A scanning electron micrograph which shows the microstructure of a plain carbon steel that contains 0.44 wt% C. The large dark areas are proeutectoid ferrite. Regions having the alternating light and dark lamellar structure are pearlite; the dark and light layers in the pearlite correspond, respectively, to ferrite and cementite phases. During etching of the surface prior to examination, the ferrite phase was preferentially dissolved; thus, the pearlite appears in topographical relief with cementite layers being elevated above the ferrite layers. 3000x. (Micrograph courtesy of Republic Steel Corporation.)

Why Study Phase Diagrams?

One reason why a knowledge and understanding of phase diagrams is important to the engineer relates to the design and control of heat treating procedures; some properties of materials are functions of their microstructures, and, consequently, of their thermal histories. Even though most phase diagrams represent stable (or equilibrium) states and microstructures, they are, nevertheless useful in understanding the development and preservation of nonequilibrium structures and their attendant properties; it is often the case that these properties are more desirable than those associated with the equilibrium state. This is aptly illustrated by the phenomenon of precipitation hardening (Sections 11.10 and 11.11).
Learning Objectives

After studying this chapter you should be able to do the following:

1. (a) Schematically sketch simple isomorphous and eutectic phase diagrams.
   (b) On these diagrams label the various phase regions.
   (c) Label liquidus, solidus, and solvus lines.
2. Given a binary phase diagram, the composition of an alloy, its temperature, and assuming that the alloy is at equilibrium, determine:
   (a) what phase(s) is (are) present;
   (b) the composition(s) of the phase(s); and
   (c) the mass fraction(s) of the phase(s).
3. For some given binary phase diagram, do the following:
   (a) locate the temperatures and compositions of all eutectic, eutectoid, peritectic, and congruent phase transformations; and
   (b) write reactions for all these transformations for either heating or cooling.
4. Given the composition of an iron–carbon alloy containing between 0.022 wt% C and 2.14 wt% C, be able to
   (a) specify whether the alloy is hypoeutectoid or hypereutectoid;
   (b) name the proeutectoid phase;
   (c) compute the mass fractions of proeutectoid phase and pearlite; and
   (d) make a schematic diagram of the microstructure at a temperature just below the eutectoid.

10.1 Introduction

The understanding of phase diagrams for alloy systems is extremely important because there is a strong correlation between microstructure and mechanical properties, and the development of microstructure of an alloy is related to the characteristics of its phase diagram. In addition, phase diagrams provide valuable information about melting, casting, crystallization, and other phenomena.

This chapter presents and discusses the following topics: (1) terminology associated with phase diagrams and phase transformations; (2) the interpretation of phase diagrams; (3) some of the common and relatively simple binary phase diagrams, including that for the iron–carbon system; and (4) the development of equilibrium microstructures, upon cooling, for several situations.

Definitions and Basic Concepts

It is necessary to establish a foundation of definitions and basic concepts relating to alloys, phases, and equilibrium before delving into the interpretation and utilization of phase diagrams. The term component is frequently used in this discussion; components are pure metals and/or compounds of which an alloy is composed. For example, in a copper–zinc brass, the components are Cu and Zn. Solute and solvent, which are also common terms, were defined in Section 5.4. A nother term used in this context is system, which has two meanings. First, “system” may refer to a specific body of material under consideration (e.g., a ladle of molten steel). Or, it may relate to the series of possible alloys consisting of the same components, but without regard to alloy composition (e.g., the iron–carbon system).

The concept of a solid solution was introduced in Section 5.4. By way of review, a solid solution consists of atoms of at least two different types; the solute atoms occupy either substitutional or interstitial positions in the solvent lattice, and the crystal structure of the solvent is maintained.
10.2 Solubility Limit

For many alloy systems and at some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution; this is called a solubility limit. The addition of solute in excess of this solubility limit results in the formation of another solid solution or compound that has a distinctly different composition. To illustrate this concept, consider the sugar–water (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}–H\textsubscript{2}O) system. Initially, as sugar is added to water, a sugar–water solution or syrup forms. As more sugar is introduced, the solution becomes more concentrated, until the solubility limit is reached, or the solution becomes saturated with sugar. At this time the solution is not capable of dissolving any more sugar, and further additions simply settle to the bottom of the container. Thus, the system now consists of two separate substances: a sugar–water syrup liquid solution and solid crystals of undissolved sugar.

This solubility limit of sugar in water depends on the temperature of the water and may be represented in graphical form on a plot of temperature along the ordinate and composition (in weight percent sugar) along the abscissa, as shown in Figure 10.1. Along the composition axis, increasing sugar concentration is from left to right, and percentage of water is read from right to left. Since only two components are involved (sugar and water), the sum of the concentrations at any composition will equal 100 wt\%. The solubility limit is represented as the nearly vertical line in the figure. For compositions and temperatures to the left of the solubility line, only the syrup liquid solution exists; to the right of the line, syrup and solid sugar coexist. The solubility limit at some temperature is the composition that corresponds to the intersection of the given temperature coordinate and the solubility limit line. For example, at 20°C the maximum solubility of sugar in water is 65 wt\%. As Figure 10.1 indicates, the solubility limit increases slightly with rising temperature.

10.3 Phases

Also critical to the understanding of phase diagrams is the concept of a phase. A phase may be defined as a homogeneous portion of a system that has uniform physical and chemical characteristics. Every pure material is considered to be a

![Figure 10.1 The solubility of sugar (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}) in a sugar–water syrup.](image)
phase; so also is every solid, liquid, and gaseous solution. For example, the sugar–
water syrup solution just discussed is one phase, and solid sugar is another. Each
has different physical properties (one is a liquid, the other is a solid); furthermore,
each is different chemically (i.e., has a different chemical composition); one is
virtually pure sugar, the other is a solution of $H_2O$ and $C_{12}H_{22}O_{11}$. If more than
one phase is present in a given system, each will have its own distinct properties,
and a boundary separating the phases will exist across which there will be a discontinu-
ous and abrupt change in physical and/or chemical characteristics. When two
phases are present in a system, it is not necessary that there be a difference in both
physical and chemical properties; a disparity in one or the other set of properties
is sufficient. When water and ice are present in a container, two separate phases
exist; they are physically dissimilar (one is a solid, the other is a liquid) but identical
in chemical makeup. Also, when a substance can exist in two or more polymorphic
forms (e.g., having both FCC and BCC structures), each of these structures is a
separate phase because their respective physical characteristics differ.

