching procedure. If the steel can be rapidly cooled past the nose of the CCT diagram, Fig. 14-7, it can then be slowly cooled through the martensite reaction or be allowed to form lower bainite.

Martempering. The most generally useful type of interrupted quenching is called martempering. It is a hardening operation that produces

* Also called marquenching.
Diagram of the cooling curve of the center of a steel bar.

**Fig. 14-17.** Two types of interrupted quenching. (a) Martempering an austenitized steel bar. (b) Producing bainite by an austempering treatment.

Martensite; it is not tempering. The steel is quenched in a molten salt bath held at a temperature near the $M_s$ point, Fig. 14-17(a). When the entire piece has reached the bath temperature and before the bainite reaction starts, the steel is removed from the bath and air cooled. The martensite that forms on air cooling is just as hard as that formed by water quenching, but serious stresses are not set up. Although subsequent tempering is not required to remove quenching stresses, it is customarily used to increase ductility. A variation of martempering is *timed quenching*, in which the steel is quenched in oil or water for a time sufficient to decrease its average temperature to about the $M_t$ temperature. It is then allowed to air cool as in martempering. The hardenability required for martempering is slightly greater than that needed for oil quenching, while timed quenching requires no increase in hardenability over that for oil or water quenching.

**Austempering.** This process involves the formation of bainite rather than martensite. Figure 14-17(b) shows that the quenching procedure is much like that used for martempering, except that the molten lead or salt bath is usually at a higher temperature and the steel is held in the bath until transformation to bainite is complete. Since the quenching bath of higher temperature has lower cooling power, a higher hardenability is needed for austempering than for martempering. Tempering is rarely needed after austempering. Besides decreasing quenching stresses, this heat treatment produces relatively high impact resistance in the high-hardness range, where hardened and tempered steels may be somewhat brittle.
TEMPERING

After completion of the hardening heat treatment, it is usually desirable to increase the ductility of the steel. This is accomplished by tempering, which consists of heating the hardened steel to some temperature below $A_1$ for about one hour to produce tempered martensite. Essentially, the tempering reaction can be pictured as the change from carbon atoms dispersed in the martensite to precipitated carbide particles of increasing size. Figure 14-18 indicates a number of stages by which this change is believed to occur. At low tempering temperatures a hexagonal close-packed carbide (called epsilon carbide) begins to form, and with this rejection of carbon the crystal structure of martensite changes ultimately from tetragonal to the body-centered cubic characteristic of ferrite. At high temperatures the epsilon carbide is converted to Fe$_3$C, which is orthorhombic in crystal structure. Prolonged tempering just below the $A_1$ temperature results in large Fe$_3$C particles in a ferrite matrix, a spheroidite structure. The tempering reaction is a function of both temperature and time, but temperature is far the more important variable, and the time of tempering usually adopted is about one hour. Figure 14-19 shows the microstructures produced by tempering a eutectoid carbon steel at two different temperatures.

Tempering also serves to eliminate the residual stresses in the hardened steel. These are of two types: (1) the macroscopic stresses produced during quenching, and (2) the microscopic stresses inherent in the martensitic structure. The origin of residual stresses and their relief by heating are discussed in Chapter 8.

Full hardening followed by tempering results in a combination of
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CHAP. 14

Fig. 14-19. Microstructures of tempered martensite in a plain carbon eutectoid steel: (a) tempered at 800°F for one hour, (b) tempered at 1100°F for one hour (both X2500; reproduced at three-fourths size). (Courtesy United States Steel Research Laboratory.)

properties generally superior to that achieved by other treatments. However, in practice some pearlite or bainite may be mixed with the martensite if the local cooling rate is less than the critical rate necessary to avoid the nose of the CCT diagram. Also, retained austenite may be present if the $M_t$ temperature is below room temperature. In either case, poorer properties are obtained after tempering. In certain high-alloy steels, the retained austenite is converted to brittle martensite on cooling from the tempering temperature, and a second tempering treatment is helpful in such cases.

Commercial tempering treatments are complicated by the presence of two little understood effects, temper brittleness and 500°F embrittlement. The term "500°F embrittlement" refers to the low ductility of steels tempered in the range of about 500 to 800°F. Tempering in this range is often avoided. Temper brittleness develops in certain alloy steels either when they are tempered in the range 800 to 1100°F, or when they are slowly cooled through this range after being tempered at a higher temperature. This embrittlement can often be prevented in critical instances by water-quenching the steel from a tempering temperature of 1100°F or above.

Although raising the tempering temperature usually produces an improvement in ductility, it also lowers the strength and hardness. Hence the useful upper tempering temperature is limited. For example, plain carbon and low-alloy tool steels that require high hardness for wear resistance are usually tempered below 500°F, and only a slight decrease in hardness results from this treatment, Fig. 14-18. On the other hand,
the superior ductility needed in medium carbon AISI steels for use in automobiles, airplanes, and other machines requires the use of high tempering temperatures that significantly decrease the hardness. The effect of tempering medium-carbon steels is shown in Fig. 14–20. Alloying elements have little effect on tempering below 500°F, but their influence in retarding softening at higher temperatures is sometimes very great, as the behavior of high-speed steels shows, Fig. 14–22. Even low-alloy steels differ somewhat from plain carbon steel during tempering, as can be seen in Fig. 14–20.

Data on tempering usually refer to an initial structure that is 100 percent martensite. Since 50 percent pearlite or bainite may be present at the center of a fully hardened steel bar, the hardness change at the center of the bar is less than that near the surface. On tempering near 1000°F, the hardness decrease for a 50 percent martensite structure is roughly 10 points $R_C$ (Rockwell C) less than that for 100% martensite. But the final hardness of the surface remains higher than that of the center, since the initial hardness difference between 100 percent martensite and 50 percent martensite is usually about 15 points $R_C$ in medium-carbon steels.

Hardness values are used to indicate the progress of tempering of AISI steels, not because hardness is an important property in itself but because it is related to design quantities such as yield strength and percent of elongation. Figure 14–21 shows some approximate relations for medium-carbon AISI steels. The endurance limit of these steels is about one-half of the tensile strength; that is, they have an endurance ratio of about 0.5. At tensile strengths above 200,000 lb/in² the endurance ratio tends to decrease slightly.

It should be strongly emphasized that the optimum properties of a steel are almost always obtained when its microstructure consists of
tempered martensite. To produce this microstructure it is first necessary to obtain martensite; here a working knowledge of hardenability is essential. When the martensite is tempered to the desired hardness, the excellent properties given in Fig. 14-21 are obtained. The poorer properties of a steel that has a pearlitic structure are clearly shown by the following data. When steel 4340 has a pearlitic structure such that the reduction in area in a tension test is 45 percent, the corresponding yield strength is only 70,000 lb/in². In contrast, from Fig. 14-21 it can be seen that the same reduction in area can be obtained with a yield strength of about 160,000 lb/in² for a structure consisting of tempered martensite. The importance of producing a martensitic structure during the hardening operation will again be evident in the following discussion of the application of steels.

Applications

In almost every use of iron-base alloys some aspect of eutectoid decomposition is considered. Steels that must be hardened before service are an outstanding example, but it is as important to avoid martensite
in many welded parts where good ductility is essential. Although the basic steel hardening reactions can occur in plain iron-carbon alloys, many applications are made possible by the special properties conferred by alloying elements. No attempt can be made here to cover the entire field of carbon and alloy steels, but a few of the principal types are briefly surveyed.

**Carbon steels.** The main advantage of unalloyed steels is their low cost. By the addition of alloying elements it is possible to obtain a steel with a better combination of properties or a longer life, but in many cases the higher cost of alloy steel cannot be justified. Consequently, carbon steel represents about 90 percent of all the steel produced in the world. Its uses are widely varied and range from massive I-beams to quality tool bits. Although most carbon steel is employed in the hot-rolled condition, other important forms are as-cast shapes, cold-finished rods and sheets, and heat-treated parts. Some properties of representative carbon steels are given in Table 6-3.

Two aspects of the behavior of hot-rolled steel deserve special mention. The first of these is the variation of the hardness of as-rolled bars with bar size. During air cooling from the rolling temperature the austenite in hypoeutectoid hot-rolled steels decomposes into a mixture of ferrite and pearlite. The cooling rate increases as the size of the steel bar decreases, and the fine pearlite produced in small bars is harder than the pearlite in larger bars. This effect becomes less important as the carbon content (and the amount of pearlite) decreases. A second characteristic of hot-rolled steels is the variation of properties with direction of testing in the bar. This directionality of properties is present because of the same "fiber" characteristic previously described in forged products. Although the strength properties are almost isotropic, the percentages of elongation and reduction in area are only about half as great in the transverse direction as they are in the direction of rolling; the effect on impact strength is even larger. These directional effects are further increased when hot-rolled steel is subjected to cold-finishing operations, such as cold rolling or cold drawing.

Compared with alloy steels, plain carbon steels have the disadvantages of lower hardenability and a poorer combination of properties in the heat-treated condition. Water quenching, with its danger of distortion and cracking, must almost always be used because of the lower hardenability, and even this drastic quench is incapable of fully hardening most carbon-steel bars greater than one inch in diameter. If a wear-resisting surface is required on larger bars, induction- or flame-hardening must be used. Moreover, when a tempered martensitic structure is successfully obtained throughout the cross section of a suitably small bar of carbon
steel, the ductility is significantly lower at a given strength value than in
the case of alloy steels. For example, in steels containing about 0.4 per­
cent carbon and tempered to a yield strength of 100,000 lb/in², the com­
parative ductilities and impact strengths are approximately as follows:

<table>
<thead>
<tr>
<th></th>
<th>Carbon steel</th>
<th>Alloy (AISI) steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Elongation</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>% Reduction of area</td>
<td>45</td>
<td>60</td>
</tr>
<tr>
<td>Izod impact strength, ft·lb</td>
<td>20</td>
<td>90</td>
</tr>
</tbody>
</table>

In spite of these disadvantages, the low cost of carbon steels encourages
their use in the heat-treated condition for many applications.

Alloy steels. Alloving elements added to a steel may act in a variety
of ways. Their effect on hardening and tempering heat treatments is con­
considered in this chapter, and previously their influence on solid-solution
hardening and carbide formation was discussed (Chapter 6). Special
effects may be produced also, such as increasing the corrosion resistance
and imparting the ability to harden by precipitation or diffusion reaction.
Although the individual alloving elements may have special attributes, it is
more convenient to divide the alloy steels into broad groups on the basis
of their principal advantages over carbon steels than on the basis of alloy
content. Such groups include the following:

<table>
<thead>
<tr>
<th>Group</th>
<th>Principal advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-alloy steels</td>
<td></td>
</tr>
<tr>
<td>AISI steels</td>
<td>Increased hardenableability</td>
</tr>
<tr>
<td>High-strength low-alloy</td>
<td>Higher yield strength in the hot-structural steels</td>
</tr>
<tr>
<td>structural steels</td>
<td></td>
</tr>
<tr>
<td>High-alloy steels</td>
<td></td>
</tr>
<tr>
<td>Tool steels</td>
<td>Higher quality with special properties</td>
</tr>
<tr>
<td>Stainless steels</td>
<td>Improved corrosion resistance</td>
</tr>
<tr>
<td>High-temperature steels</td>
<td>Improved properties at high temperatures</td>
</tr>
<tr>
<td>Special purpose steels</td>
<td>Special magnetic or other properties</td>
</tr>
</tbody>
</table>

The stainless, high-temperature, and special purpose steels have been
considered in earlier chapters, and only the three remaining groups are discussed here.