Sometimes, a single-phase system is termed “homogeneous.” Systems com-
posed of two or more phases are termed “mixtures” or “heterogeneous systems.”
Most metallic alloys, and, for that matter, ceramic, polymeric, and composite systems
are heterogeneous. Ordinarily, the phases interact in such a way that the property
combination of the multiphase system is different from, and more attractive than,
either of the individual phases.

### 10.4 Microstructure

Many times, the physical properties and, in particular, the mechanical behavior
of a material depend on the microstructure. Microstructure is subject to direct
microscopic observation, using optical or electron microscopes; (this topic was
touched on in Section 5.12.) In metal alloys, microstructure is characterized by the
number of phases present, their proportions, and the manner in which they are
distributed or arranged. The microstructure of an alloy depends on such variables
as the alloying elements present, their concentrations, and the heat treatment of
the alloy (i.e., the temperature, the heating time at temperature, and the rate of
cooling to room temperature).

(The procedure of specimen preparation for microscopic examination was
briefly outlined in Section 5.12. After appropriate polishing and etching, the different
phases may be distinguished by their appearance.) For example, for a two-phase
alloy, one phase may appear light, and the other phase dark, as in the chapter-
opening photograph for this chapter. When only a single phase or solid solution is
present, the texture will be uniform, except for grain boundaries that may be
revealed (Figure 5.16b).

### 10.5 Phase Equilibria

Equilibrium is another essential concept. It is best described in terms of a thermody-
namic quantity called the free energy. In brief, free energy is a function of the
internal energy of a system, and also the randomness or disorder of the atoms or
molecules (or entropy). A system is at equilibrium if its free energy is at a minimum
under some specified combination of temperature, pressure, and composition. In
a macroscopic sense, this means that the characteristics of the system do not change
with time but persist indefinitely; that is, the system is stable. A change in tempera-
ture, pressure, and/or composition for a system in equilibrium will result in an
increase in the free energy and in a possible spontaneous change to another state whereby the free energy is lowered.

The term phase equilibrium, often used in the context of this discussion, refers to equilibrium as it applies to systems in which more than one phase may exist. Phase equilibrium is reflected by a constancy with time in the phase characteristics of a system. Perhaps an example best illustrates this concept. Suppose that a sugar–water syrup is contained in a closed vessel and the solution is in contact with solid sugar at 20°C. If the system is at equilibrium, the composition of the syrup is 65 wt% C$_{12}$H$_{22}$O$_{11}$–35 wt% H$_2$O (Figure 10.1), and the amounts and compositions of the syrup and solid sugar will remain constant with time. If the temperature of the system is suddenly raised—say, to 100°C—this equilibrium or balance is temporarily upset in that the solubility limit has been increased to 80 wt% C$_{12}$H$_{22}$O$_{11}$ (Figure 10.1). Thus, some of the solid sugar will go into solution in the syrup. This will continue until the new equilibrium syrup concentration is established at the higher temperature.

This sugar–syrup example has illustrated the principle of phase equilibrium using a liquid–solid system. In many metallurgical and materials systems of interest, phase equilibrium involves just solid phases. In this regard the state of the system is reflected in the characteristics of the microstructure, which necessarily include not only the phases present and their compositions but, in addition, the relative phase amounts and their spatial arrangement or distribution.

Free energy considerations and diagrams similar to Figure 10.1 provide information about the equilibrium characteristics of a particular system, which is important; but they do not indicate the time period necessary for the attainment of a new equilibrium state. It is often the case, especially in solid systems, that a state of equilibrium is never completely achieved because the rate of approach to equilibrium is extremely slow; such a system is said to be in a nonequilibrium or metastable state. A metastable state or microstructure may persist indefinitely, experiencing only extremely slight and almost imperceptible changes as time progresses. Often, metastable structures are of more practical significance than equilibrium ones. For example, some steel and aluminum alloys rely for their strength on the development of metastable microstructures during carefully designed heat treatments (Sections 11.5 and 11.10).

Thus not only is an understanding of equilibrium states and structures important, but the speed or rate at which they are established and, in addition, the factors that affect the rate must be considered. This chapter is devoted almost exclusively to equilibrium structures; the treatment of reaction rates and nonequilibrium structures is deferred to Chapter 11.

**EQUILIBRIUM PHASE DIAGRAMS**

Much of the information about the control of microstructure or phase structure of a particular alloy system is conveniently and concisely displayed in what is called a phase diagram, also often termed an equilibrium or constitutional diagram. Many microstructures develop from phase transformations, the changes that occur between phases when the temperature is altered (ordinarily upon cooling). This may involve the transition from one phase to another, or the appearance or disappearance of a phase. Phase diagrams are helpful in predicting phase transformations and the resulting microstructures, which may have equilibrium or nonequilibrium character.
Equilibrium phase diagrams represent the relationships between temperature and the compositions and the quantities of phases at equilibrium. There are several different varieties; but in the present discussion, temperature and composition are the variable parameters, for binary alloys. A binary alloy is one that contains two components. If more than two components are present, phase diagrams become extremely complicated and difficult to represent. The principles of microstructural control with the aid of phase diagrams can be illustrated with binary alloys even though, in reality, most alloys contain more than two components. External pressure is also a parameter that influences the phase structure. However, in practicality, pressure remains virtually constant in most applications; thus, the phase diagrams presented here are for a constant pressure of one atmosphere (1 atm).

10.6 Binary Isomorphous Systems

Possibly the easiest type of binary phase diagram to understand and interpret is that which is characterized by the copper–nickel system (Figure 10.2a). Temperature is plotted along the ordinate, and the abscissa represents the composition of the alloy, in weight percent (bottom) and atom percent (top) of nickel. The composition ranges from 0 wt% Ni (100 wt% Cu) on the left horizontal extremity to 100 wt% Ni (0 wt% Cu) on the right. Three different phase regions, or fields, appear on the diagram, an alpha (α) field, a liquid (L) field, and a two-phase α + L field. Each region is defined by the phase or phases that exist over the range of temperatures and compositions delimited by the phase boundary lines.

The liquid L is a homogeneous liquid solution composed of both copper and nickel. The α phase is a substitutional solid solution consisting of both Cu and Ni atoms, and having an FCC crystal structure. At temperatures below about 1080°C, copper and nickel are mutually soluble in each other in the solid state for all compositions. This complete solubility is explained by the fact that both Cu and Ni have the same crystal structure (FCC), nearly identical atomic radii and electronegativities, and similar valences, as discussed in Section 5.4. The copper–nickel system is termed isomorphous because of this complete liquid and solid solubility of the two components.