**AISI steels.** This group of steels can be roughly described as containing a total of less than about five percent alloying elements and as being used, most often after heat treatment, in machine construction by such industries as automobile manufacturing. In fact, the basis of the AISI classification is the similar standardization made earlier by the Society of Automotive Engineers, and many of the steels can also be termed SAE steels. A standard number is used for each steel; the first two digits refer to the alloy content, and the last two (or three) digits express the carbon content in points of carbon, where one point is equal to one-hundredth of one percent. Permissible variations in composition are established for each steel. A letter may precede the numbers to indicate the steelmaking process used or a special chemical analysis.* An H following the numbers designates a steel produced to a hardenability specification, and wider composition ranges are allowed for these steels.

A typical AISI steel designation is A3145; it has the following interpretation:

```
A3145
```

- **Basic open-hearth alloy steel**
- **Chromium-nickel steel**
- **45 points of carbon**
- **Cr = 0.70—0.90%**
- **Ni = 1.10—1.40%**
- **C = 0.43—0.48%**

Brief descriptions of the principal AISI steels are given in Table 14-3. Complete composition limits can be found in the Metals Handbook.

The variable of principal importance in AISI steels is the hardenability. Average ideal critical diameter values are given in Table 14-3. In a specific case it is of course necessary to achieve a minimum yield strength, elongation, etc. However, to a good approximation the combination of properties shown in Fig. 14-21 is obtained when any one of these low-alloy steels is fully hardened and then tempered to a given hardness. For example, assume that the final hardness is 320 Brinell. By reading down from this value in Fig. 14-21, we can estimate that the corresponding Rockwell hardness is about 35, the yield strength is about 140,000 lb/in², the reduction in area is 52 percent, the impact strength is 50 ft-lb, and the elongation is 17 percent. Other properties such as machinability,

* *A* = basic open-hearth alloy steel  
* B = acid-Bessemer carbon steel  
* C = basic open-hearth carbon steel  
* D = acid open-hearth carbon steel  
* E = electric furnace steel  
* X = special chemical analysis  
* T =
susceptibility to temper brittleness, wear resistance, weldability, and formability are of varying significance in different applications, but the lowest-cost steel having adequate hardenability appears to be suitable for most purposes. This conclusion is supported by the fact that the same gear or shaft is usually made from a range of AISI steels by the various automobile manufacturers.

High-strength, low-alloy structural steels. This group of materials is essentially ordinary structural steel with one or two percent of alloying elements added. Since it is not feasible to quench and temper the large structural steel beams used in bridges and large buildings, it may be asked why alloying is used in these steels. In most instances the purpose is threefold:

1. Ordinary low-carbon structural steel has a yield strength of only 25,000 to 30,000 lb/in². This value can be doubled by solid-solution alloying without greatly affecting the cold formability of the steel.

2. The character of austenite decomposition can be balanced between the desirability of (a) increasing the strength by forming fine pearlite (mixed with proeutectoid ferrite) during cooling from the hot-rolling operation, and (b) avoiding hardening and the accompanying embrittlement when welding is used as a method of fabrication.

3. The resistance to atmospheric corrosion can be increased by the use of a combination of copper, phosphorus, and chromium.

Many different compositions that achieve these purposes are marketed under various trade names, but typically these steels contain about 0.12% carbon, 0.6% manganese, 0.5% copper, 0.5% nickel, 0.1% phosphorus, and perhaps additions of chromium, molybdenum, zirconium, vanadium, or titanium. The properties are usually in the following range: yield strength, 50,000-60,000 lb/in²; tensile strength, 70,000-80,000 lb/in²; and 28-33% elongation in 8 inches. Since the cost of these steels usually exceeds that of low-carbon structural steel by less than 50 percent, it is often economical to use them, particularly when weight saving is of principal concern.

Tool steels. Depending on the design of the tool and its intended use, the characteristics of a suitable steel for its manufacture are widely variable. These characteristics include hardenability, wear resistance, nondeforming properties,* and resistance to softening on heating. All tool steels, however, are alike in being of high quality. Most tool steels are manufactured in electric furnaces and therefore have fewer nonmetallic

* All steels deform somewhat during hardening heat treatments. However, some steels exhibit a minimum of distortion and therefore can be machined almost to final size before hardening. Such nondeforming steels are especially useful for complex dies.
inclusions than alloy steels made in open-hearth furnaces. Especially careful hot-working and surface-cleaning operations guard against internal or external flaws. The resulting tool-steel-quality material minimizes the danger of cracking during the heat treatment of complex shapes, and it also produces greater toughness at the high-hardness levels necessary in most tool applications.

Tool steels are largely sold under trade names, and about a thousand different steels are available in this country. Most of these can be grouped adequately in about thirty categories, and a still shorter list of the principal types of tool steel is given in Table 14-4. The relation between the properties of a given type of steel and its applications should be noted. Heat treatment of most tool steels that operate at ordinary temperatures is not essentially different from that previously described for carbon and low-alloy steels. Greater care is used in heating and quenching because of the inherent brittleness of high-carbon tool steels, and tempering is done at a low temperature that only slightly decreases the hardness while significantly increasing the toughness.

Certain tool steels, especially those used at temperatures near 1000°F, must be given a special heat treatment to develop their unusual properties. As an example, the most popular high-speed steel, 18-4-1 (see Table 14-4), is considered here. Although the equilibrium phase relations in this multicomponent system are not completely known, it appears that austenitizing temperatures near the melting range must be used to obtain austenite with sufficient carbon and alloying elements in solution to produce martensite of the necessary hot hardness. Since this austenitizing temperature is about 2350°F, it is usual to preheat steel parts to 1500°F before placing them in the high-temperature furnace. Oil quenching from the austenitizing temperature is common, but quenching in a molten salt bath or air cooling may also be used. To reduce the danger of cracking, the steel is tempered immediately upon cooling to near room temperature.

High-speed steel that is ready for tempering has the following constituents: (1) carbides that were undissolved at the austenitizing temperature and were unaffected by quenching, (2) martensite that formed from a portion of the austenite on cooling below the $M_s$ temperature, and (3) austenite that failed to transform to martensite. The amount of this retained austenite depends on such factors as the composition and the austenitizing temperature; about 20 percent is present in commercial practice. The behavior both of the martensite and of the retained austenite influences the course of tempering. Figure 14-22 shows that the usual decrease in hardness occurs on tempering up to about 600°F. This effect is

* Hot hardness is hardness as measured at elevated temperatures.
Table 14-4
CHARACTERISTICS OF SOME PRINCIPAL TYPES OF TOOL STEEL*

<table>
<thead>
<tr>
<th>Type of tool steel</th>
<th>Principal alloy content</th>
<th>Relative hardenability</th>
<th>Quenching medium</th>
<th>Satisfactory hardness</th>
<th>Non-ductile fracture</th>
<th>Toughness</th>
<th>Resilience to softening on heating</th>
<th>Wear resistance</th>
<th>Machinability</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>1.00 0.35</td>
<td>poor</td>
<td>water</td>
<td>fair</td>
<td>poor</td>
<td>poor</td>
<td>fair</td>
<td>good</td>
<td>good</td>
<td>Drill, reamer, small dies, cutters, etc.</td>
</tr>
<tr>
<td>Oil hardening</td>
<td>0.95 1.20 0.50 0.30</td>
<td>fair</td>
<td>oil</td>
<td>very good</td>
<td>fair</td>
<td>poor</td>
<td>fair</td>
<td>good</td>
<td>good</td>
<td>General tool and die applications in which resistance to distortion or cracking is needed.</td>
</tr>
<tr>
<td>Air hardening</td>
<td>1.00 0.50 5.00 0.75</td>
<td>good</td>
<td>air</td>
<td>best</td>
<td>fair</td>
<td>fair</td>
<td>very good</td>
<td>fair</td>
<td>fair</td>
<td>Pneumatic chisels, concrete breakers, rivet sets</td>
</tr>
<tr>
<td>Tungsten steel</td>
<td>0.80 0.35 2.50 0.35</td>
<td>fair</td>
<td>oil</td>
<td>good</td>
<td>fair</td>
<td>very good</td>
<td>fair</td>
<td>fair</td>
<td>fair</td>
<td>Taps for hard-turning machines, honing, finishing tools</td>
</tr>
<tr>
<td>Chromium tool steel</td>
<td>0.50 0.30 4.00 0.75</td>
<td>good</td>
<td>air</td>
<td>good</td>
<td>good</td>
<td>fair</td>
<td>good</td>
<td>fair</td>
<td>fair</td>
<td>General purpose for tool operating at high cutting speeds</td>
</tr>
<tr>
<td>H-1 high speed</td>
<td>0.70 0.30 10.00 1.00</td>
<td>good</td>
<td>oil, air, salt bath</td>
<td>good</td>
<td>poor</td>
<td>very good</td>
<td>very good</td>
<td>fair</td>
<td>fair</td>
<td></td>
</tr>
</tbody>
</table>

* Largely adapted from the section on tool steels in the 1949 Metals Handbook.
apparently analogous to that found in carbon steels. However, as the tempering temperature is increased, the hardness measured at room temperature increases to a maximum at about 1000°F. The principal cause of this secondary hardening is the formation of complex carbides, possibly in a manner that produces precipitation hardening. Further hardening is due to martensite produced by decomposition of the retained austenite on cooling from the tempering temperature. Since the steel is toughened by tempering this martensite, high-speed steel is frequently double tempered by heating at about 1050°F for two hours, air cooling, and then repeating the tempering treatment.

**Fig. 14–22.** A typical tempering curve for 18-4-1 high-speed steel.

![Tempering Curve](image-url)

**REFERENCES**

1. Make phase analyses for (a) 0.4% C, (b) 0.8% C, and (c) 1.2% C steels under equilibrium conditions at (1) a temperature in the austenite region, (2) 1335°F, (3) 1330°F, and sketch the corresponding microstructures. How much pearlite is present at 1330°F in each of these steels?

2. (a) In the portion of the Cu-Al diagram shown in Fig. 14–23 there are two eutectoid reactions. Specify their locations by giving the temperature and composition of each of the eutectoid points. (b) In Table 6-6 the composition of the hardenable aluminum bronze is given as 10.5% Al. Give a possible reason for the choice of this composition. (Note the elongation values of the 5% and 10.5% Al alloys in Table 6-6.) (c) Make phase analyses for the 10.5% Al alloy under equilibrium conditions at the following temperatures: (1) 1600°F, (2) 1300°F, (3) 1055°F, (4) 1045°F, and sketch the corresponding microstructures. (d) How much eutectoid microconstituent (analogous to pearlite) is present at 1045°F?

3. (a) In a steel to be austenitized, is it preferable that the initial structure be coarse spheroidite or fine pearlite? (b) Explain your answer in terms of the mechanism of isothermal austenite formation. (c) Specify the heat-treating conditions (time, temperature, cooling rate, etc.) suitable for (1) annealing, (2) normalizing, (3) spheroidizing a bar of hot-rolled 0.8% C steel one inch in diameter.

Fig. 14–23. A portion of the copper-aluminum equilibrium diagram.
4. (a) Describe a practical procedure for determining experimentally the isothermal reaction curve for the decomposition of austenite in a given steel at 700°F. (b) Sketch a typical reaction curve. (c) Show that most of the information given by this curve can be recorded in the TTT diagram for the steel.