A couple of comments are in order regarding nomenclature. First, for metallic alloys, solid solutions are commonly designated by lowercase Greek letters (α, β, γ, etc.). Furthermore, with regard to phase boundaries, the line separating the L and α + L phase fields is termed the liquidus line, as indicated in Figure 10.2a; the liquid phase is present at all temperatures and compositions above this line. The solidus line is located between the α and α + L regions, below which only the solid α phase exists.

For Figure 10.2a, the solidus and liquidus lines intersect at the two composition extremities; these correspond to the melting temperatures of the pure components. For example, the melting temperatures of pure copper and nickel are 1085°C and 1453°C, respectively. Heating pure copper corresponds to moving vertically up the left-hand temperature axis. Copper remains solid until its melting temperature is reached. The solid-to-liquid transformation takes place at the melting temperature, and no further heating is possible until this transformation has been completed.

For any composition other than pure components, this melting phenomenon will occur over the range of temperatures between the solidus and liquidus lines;
both solid $\alpha$ and liquid phases will be in equilibrium within this temperature range. For example, upon heating an alloy of composition 50 wt% Ni–50 wt% Cu (Figure 10.2a), melting begins at approximately 1280°C (2340°F); the amount of liquid phase continuously increases with temperature until about 1320°C (2410°F), at which the alloy is completely liquid.
10.7 Interpretation of Phase Diagrams

For a binary system of known composition and temperature that is at equilibrium, at least three kinds of information are available: (1) the phases that are present, (2) the compositions of these phases, and (3) the percentages or fractions of the phases. The procedures for making these determinations will be demonstrated using the copper–nickel system.

Phases Present

The establishment of what phases are present is relatively simple. One just locates the temperature–composition point on the diagram and notes the phase(s) with which the corresponding phase field is labeled. For example, an alloy of composition 60 wt% Ni–40 wt% Cu at 1100°C would be located at point A in Figure 10.2a; since this is within the α region, only the single α phase will be present. On the other hand, a 35 wt% Ni–65 wt% Cu alloy at 1250°C (point B) will consist of both α and liquid phases at equilibrium.

Determination of Phase Compositions

The first step in the determination of phase compositions (in terms of the concentrations of the components) is to locate the temperature–composition point on the phase diagram. Different methods are used for single- and two-phase regions. If only one phase is present, the procedure is trivial: the composition of this phase is simply the same as the overall composition of the alloy. For example, consider the 60 wt% Ni–40 wt% Cu alloy at 1100°C (point A, Figure 10.2a). At this composition and temperature, only the α phase is present, having a composition of 60 wt% Ni–40 wt% Cu.

For an alloy having composition and temperature located in a two-phase region, the situation is more complicated. In all two-phase regions (and in two-phase regions only), one may imagine a series of horizontal lines, one at every temperature; each of these is known as a tie line, or sometimes as an isotherm. These tie lines extend across the two-phase region and terminate at the phase boundary lines on either side. To compute the equilibrium concentrations of the two phases, the following procedure is used:

1. A tie line is constructed across the two-phase region at the temperature of the alloy.
2. The intersections of the tie line and the phase boundaries on either side are noted.
3. Perpendiculars are dropped from these intersections to the horizontal composition axis, from which the composition of each of the respective phases is read.

For example, consider again the 35 wt% Ni–65 wt% Cu alloy at 1250°C, located at point B in Figure 10.2b and lying within the α + L region. Thus, the problem is to determine the composition (in wt% Ni and Cu) for both the α and liquid phases. The tie line has been constructed across the α + L phase region, as shown in Figure 10.2b. The perpendicular from the intersection of the tie line with the liquidus boundary meets the composition axis at 31.5 wt% Ni–68.5 wt% Cu, which is the composition of the liquid phase, C_L. Likewise, for the solidus–tie line intersection, we find a composition for the α solid-solution phase, C_α, of 42.5 wt% Ni–57.5 wt% Cu.
10.7 Interpretation of Phase Diagrams

DETERMINATION OF PHASE AMOUNTS

The relative amounts (as fraction or as percentage) of the phases present at equilibrium may also be computed with the aid of phase diagrams. Again, the single- and two-phase situations must be treated separately. The solution is obvious in the single-phase region: Since only one phase is present, the alloy is composed entirely of that phase; that is, the phase fraction is 1.0 or, alternatively, the percentage is 100%. From the previous example for the 60 wt% Ni–40 wt% Cu alloy at 1100°C (point A in Figure 10.2a), only the α phase is present; hence, the alloy is completely or 100% α.

If the composition and temperature position is located within a two-phase region, things are more complex. The tie line must be utilized in conjunction with a procedure that is often called the lever rule (or the inverse lever rule), which is applied as follows:

1. The tie line is constructed across the two-phase region at the temperature of the alloy.
2. The overall alloy composition is located on the tie line.
3. The fraction of one phase is computed by taking the length of tie line from the overall alloy composition to the phase boundary for the other phase, and dividing by the total tie line length.
4. The fraction of the other phase is determined in the same manner.
5. If phase percentages are desired, each phase fraction is multiplied by 100. When the composition axis is scaled in weight percent, the phase fractions computed using the lever rule are mass fractions—the mass (or weight) of a specific phase divided by the total alloy mass (or weight). The mass of each phase is computed from the product of each phase fraction and the total alloy mass.

In the employment of the lever rule, tie line segment lengths may be determined either by direct measurement from the phase diagram using a linear scale, preferably graduated in millimeters, or by subtracting compositions as taken from the composition axis.

Consider again the example shown in Figure 10.2b, in which at 1250°C both α and liquid phases are present for a 35 wt% Ni–65 wt% Cu alloy. The problem is to compute the fraction of each of the α and liquid phases. The tie line has been constructed that was used for the determination of α and L phase compositions. Let the overall alloy composition be located along the tie line and denoted as C₀, and mass fractions be represented by W_L and W_α for the respective phases. From the lever rule, W_L may be computed according to

\[ W_L = \frac{S}{R + S} \quad (10.1a) \]

or, by subtracting compositions,

\[ W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L} \quad (10.1b) \]

Composition need be specified in terms of only one of the constituents for a binary alloy; for the computation above, weight percent nickel will be used (i.e., C₀ = 35
wt% Ni, \( C_\alpha = 42.5 \text{ wt% Ni} \), and \( C_L = 31.5 \text{ wt% Ni} \), and

\[
W_L = \frac{42.5 - 35}{42.5 - 31.5} = 0.68
\]

Similarly, for the \( \alpha \) phase,

\[
W_\alpha = \frac{R}{R + S} = \frac{C_0 - C_L}{C_\alpha - C_L} = \frac{35 - 31.5}{42.5 - 31.5} = 0.32
\]

Of course, identical answers are obtained if compositions are expressed in weight percent copper instead of nickel.