5. (a) If a hot-rolled 0.8% C steel bar one inch in diameter is heated to 1200°F, held for 15 seconds, and quenched in water, can the TTT diagram of Fig. 14-5 be used to predict the structure produced? (b) Explain.

6. Since the austenite grain size influences such properties as impact strength and hardenability, it is often necessary to determine the grain size of the austenite in a given heat of steel at the austenitizing temperature. Making use of the fact that pearlite, proeutectoid ferrite, and proeutectoid cementite form preferentially at the austenite grain boundaries, suggest possible procedures for determining the austenite grain size in steels containing (a) 0.4% C, (b) 0.8% C, and (c) 1.2% C. (Note: A completely pearlitic structure is not convenient for determining grain size.)

7. Compare the usefulness of (a) the equilibrium diagram, (b) the TTT diagram, and (c) the CCT diagram in predicting the effect of normalizing a one-inch bar of eutectoid steel.

8. "Steel is made hard by quenching." List at least three requirements that must be met to justify this statement.

9. Determine the ideal critical diameter (IE) of AISI 6145 steel that has a No. 8 grain size. An average composition is

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.45</td>
</tr>
<tr>
<td>Mn</td>
<td>0.8</td>
</tr>
<tr>
<td>Cr</td>
<td>0.2</td>
</tr>
<tr>
<td>Ni</td>
<td>0.3</td>
</tr>
</tbody>
</table>

(Note: The effect of vanadium is variable and may be neglected here.)

10. What diameter bars of the steel of Problem 9 could be fully hardened (50% martensite at the center) using each of the following quenching media: (a) still air, (b) still oil, (c) still water, and (d) agitated brine?

11. A one-inch diameter shaft of AISI 6145 steel is to be oil quenched and then tempered for one hour at 800°F. Estimate the final surface and center hardness. (Hint: Figures 14-12, 14-15, 14-16(a), and 14-20 contain relevant information.)

12. A suitable steel for a shaft 1½ inches in diameter is to be chosen. The shaft must be oil quenched, tempered at 1000°F, and must have a minimum Rockwell C hardness of 35 at the surface and 30 at the center. Specify a 0.45% C steel for this application.

13. A steel shaft two inches in diameter must have a minimum yield strength of 180,000 lb/ln² in tension. If oil quenching were used with an AISI 5145 steel, what is the maximum tempering temperature that could be used?
APPENDIX

LITERATURE OF METALLURGY

"Knowledge is of two kinds. We know a subject ourselves, or we know where we can find information upon it."

SAMUEL JOHNSON

WANTED: INFORMATION

The practical application of metallurgy often consists in answering the question "What metal is suitable for this job?" Usually the answer is not obvious. Required mechanical, physical, and chemical properties vary widely depending on the particular application; the nature of a suitable alloy varies accordingly. Even the basic engineering requirement that lowest cost be achieved is not necessarily satisfied by choosing the least expensive material. Platinum, which costs a hundred dollars an ounce, may be the proper choice even though cast iron costs only a few cents a pound. Although each instance of adapting metals for a given purpose is an individual problem, there is a general pattern often followed in obtaining a solution.

First, from a consideration of basic principles (economic, physical, chemical, and metallurgical) a relatively small number of alloys can be chosen for study. For example, only silver, copper, gold, aluminum, or alloys based on these metals are useful in applications that require high electrical conductivity. Furthermore, the high cost of silver and gold eliminates these metals from consideration in most cases. Such initial restriction of the field of study is a practical necessity, since there are thousands of commercial alloys and an infinity of possible combinations of known metals. This first step also determines the critical properties on which the final choice of alloy depends. Hardenability, creep strength, oxidation resistance, and endurance limit are typical properties of primary interest.

The second step in choosing a suitable metal is to determine what is known about the materials and properties in question. While the ideal way to do this might be to ask the men who know, a close approach to this unattainable ideal is to read what they have contributed to the technical literature. To do this effectively it is necessary first to be able to find the pertinent writings and then to understand the results given in
them. Both tasks present difficulties. The immense volume and diversity of the metallurgical literature are obstacles to its use. This appendix can aid in this respect by serving as a convenient guide to pertinent information within this extensive literature. The purpose of the entire textbook is to overcome the second difficulty by supplying sufficient background for competent reading of the significant technical books and articles.

In some cases a reasonable search of the recorded work of others fails to produce sufficient information for a logical choice of the best alloy. The third step, running a testing program, may then be undertaken. This procedure has undeniable advantages, especially in permitting simultaneous control of the many variables, such as composition, temperature, stress conditions, corroding atmosphere, etc., that influence actual applications. The cost and difficulty of an adequate investigation, however, are great, and it is foolish to waste effort in obtaining information that is already available.

**LITERATURE SOURCES**

Since the technical literature is of such tremendous importance in solving practical problems of alloy application, a working guide to it is given here. The laboratory for literature research is a library with its card catalogs, indexes, and reference books. Reasonable proficiency in using these facilities is easily acquired. The librarian can be helpful in the solution of more difficult search problems. He has valuable knowledge of the local library collection, and he can borrow specialized volumes on inter-library loan. In the following sections the extensive technical literature is considered in convenient divisions.

**Textbooks.** An effective start on a literature search can be made with textbooks, which are introductory and explanatory, and usually assume little previous knowledge of the subject. Characteristically, they give a superficial survey of a wide field or a range of subjects, rather than an intensive treatment of a single subject. Ordinarily, suitable textbooks can be located by using the library subject index cards. If the library shelves are searched directly, it is convenient to know the principal Dewey and Library of Congress classification numbers:

<table>
<thead>
<tr>
<th>Dewey Classification</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>669</td>
<td>General Metallurgy</td>
</tr>
<tr>
<td>670-673</td>
<td>Metal Manufacture</td>
</tr>
<tr>
<td>739</td>
<td>Metal Arts</td>
</tr>
<tr>
<td>620.1</td>
<td>Engineering Properties of Metals</td>
</tr>
</tbody>
</table>
If a more thorough search for a textbook must be made, two bibliographies can be used. Warren lists metallurgical books published from 1936 to 1946, and Rimbach lists those published before 1936.


Each of these bibliographies has a subject and an author index. Textbooks published after 1946 can be found with the aid of an abstract service such as Chemical Abstracts, Metallurgical Abstracts, or the ASM Review of Metal Literature. The Cumulative Book Index is a useful guide to books published in the English language, and Whitaker's Cumulative Book List covers British books.

Handbooks. These volumes have concise, detailed information on a broad range of subjects and are designed to aid the average worker. The Metals Handbook is outstanding for general metallurgical work. At the time of this writing a new edition is in preparation; only the 1948 edition and its supplements are currently available.


This book has been called the metallurgists' Bible, and no search of the literature could be considered complete without its use. However, like most of the remaining literature sources, effective use of the Metals Handbook requires a preliminary study of the particular subject and of general metallurgy. Other handbooks and similar works containing metallurgical data are the following:

Monographs. These books are written on a single subject, and therefore they are usually complete, advanced treatments. Although no sharp division can be made between textbooks and monographs, a textbook usually covers the important aspects of a broad field while a monograph treats a small part of this field in great detail. For example, a textbook on general metallurgy may devote only a few pages to the extraction of copper from its ore, while the same subject is the sole content of several monographs on the metallurgy of copper. An outstanding monograph series is The Alloys of Iron and its successor, Alloys of Iron Research. Individual volumes in this series treat the following alloying elements in iron: carbon, molybdenum, copper, tungsten, silicon, chromium, titanium, nickel, aluminum, and additional elements such as boron. Metallurgy of the Rarer Metals is another monograph series that to date includes volumes on chromium, zirconium, manganese, titanium, and molybdenum.

For many purposes no distinction is made between textbooks and monographs, and both are listed in the bibliographies given above. In spite of the evident merit of monographs as sources of information, they have two disadvantages. The more serious one is that many aspects of metallurgy are not treated in monographs. This situation appears inevitable in view of the diversity and complexity of metallurgical interests.
Moreover, monographs rarely appear in revised or new editions, so that the latest monograph may be many years out of date.

A literature source that is similar to a monograph in being a specialized, advanced treatment of a specific topic is the review article. Each annual volume of the following series contains a number of reviews.

**Metallurgical Reviews.** London: Institute of Metals. (Individual numbers are published bimonthly.)


Textbooks, handbooks, and monographs are easily located and their presentations are reasonably complete; however, they are several months to several years behind the latest information, and frequently they fail to supply the specific facts needed. Superior on both counts are the original literature sources, especially the journals. Since thousands of original articles of metallurgical interest appear each year, there are few subjects on which published information does not exist. Unfortunately, the task of locating the available data is not easy, but with the help of a few library aids a thorough search can be made in a reasonable time. The indispensable guides to this metallurgical literature are treated in the following section.

**Abstracts and indexes.** Several journals are wholly or partly devoted to summarizing the current literature of a given field (literature that consists of government publications, patents, and books, as well as journal articles). The main purpose of these abstracting and indexing journals is to allow the reader to survey the current literature. When the reader finds a reference to an article of special interest to him, he can then locate a copy of the article and obtain full information from it. The more complete abstract services have another use. In some cases it is inconvenient to refer to the original article (if it is in a foreign language, for example), and the abstract itself may then be a useful source of information.

**Metallurgical Abstracts** appears monthly as a section of the *Journal of the Institute of Metals* (British) and as a separate annual volume. This excellent abstract service, especially of foreign literature, has appeared since 1909. Cumulative indexes cover the periods 1909–1921, 1921–1933, and 1934–1943. Typical of the abstracts is the following:

*Construction and Applications of a Hot Stage for High-Temperature Metallography.* Ernst Pfeiffer (Z. Metallkunde, 1957, 48, (4), 171–175).—A vacuum hot-stage capable of maintaining temperature up to 1100°C is described. The specimen structure is revealed by thermal etching. Photo-
Micrographs illustrate some examples of its use, viz. the study of grain-boundary movements in a Ni-Fe alloy, the \( \beta \rightarrow \alpha \) transformation in Ti, and dissolution of impurities in a magnet alloy of high permeability.

Metallurgical Abstracts covers general and nonferrous metallurgy, and a similar abstract section in the Journal of the Iron and Steel Institute (British) surveys the literature of the iron and steel industry.

ASM Review of Metal Literature is published as a yearly volume by the American Society for Metals; the first volume appeared in 1944. The individual numbers from which the annual volume is made are published monthly as the "Metals Review." During the early years of this literature service its brief abstracts were intended to serve only as a guide to the general nature of the articles. Recently, however, many of the abstracts have also reported specific results, as the following example illustrates:


Preliminary investigation of inverse grayness occurring in certain types of commercially produced blackheart malleable castings, factors affecting the incidence of this defect in thin sections attached to a relatively heavier section of a test casting. Inverse grayness was found to increase simultaneously with mottle in the heavy section when the Al, Si, C, or Mn content was increased. High casting temperatures and an increase in the thickness of the thin section also aggravated the defect. 3 ref.

Many of the abstracts in the ASM Review of Metal Literature appear also in Crerar Metals Abstracts, a literature service devoted to metals now coming into prominence, such as titanium.