Thus, the lever rule may be employed to determine the relative amounts or fractions of phases in any two-phase region for a binary alloy if the temperature and composition are known and if equilibrium has been established. Its derivation is presented as an example problem.

It is easy to confuse the foregoing procedures for the determination of phase compositions and fractional phase amounts; thus, a brief summary is warranted. Compositions of phases are expressed in terms of weight percents of the components (e.g., wt% Cu, wt% Ni). For any alloy consisting of a single phase, the composition of that phase is the same as the total alloy composition. If two phases are present, the tie line must be employed, the extremities of which determine the compositions of the respective phases. With regard to fractional phase amounts (e.g., mass fraction of the \( \alpha \) or liquid phase), when a single phase exists, the alloy is completely that phase. For a two-phase alloy, on the other hand, the lever rule is utilized, in which a ratio of tie line segment lengths is taken.

**Example Problem 10.1**

**Derive the lever rule.**

**Solution**

Consider the phase diagram for copper and nickel (Figure 10.2b) and alloy of composition \( C_0 \) at 1250°C, and let \( C_\alpha \), \( C_L \), \( W_\alpha \), and \( W_L \) represent the same parameters as above. This derivation is accomplished through two conservation-of-mass expressions. With the first, since only two phases are present, the sum of their mass fractions must be equal to unity, that is,

\[
W_\alpha + W_L = 1 \tag{10.3}
\]

For the second, the mass of one of the components (either Cu or Ni) that is present in both of the phases must be equal to the mass of that component in the total alloy, or

\[
W_\alpha C_\alpha + W_L C_L = C_0 \tag{10.4}
\]
Simultaneous solution of these two equations leads to the lever rule expressions for this particular situation, Equations 10.1b and 10.2b:

\[
W_L = \frac{C_a - C_0}{C_a - C_L} \\
W_L = \frac{C_0 - C_L}{C_a - C_L}
\]  (10.1b)

(10.2b)

For multiphase alloys, it is often more convenient to specify relative phase amount in terms of volume fraction rather than mass fraction. Phase volume fractions are preferred because they (rather than mass fractions) may be determined from examination of the microstructure; furthermore, the properties of a multiphase alloy may be estimated on the basis of volume fractions.

For an alloy consisting of \(a\) and \(b\) phases, the volume fraction of the \(a\) phase, \(V_a\), is defined as

\[
V_a = \frac{v_a}{v_a + v_b}
\]  (10.5)

where \(v_a\) and \(v_b\) denote the volumes of the respective phases in the alloy. Of course, an analogous expression exists for \(V_b\); and, for an alloy consisting of just two phases, it is the case that \(V_a + V_b = 1\).

On occasion conversion from mass fraction to volume fraction (or vice versa) is desired. Equations that facilitate these conversions are as follows:

\[
V_a = \frac{W_a}{W_a + W_b} \frac{\rho_a}{\rho_a + \rho_b} \]  (10.6a)

and

\[
V_b = \frac{W_b}{W_a + W_b} \frac{\rho_b}{\rho_a + \rho_b} \]  (10.6b)

\[
W_a = \frac{V_a \rho_a}{V_a \rho_a + V_b \rho_b} \]  (10.7a)

and

\[
W_b = \frac{V_b \rho_b}{V_a \rho_a + V_b \rho_b} \]  (10.7b)

In these expressions, \(\rho_a\) and \(\rho_b\) are the densities of the respective phases; these may be determined approximately using Equations 5.10a and 5.10b.

When the densities of the phases in a two-phase alloy differ significantly, there will be quite a disparity between mass and volume fractions; conversely, if the phase densities are the same, mass and volume fractions are identical.
10.8 Development of Microstructure in Isomorphous Alloys

Equilibrium Cooling (CD-ROM)

Nonequilibrium Cooling (CD-ROM)

10.9 Mechanical Properties of Isomorphous Alloys

We shall now briefly explore how the mechanical properties of solid isomorphous alloys are affected by composition as other structural variables (e.g., grain size) are held constant. For all temperatures and compositions below the melting temperature of the lowest-melting component, only a single solid phase will exist. Therefore, each component will experience solid-solution strengthening (Section 8.10), or an increase in strength and hardness by additions of the other component. This effect is demonstrated in Figure 10.5a as tensile strength versus composition for the copper–nickel system at room temperature; at some intermediate composition, the curve necessarily passes through a maximum. Plotted in Figure 10.5b is the ductility (% EL)–composition behavior, which is just the opposite of tensile strength; that is, ductility decreases with additions of the second component, and the curve exhibits a minimum.

10.10 Binary Eutectic Systems

Another type of common and relatively simple phase diagram found for binary alloys is shown in Figure 10.6 for the copper–silver system; this is known as a binary eutectic phase diagram. A number of features of this phase diagram are important and worth noting. First of all, three single-phase regions are found on the diagram: \( \alpha \), \( \beta \), and liquid. The \( \alpha \) phase is a solid solution rich in copper; it has silver as the solute component and an FCC crystal structure. The \( \beta \) phase solid solution also

---

**Figure 10.5** For the copper–nickel system, (a) tensile strength versus composition, and (b) ductility (% EL) versus composition at room temperature. A solid solution exists over all compositions for this system.
has an FCC structure, but copper is the solute. The $\alpha$ and $\beta$ phases are considered to include pure copper and pure silver, respectively.

Thus, the solubility in each of these solid phases is limited, in that at any temperature below line $B\ E\ G$ only a limited concentration of silver will dissolve in copper (for the $\alpha$ phase), and similarly for copper in silver (for the $\beta$ phase). The solubility limit for the $\alpha$ phase corresponds to the boundary line, labeled $C\ B\ A$, between the $\alpha/(\alpha + \beta)$ and $\alpha/(\alpha + L)$ phase regions; it increases with temperature to a maximum [8.0 wt% Ag at 779°C (1434°F)] at point $B$, and decreases back to zero at the melting temperature of pure copper, point $A$ [1085°C (1985°F)]. At temperatures below 779°C (1434°F), the solid solubility limit line separating the $\alpha$ and $\alpha + L$ phase regions is termed a solvus line; the boundary $A\ B$ between the $\alpha$ and $\alpha + L$ fields is the solidus line, as indicated in Figure 10.6. For the $\beta$ phase, both solvus and solidus lines also exist, $H\ G$ and $G\ F$, respectively, as shown. The maximum solubility of copper in the $\beta$ phase, point $G$ (8.8 wt% Cu), also occurs at 779°C (1434°F). This horizontal line $B\ E\ G$, which is parallel to the composition axis and extends between these maximum solubility positions, may also be considered to be a solidus line; it represents the lowest temperature at which a liquid phase may exist for any copper-silver alloy that is at equilibrium.

There are also three two-phase regions found for the copper-silver system (Figure 10.6): $\alpha + L$, $\beta + L$, and $\alpha + \beta$. The $\alpha$ and $\beta$ phase solid solutions coexist for all compositions and temperatures within the $\alpha + \beta$ phase field; the $\alpha +$ liquid

---

**Figure 10.6** The copper-silver phase diagram. (Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)
and $\beta$ + liquid phases also coexist in their respective phase regions. Furthermore, compositions and relative amounts for the phases may be determined using tie lines and the lever rule as outlined previously.

As silver is added to copper, the temperature at which the alloys become totally liquid decreases along the liquidus line, line $AE$; thus, the melting temperature of copper is lowered by silver additions. The same may be said for silver: the introduction of copper reduces the temperature of complete melting along the other liquidus line, $FE$. These liquidus lines meet at the point $E$ on the phase diagram, through which also passes the horizontal isotherm line $BEG$. Point $E$ is called an **invariant point**, which is designated by the composition $C_E$ and temperature $T_E$; for the copper–silver system, the values of $C_E$ and $T_E$ are 71.9 wt% Ag and 779°C ($1434^\circ$F), respectively.

An important reaction occurs for an alloy of composition $C_E$ as it changes temperature in passing through $T_E$; this reaction may be written as follows:

$$L(C_E) \xrightarrow{\text{cooling}} \alpha(C_{\alpha E}) + \beta(C_{\beta E}) \xrightarrow{\text{heating}}$$

Or, upon cooling, a liquid phase is transformed into the two solid $\alpha$ and $\beta$ phases at the temperature $T_E$; the opposite reaction occurs upon heating. This is called a **eutectic reaction** (eutectic means easily melted), and $C_E$ and $T_E$ represent the eutectic composition and temperature, respectively; $C_{\alpha E}$ and $C_{\beta E}$ are the respective compositions of the $\alpha$ and $\beta$ phases at $T_E$. Thus, for the copper–silver system, the eutectic reaction, Equation 10.8, may be written as follows:

$$L(71.9 \text{ wt}\% \text{ Ag}) \xrightarrow{\text{cooling}} \alpha(8.0 \text{ wt}\% \text{ Ag}) + \beta(91.2 \text{ wt}\% \text{ Ag}) \xrightarrow{\text{heating}}$$

Often, the horizontal solidus line at $T_E$ is called the eutectic isotherm.

The eutectic reaction, upon cooling, is similar to solidification for pure components in that the reaction proceeds to completion at a constant temperature, or isothermally, at $T_E$. However, the solid product of eutectic solidification is always two solid phases, whereas for a pure component only a single phase forms. Because of this eutectic reaction, phase diagrams similar to that in Figure 10.6 are termed eutectic phase diagrams; components exhibiting this behavior comprise a eutectic system.

In the construction of binary phase diagrams, it is important to understand that one or at most two phases may be in equilibrium within a phase field. This holds true for the phase diagrams in Figures 10.2a and 10.6. For a eutectic system, three phases ($\alpha$, $\beta$, and $L$) may be in equilibrium, but only at points along the eutectic isotherm. A nother general rule is that single-phase regions are always separated from each other by a two-phase region that consists of the two single phases that it separates. For example, the $\alpha + \beta$ field is situated between the $\alpha$ and $\beta$ single-phase regions in Figure 10.6.

A nother common eutectic system is that for lead and tin; the phase diagram (Figure 10.7) has a general shape similar to that for copper–silver. For the lead–tin system the solid solution phases are also designated by $\alpha$ and $\beta$; in this case, $\alpha$ represents a solid solution of tin in lead, and for $\beta$, tin is the solvent and lead is the solute. The eutectic invariant point is located at 61.9 wt% Sn and 183°C ($361^\circ$F). Of course, maximum solid solubility compositions as well as component melting temperatures will be different for the copper–silver and lead–tin systems, as may be observed by comparing their phase diagrams.
On occasion, low-melting-temperature alloys are prepared having near-eutectic compositions. A familiar example is the 60–40 solder, containing 60 wt% Sn and 40 wt% Pb. Figure 10.7 indicates that an alloy of this composition is completely molten at about 185°C (365°F), which makes this material especially attractive as a low-temperature solder, since it is easily melted.

**EXAMPLE PROBLEM 10.2**

For a 40 wt% Sn–60 wt% Pb alloy at 150°C (300°F), (a) What phase(s) is (are) present? (b) What is (are) the composition(s) of the phase(s)?

**Solution**

(a) Locate this temperature–composition point on the phase diagram (point B in Figure 10.8). Inasmuch as it is within the α + β region, both α and β phases will coexist.

(b) Since two phases are present, it becomes necessary to construct a tie line across the α + β phase field at 150°C, as indicated in Figure 10.8. The composition of the α phase corresponds to the tie line intersection with the α/(α + β) solvus phase boundary—about 10 wt% Sn–90 wt% Pb, denoted as Cα. Similarly, for the β phase, which will have a composition approximately 98 wt% Sn–2 wt% Pb (Cβ).

![Figure 10.7 The lead–tin phase diagram. (Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)](image-url)
EXAMPLE PROBLEM 10.3

For the lead–tin alloy in Example Problem 10.2, calculate the relative amount of each phase present in terms of (a) mass fraction and (b) volume fraction. At 150°C take the densities of Pb and Sn to be 11.23 and 7.24 g/cm³, respectively.