The most complete abstracting of metallurgical literature is provided by the Russian publication Referativnyj Zhurnal Metallurgii. Each monthly number is about 300 pages and the yearly volume contains over 20,000 abstracts. A translation of the abstracts of Russian articles appearing in this journal is available as The Abstracts Journal of Metallurgy. Typical of these abstracts is the following:


Using a Müller field-emission electron-microscope, a study was made of the allotropic transformation \( \alpha \) (hexagonal close-packed) \( \Rightarrow \beta \) (b.c.c.). This technique provides visual observation of metallic phase transformations in crystallites in the size range \( 10^{-4} - 10^{-5} \) cm, with a resolution of 20-100Å. When a needle of Zr was heated above transformation temperature (862°C) it formed a \( \beta \)-Zr single crystal, which on cooling below this temperature transformed to an \( \alpha \)-Zr single crystal. The process of \( \beta \rightarrow \alpha \) transformation was not always
geometrically reversible. However in all cases the mutual orientations of the crystals of initial and final phases obeyed the relationship discovered by Burgers: (0001)_β // (110)_α and [1120]_β // [111]_α. These relationships permit the occurrence of 12 orientations of the new phase in the $\beta \rightarrow \alpha$ change, and of 6 orientations in the $\alpha \rightarrow \beta$ change, for a given orientation of the initial phase. In practice one (occasionally 2) of the possible orientations of the new phase was realized, namely that leading to the minimum change in surface energy.

Chemical Abstracts contains much of metallurgical interest, most of it in Section 9, Metallurgy. The abstracts are factual and are of especial value for foreign publications, as the following example shows:

The mechanism of oxidation reactions of metals and alloys at high temperatures. Jacques Bénard (Univ. Paris). Trabajos reunion intern. reactividad solidos, 3°, Madrid, 1956, 1, 153-70 (Pub. 1957) (in French).—The formation of oxide nuclei in the oxidation of NiCr and FeCr alloys at high temp. (900-1200°) in an atm. of $H_2$ containing a small partial pressure of $H_2O$ is reviewed. The striations of the metal surface appearing between the nuclei when these coalesce are investigated. It is concluded that the striations occur owing to a reduction of surface energy of the metal by oxide films and by layers of adsorbed $O$.

It is necessary to search the individual issues of Chemical Abstracts for just the current year, since author and subject indexes are published annually, and indexes covering a ten-year period are available for 1916, 1926, 1936, 1946 and 1956.

Engineering Index appears as an annual volume with numbers going back to 1884, and is primarily an index to technical, industrial, and commercial literature, with emphasis on publications in English. The references for the current year are also available as a card file to which additions are continually made during the year. The short annotation accompanying each reference is useful in determining the character of the article; for example:

Metallurgy, vacuum applications


Different fields of application and advantages of vacuum procedures; annealing and degassing, sintering, melting and alloying, sublimation and distillation, vacuum coating.

Applied Science & Technology Index is issued monthly and as an annual bound volume. (Prior to 1958 this service was called the Industrial Arts Index.) The articles it indexes, mainly from American technical journals, are conveniently listed alphabetically under suitable subject headings. Since little information other than the title is given, the actual content of indexed articles is largely unknown. The following entry illustrates the procedure used:
Metals, Nonferrous

Planning the melting department of a nonferrous foundry. ill diag Foundry 85:160-1 + N '57.

In addition to the relatively complete abstracting and indexing periodicals given above, there are scores of more specialised ones, like the following:

<table>
<thead>
<tr>
<th>Periodical</th>
<th>Subject</th>
</tr>
</thead>
<tbody>
<tr>
<td>Science Abstracts, Section A</td>
<td>Physics</td>
</tr>
<tr>
<td>Science Abstracts, Section B</td>
<td>Electrical engineering</td>
</tr>
<tr>
<td>Nickel Bulletin</td>
<td>Nickel and its alloys</td>
</tr>
<tr>
<td>Engineers' Digest</td>
<td>Foreign engineering literature</td>
</tr>
<tr>
<td>Bibliographical Bulletin for Welding and Allied</td>
<td>Welding</td>
</tr>
<tr>
<td>Processes</td>
<td></td>
</tr>
<tr>
<td>Nuclear Science Abstracts</td>
<td>Atomic energy</td>
</tr>
</tbody>
</table>

An especially useful index to the literature of a narrow field is a recent bibliography (list of books, journal articles, patents, etc.) of that field. Examples of such bibliographies are


Bibliographies are indexed in the regular abstract and index journals, and are especially well listed in the Bibliographic Index. There are few formal, complete bibliographies, but most journal articles and technical books give a partial list of the references in the field, with special attention to the latest publications. Therefore it is often possible to build up a practical bibliography on a specialized subject by locating a few of the more recent articles and tracing back through the references given in them.

Original sources. Technical journals, government publications, and patents constitute the original literature sources. It is principally to these that the abstract services refer. Also, textbooks and monographs are
compiled from these literature sources. The chief practical value of this original literature is its detailed treatments of a tremendous variety of subjects, including their most recent developments. In addition, study of the current and older journals gives a perspective of the field that permits a just evaluation of the newer work.