SOLUTION

(a) Since the alloy consists of two phases, it is necessary to employ the lever rule. If \( C_1 \) denotes the overall alloy composition, mass fractions may be computed by subtracting compositions, in terms of weight percent tin, as follows:

\[
W_w = \frac{C_\beta - C_1}{C_\beta - C_\alpha} = \frac{98 - 40}{98 - 10} = 0.66
\]

\[
W_\mu = \frac{C_1 - C_\alpha}{C_\beta - C_\alpha} = \frac{40 - 10}{98 - 10} = 0.34
\]

(b) To compute volume fractions it is first necessary to determine the density of each phase (using Equation 5.10a). Thus

\[
\rho_w = \frac{100}{\frac{C_{Sn(\alpha)}}{\rho_{Sn}} + \frac{C_{Pb(\alpha)}}{\rho_{Pb}}}
\]

where \( C_{Sn(\alpha)} \) and \( C_{Pb(\alpha)} \) denote the concentrations in weight percent of tin and lead, respectively, in the \( \alpha \) phase. From Example Problem 10.2, these values...
10.12 Equilibrium Diagrams Having Intermediate Phases or Compounds

are 10 wt% and 90 wt%. Incorporation of these values along with the densities of the two components lead to

\[
\rho_\alpha = \frac{100}{7.24 \text{ g/cm}^3} + \frac{90}{11.23 \text{ g/cm}^3} = 10.64 \text{ g/cm}^3
\]

Similarly for the \( \beta \) phase

\[
\rho_\beta = \frac{100}{7.24 \text{ g/cm}^3} + \frac{2}{11.23 \text{ g/cm}^3} = 7.29 \text{ g/cm}^3
\]

Now it becomes necessary to employ Equations 10.6a and 10.6b to determine \( V_\alpha \) and \( V_\beta \) as

\[
V_\alpha = \frac{W_\alpha}{\rho_\alpha} = \frac{0.66}{10.64 \text{ g/cm}^3} = 0.06 \approx 0.57
\]

\[
V_\beta = \frac{W_\beta}{\rho_\beta} = \frac{0.34}{7.29 \text{ g/cm}^3} = 0.046 \approx 0.43
\]

10.11 Development of Microstructure in Eutectic Alloys (CD-ROM)

10.12 Equilibrium Diagrams Having Intermediate Phases or Compounds

The isomorphous and eutectic phase diagrams discussed thus far are relatively simple, but those for many binary alloy systems are much more complex. The eutectic copper–silver and lead–tin phase diagrams (Figures 10.6 and 10.7) have only two solid phases, \( \alpha \) and \( \beta \); these are sometimes termed terminal solid solutions,
because they exist over composition ranges near the concentration extremities of the phase diagram. For other alloy systems, intermediate solid solutions (or intermediate phases) may be found at other than the two composition extremes. Such is the case for the copper–zinc system. Its phase diagram (Figure 10.17) may at first appear formidable because there are some invariant points and reactions similar to the eutectic that have not yet been discussed. In addition, there are six different solid solutions—two terminal (α and η) and four intermediate (β, γ, δ, and ε). (The β′ phase is termed an ordered solid solution, one in which the copper and zinc atoms are situated in a specific and ordered arrangement within each unit cell.) Some phase boundary lines near the bottom of Figure 10.17 are dashed to indicate that their positions have not been exactly determined. The reason for this is that at low temperatures, diffusion rates are very slow and inordinately long times are required for the attainment of equilibrium. A gain, only single- and two-phase regions are found on the diagram, and the same rules outlined in Section 10.7 are utilized for computing phase compositions and relative amounts. The commercial brasses are copper-rich copper–zinc alloys; for example, cartridge brass has a composition of 70 wt% Cu–30 wt% Zn and a microstructure consisting of a single α phase.

For some systems, discrete intermediate compounds rather than solid solutions may be found on the phase diagram, and these compounds have distinct chemical formulas; for metal–metal systems, they are called intermetallic compounds. For example, consider the magnesium–lead system (Figure 10.18). The compound Mg2Pb has a composition of 19 wt% Mg–81 wt% Pb (33 at% Pb), and is represented as a vertical line on the diagram, rather than as a phase region of finite width; hence, Mg2Pb can exist by itself only at this precise composition. Several other characteristics are worth noting for this magnesium–lead system. First, the compound Mg2Pb melts at approximately 550°C (1020°F), as indicated by point M in Figure 10.18. Also, the solubility of lead in magnesium is rather extensive, as indicated by the relatively large composition span for the α phase field. On the other hand, the solubility of magnesium in lead is extremely limited. This is evident from the very narrow β terminal solid-solution region on the right or lead-rich side of the diagram. Finally, this phase diagram may be thought of as two simple eutectic diagrams joined back to back, one for the Mg–Mg2Pb system, the other for Mg2Pb–Pb; as such, the compound Mg2Pb is really considered to be a component. This separation of complex phase diagrams into smaller-component units may simplify them and, furthermore, expedite their interpretation.

10.13 Eutectoid and Peritectic Reactions

In addition to the eutectic, other invariant points involving three different phases are found for some alloy systems. One of these occurs for the copper–zinc system (Figure 10.17) at 560°C (1040°F) and 74 wt% Zn–26 wt% Cu. A portion of the phase diagram in this vicinity appears enlarged in Figure 10.19. Upon cooling, a solid δ phase transforms into two other solid phases (γ and ε) according to the reaction

\[
\text{δ cooling } \rightarrow \text{ γ + ε}
\]

(10.14)

The reverse reaction occurs upon heating. It is called a eutectoid (or eutecticlike) reaction, and the invariant point (point E, Figure 10.19) and the horizontal tie line
10.13 Eutectoid and Peritectic Reactions

**Figure 10.17** The copper–zinc phase diagram. (Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 2, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)
**Chapter 10 / Phase Diagrams**

**Figure 10.18** The magnesium–lead phase diagram. (Adapted from Phase Diagrams of Binary Magnesium Alloys, A. A. Nayeb-Hashemi and J. B. Clark, Editors, 1988. Reprinted by permission of ASM International, Materials Park, OH.)

**Figure 10.19** A region of the copper–zinc phase diagram that has been enlarged to show eutectoid and peritectic invariant points, labeled E (560°C, 74 wt% Zn) and P (598°C, 78.6 wt% Zn), respectively. (Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 2, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)
at 560°C are termed the eutectoid and eutectoid isotherm, respectively. The feature distinguishing "eutectoid" from "eutectic" is that one solid phase instead of a liquid transforms into two other solid phases at a single temperature. A eutectoid reaction is found in the iron–carbon system (Section 10.18) that is very important in the heat treating of steels.