Journals. Most journals publish several numbers or issues each year, usually one a month, and each number contains about ten articles in the field of the given journal. The numbers for one year are bound with an index for easy reference, and frequently indexes covering ten years or more are available. Only a fraction of the edition of each journal is sold to libraries; many engineers subscribe for the monthly issues in order to keep informed of the latest advances. Technical societies publish many of the important journals for their members. The Metallurgical Society of AIME (American Institute of Mining, Metallurgical and Petroleum Engineers) publishes the Journal of Metals and the Transactions of the Metallurgical Society of AIME. The American Society for Metals (ASM) publishes Metal Progress and the Transactions of ASM. Other representatives of the numerous journals of interest to metallurgists are the following:

- Acta Metallurgica
- Physika Metalloc i Metallovedenie (Russian)
- Iron Age
- Journal of the Institute of Metals (British)
- Journal of the Japan Institute of Metals
- Journal of the Iron and Steel Institute (British)
- Light Metal Age
- Metallovedenie i Oborotka Metalloc (Russian)
- Metallurgia (British)
- Revue de Metallurgie (French)
- Stahl und Eisen (German)
- Stal' (Russian)
- Steel
- Welding Journal
- Zeitschrift für Metallkunde (German)

Government publications. The federal and state governments and foreign governments publish thousands of articles each year, many of them on metallurgy. Although abstract services list many of these publications, there is no convenient guide or index to all of this literature. Current American literature can be followed by means of two Government Printing Office publications:

- Monthly Catalog of United States Government Publications
- Monthly Checklist of State Publications

The government publications in a given field can be covered most con-
veniently by means of bulletins issued by the individual bureaus. Those of special interest for metallurgy are

List of Publications, Bureau of Mines

An important type of technical report is that issued by university and industrial laboratories reporting the results of research sponsored by the federal government. These and other government reports are made available to the public by the Office of Technical Services and are listed in the monthly publication U. S. Government Research Reports. The yearly volume contains a detailed index.

**Patents.** Since the subject matter contained in a patent is ordinarily not described in the previous literature, patents would seem to be an excellent source of new information. However, this fund of metallurgical knowledge is frequently obscured by legal jargon and the desire of the author to obtain maximum protection with minimum disclosure. Even so, the patent literature frequently yields valuable material. One of the most practical indexes to metallurgical patents is Chemical Abstracts, which abstracts them in the same way it does journal articles; for example:

*Stainless steel for deep drawing.* Wallace B. Leffingwell and Carl W. Weesner (to Sharon Steel Corp.). U. S. 2,808,353, Oct. 1, 1957. The 17%-Cr steels of the 430 and 442 types, when severely stretched or strained in forming, have the disadvantage of forming directional lines or bands sometimes called "roping" or "washboard." A phase-redistribution heat-treatment helps produce a strip product having a min. of directional tendency and better ductility. The treatment consists of passing the strip through and heating it in a continuous furnace at 1950°F for 1–10 min., followed by air cooling.

When more information concerning the patent is desired, the patent number indicates the entry in the Official Gazette of the U. S. Patent Office. This weekly publication does not print the entire patent but only the essential drawing and the most important claims. It also contains the following indexes: (1) names of patentees, and (2) classification of patents according to use. A cumulative Annual Index is available for each year. If study of the entire patent is necessary, a copy can be purchased from the Commissioner of Patents or found in one of the several libraries having patent files.

**Manufacturers' literature.** In addition to publications by their engineers and scientists in the technical journals, many manufacturers contribute useful information to the metallurgical literature by means of bulletins, pamphlets, books, and motion pictures. These are usually available free on request to those who have a real need for them. Because of the tendency toward one-sided presentation of these company publications, it is advisable to study them after obtaining a thorough grounding in the subject from
other sources. However, many of these publications supply excellent treatments of manufacturing procedure, operation of equipment, application of alloys, etc.

Convenient sources of the names of the larger manufacturers in various fields are the advertisements in current issues of such journals as Metal Progress, Journals of Metals, and Iron Age. More complete lists are given in such general references as

MacRae's Blue Book
Sweet's File
Thomas' Register of American Manufacturers

Many libraries have a trade catalog collection, usually indexed according to subject. However, the diversity of subject matter and the frequency with which new editions or publications appear seriously limit the usefulness of this source of manufacturers' literature.

Specifications and standards play an important part in the purchase of metallurgical products. The most important source of standards and specifications is the American Society for Testing Materials (ASTM), but many of the larger companies have their own requirements. In the ASTM Standards volumes for ferrous and nonferrous metals, there are methods of testing, recommended practices, and detailed specifications covering the purchase of materials. Other sources of metal standards include

Alloy Casting Institute
Society of Automotive Engineers
U. S. Bureau of Standards
U. S. Government Specifications
American Standards Association

Practical use of the literature. Perhaps this recital of literature sources explains the paradox that many people do not use the literature because there is too much of it. A typical result of this practice, cited by Rimbach, was the repeated proposal or actual construction of rectangular iron blast furnaces in 1857 (Prussia), 1863 (Russia), 1889 and 1910 (Germany), and 1925 (United States). The new furnaces were eventually replaced by the conventional circular ones because of difficulties in charging the ore, coke, and limestone, and in collecting the exhaust gases.

Although it is impractical to set a normal length of time for searching the literature in a given instance, it is safe to say that rarely is too long a period used for this purpose. Considering the months or years of able, diligent effort that underlie each technical article, certainly a few hours or days spent in locating and reading the work are worth while. Even a routine problem merits some literature search, while an indispensable part of an extensive investigation is thorough coverage of previous work. In addition
to the sources of information given here, such coverage may include
doctoral dissertations, privately published company reports, foreign
patents, and other sources, some of which are described in the references
at the end of this appendix.

In obtaining information on a new subject, an effective procedure is to
consult textbooks, handbooks, monographs, abstract services, original
sources, and manufacturers' literature, in that order. The most recent
literature should be read first, since it frequently summarizes the older
work and gives references to it. How far back in time it is profitable to
search is determined by the subject matter. (The history of metal spraying,
for example, is short compared with that of foundry processes.) It is con­
venient to record each reference in a form suitable for use in a bibliography,
 together with adequate notes on its contents. From such notes a survey of
the field can be prepared either for immediate application or as the basis for
new developmental or research work.

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PROBLEMS

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obtaining information on permanent
magnet alloys.
2. What are the disadvantages of
using an abstract instead of the original
article?
3. How can useful data on a patent
be obtained without access to a copy
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