The peritectic reaction is yet another invariant reaction involving three phases at equilibrium. With this reaction, upon heating, one solid phase transforms into a liquid phase and another solid phase. A peritectic exists for the copper–zinc system (Figure 10.19, point P) at 598°C (1108°F) and 78.6 wt% Zn–21.4 wt% Cu; this reaction is as follows:

\[ \delta + L \xrightarrow{\text{cooling}} \epsilon \]

Heating

The low-temperature solid phase may be an intermediate solid solution (e.g., ε in the above reaction), or it may be a terminal solid solution. One of the latter peritectics exists at about 97 wt% Zn and 435°C (815°F) (see Figure 10.17), wherein the \( \gamma \) phase, when heated, transforms to \( \epsilon \) and liquid phases. Three other peritectics are found for the Cu–Zn system, the reactions of which involve \( \beta \), \( \delta \), and \( \gamma \) intermediate solid solutions as the low-temperature phases that transform upon heating.

\section*{10.14 Congruent Phase Transformations}

Phase transformations may be classified according to whether or not there is any change in composition for the phases involved. Those for which there are no compositional alterations are said to be congruent transformations. Conversely, for incongruent transformations, at least one of the phases will experience a change in composition. Examples of congruent transformations include allotropic transformations (Section 3.10) and melting of pure materials. Eutectic and eutectoid reactions, as well as the melting of an alloy that belongs to an isomorphous system, all represent incongruent transformations.

Intermediate phases are sometimes classified on the basis of whether they melt congruently or incongruently. The intermetallic compound Mg2Pb melts congruently at the point designated M on the magnesium–lead phase diagram, Figure 10.18. Also, for the nickel–titanium system, Figure 10.20, there is a congruent melting point for the \( \beta \) solid solution that corresponds to the point of tangency for the pairs of liquidus and solidus lines, at 1310°C and 44.9 wt% Ti. Furthermore, the peritectic reaction is an example of incongruent melting for an intermediate phase.

\section*{10.15 Ceramic Phase Diagrams (CD-ROM)}

\section*{10.16 Ternary Phase Diagrams}

Phase diagrams have also been determined for metallic (as well as ceramic) systems containing more than two components; however, their representation and interpretation may be exceedingly complex. For example, a ternary, or three-component, composition–temperature phase diagram in its entirety is depicted by a three-dimensional model. Portrayal of features of the diagram or model in two dimensions is possible but somewhat difficult.
10.17 **The Gibbs Phase Rule (CD-ROM)**

The Iron–Carbon System

Of all binary alloy systems, the one that is possibly the most important is that for iron and carbon. Both steels and cast irons, primary structural materials in every technologically advanced culture, are essentially iron–carbon alloys. This section is devoted to a study of the phase diagram for this system and the development of several of the possible microstructures. The relationships between heat treatment, microstructure, and mechanical properties are explored in Chapter 11.

10.18 **The Iron-Iron Carbide (Fe–Fe₃C) Phase Diagram**

A portion of the iron–carbon phase diagram is presented in Figure 10.26. Pure iron, upon heating, experiences two changes in crystal structure before it melts. At room temperature the stable form, called ferrite, or \( \alpha \) iron, has a BCC crystal structure. Ferrite experiences a polymorphic transformation to FCC austenite, or \( \gamma \) iron, at 912°C (1674°F). This austenite persists to 1394°C (2541°F), at which temperature the FCC austenite reverts back to a BCC phase known as \( \delta \) ferrite, which finally melts at 1538°C (2800°F). All these changes are apparent along the left vertical axis of the phase diagram.

The composition axis in Figure 10.26 extends only to 6.70 wt% C; at this concentration the intermediate compound iron carbide, or cementite (Fe₃C), is
formed, which is represented by a vertical line on the phase diagram. Thus, the iron–carbon system may be divided into two parts: an iron-rich portion, as in Figure 10.26; and the other (not shown) for compositions between 6.70 and 100 wt% C (pure graphite). In practice, all steels and cast irons have carbon contents less than 6.70 wt% C; therefore, we consider only the iron–iron carbide system. Figure 10.26 would be more appropriately labeled the Fe–Fe₃C phase diagram, since Fe₃C is now considered to be a component. Convention and convenience dictate that composition still be expressed in “wt% C” rather than “wt% Fe₃C”; 6.70 wt% C corresponds to 100 wt% Fe₃C.

Carbon is an interstitial impurity in iron and forms a solid solution with each of α and δ ferrites, and also with austenite, as indicated by the α, δ, and γ single-phase fields in Figure 10.26. In the BCC α ferrite, only small concentrations of carbon are soluble; the maximum solubility is 0.022 wt% at 727°C (1341°F). The limited solubility is explained by the shape and size of the BCC interstitial positions, which make it difficult to accommodate the carbon atoms. Even though present in relatively low concentrations, carbon significantly influences the mechanical properties of ferrite. This particular iron–carbon phase is relatively soft, may be made magnetic at temperatures below 768°C (1414°F), and has a density of 7.88 g/cm³. Figure 10.27a is a photomicrograph of α ferrite.

The austenite, or γ phase of iron, when alloyed with just carbon, is not stable below 727°C (1341°F), as indicated in Figure 10.26. The maximum solubility of
carbon in austenite, 2.14 wt%, occurs at 1147°C (2097°F). This solubility is approximately 100 times greater than the maximum for BCC ferrite, since the FCC interstitial positions are larger (see the results of Problem 5.9), and, therefore, the strains imposed on the surrounding iron atoms are much lower. As the discussions that follow demonstrate, phase transformations involving austenite are very important in the heat treating of steels. In passing, it should be mentioned that austenite is nonmagnetic. Figure 10.27 shows a photomicrograph of this austenite phase.

The δ ferrite is virtually the same as α ferrite, except for the range of temperatures over which each exists. Since the δ ferrite is stable only at relatively high temperatures, it is of no technological importance and is not discussed further.

Cementite (Fe₃C) forms when the solubility limit of carbon in α ferrite is exceeded below 727°C (1341°F) (for compositions within the Fe₃C phase region). As indicated in Figure 10.26, Fe₃C will also coexist with the γ phase between 727 and 1147°C (1341 and 2097°F). Mechanically, cementite is very hard and brittle; the strength of some steels is greatly enhanced by its presence.

Strictly speaking, cementite is only metastable; that is, it will remain as a compound indefinitely at room temperature. But if heated to between 650 and 700°C (1200 and 1300°F) for several years, it will gradually change or transform into α iron and carbon, in the form of graphite, which will remain upon subsequent cooling to room temperature. Thus, the phase diagram in Figure 10.26 is not a true equilibrium one because cementite is not an equilibrium compound. However, inasmuch as the decomposition rate of cementite is extremely sluggish, virtually all the carbon in steel will be as Fe₃C instead of graphite, and the iron–iron carbide phase diagram is, for all practical purposes, valid. As will be seen in Section 13.2, addition of silicon to cast irons greatly accelerates this cementite decomposition reaction to form graphite.

The two-phase regions are labeled in Figure 10.26. It may be noted that one eutectic exists for the iron–iron carbide system, at 4.30 wt% C and 1147°C (2097°F);
for this eutectic reaction,

\[ L \xrightarrow{\text{cooling}} \gamma + \text{Fe}_3\text{C} \]  

(10.18)

the liquid solidifies to form austenite and cementite phases. Of course, subsequent cooling to room temperature will promote additional phase changes.

It may be noted that a eutectoid invariant point exists at a composition of 0.76 wt \% C and a temperature of 727°C (1341°F). This eutectoid reaction may be represented by

\[ \gamma(0.76 \text{ wt } \% \text{ C}) \xrightarrow{\text{cooling}} \alpha(0.022 \text{ wt } \% \text{ C}) + \text{Fe}_3\text{C} (6.7 \text{ wt } \% \text{ C}) \]  

(10.19)

or, upon cooling, the solid \( \gamma \) phase is transformed into \( \alpha \) iron and cementite. (Eutectoid phase transformations were addressed in Section 10.13.) The eutectoid phase changes described by Equation 10.19 are very important, being fundamental to the heat treatment of steels, as explained in subsequent discussions.

Ferrous alloys are those in which iron is the prime component, but carbon as well as other alloying elements may be present. In the classification scheme of ferrous alloys based on carbon content, there are three types: iron, steel, and cast iron. Commercially pure iron contains less than 0.008 wt \% C and, from the phase diagram, is composed almost exclusively of the ferrite phase at room temperature. The iron–carbon alloys that contain between 0.008 and 2.14 wt \% C are classified as steels. In most steels the microstructure consists of both \( \alpha \) and \( \text{Fe}_3\text{C} \) phases. Upon cooling to room temperature, an alloy within this composition range must pass through at least a portion of the \( \gamma \) phase field; distinctive microstructures are subsequently produced, as discussed below. Although a steel alloy may contain as much as 2.14 wt \% C, in practice, carbon concentrations rarely exceed 1.0 wt \%. The properties and various classifications of steels are treated in Section 13.2. Cast irons are classified as ferrous alloys that contain between 2.14 and 6.70 wt \% C. However, commercial cast irons normally contain less than 4.5 wt \% C. These alloys are also discussed in Section 13.2.

### 10.19 Development of Microstructures in Iron–Carbon Alloys

Several of the various microstructures that may be produced in steel alloys and their relationships to the iron–iron carbon phase diagram are now discussed, and it is shown that the microstructure that develops depends on both the carbon content and heat treatment. The discussion is confined to very slow cooling of steel alloys, in which equilibrium is continuously maintained. A more detailed exploration of the influence of heat treatment on microstructure, and ultimately on the mechanical properties of steels, is contained in Chapter 11.

Phase changes that occur upon passing from the \( \gamma \) region into the \( \alpha + \text{Fe}_3\text{C} \) phase field (Figure 10.26) are relatively complex (and similar to those described for the eutectic systems in Section 10.11.) Consider, for example, an alloy of eutectoid composition (0.76 wt \% C) as it is cooled from a temperature within the \( \gamma \) phase region, say, 800°C, that is, beginning at point \( a \) in Figure 10.28 and moving down the vertical line \( xx' \). Initially, the alloy is composed entirely of the austenite phase...
having a composition of 0.76 wt% C and corresponding microstructure, also indicated in Figure 10.28. As the alloy is cooled, there will occur no changes until the eutectoid temperature (727°C) is reached. Upon crossing this temperature to point b, the austenite transforms according to Equation 10.19.

The microstructure for this eutectoid steel that is slowly cooled through the eutectoid temperature consists of alternating layers or lamellae of the two phases \((\alpha + \gamma)\) that form simultaneously during the transformation. In this case, the relative layer thickness is approximately 8 to 1. This microstructure, represented schematically in Figure 10.28, point b, is called pearlite because it has the appearance of mother of pearl when viewed under the microscope at low magnifications. Figure 10.29 is a photomicrograph of a eutectoid steel showing the pearlite. The pearlite exists as grains, often termed “colonies”; within each colony the layers are oriented in essentially the same direction, which varies from one colony to another. The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which appear dark. Many cementite layers are so thin that adjacent phase boundaries are indistinguishable, which layers appear dark at this magnification. Mechanically, pearlite has properties intermediate between the soft, ductile ferrite and the hard, brittle cementite.

The alternating \(\alpha\) and \(\text{Fe}_3\text{C}\) layers in pearlite form (as such for the same reason that the eutectic structure (Figures 10.11 and 10.12) forms)—because the composition of the parent phase [in this case austenite (0.76 wt% C)] is different from either of the product phases [ferrite (0.022 wt% C) and cementite (6.7 wt% C)], and the phase transformation requires that there be a redistribution of the carbon by diffusion. Figure 10.30 illustrates schematically microstructural changes that accompany this eutectoid reaction; here the directions of carbon diffusion are
indicated by arrows. Carbon atoms diffuse away from the 0.022 wt% ferrite regions and to the 6.7 wt% cementite layers, as the pearlite extends from the grain boundary into the unreacted austenite grain. The layered pearlite forms because carbon atoms need diffuse only minimal distances with the formation of this structure.

Furthermore, subsequent cooling of the pearlite from point b in Figure 10.28 will produce relatively insignificant microstructural changes.

HYPOEUTECTOID ALLOYS

Microstructures for iron–iron carbide alloys having other than the eutectoid composition are now explored; these are analogous to the fourth case described in Section 10.11 and illustrated in Figure 10.14 for the eutectic system. Consider a composition \( C_0 \) to the left of the eutectoid, between 0.022 and 0.76 wt% C; this is termed a hypoeutectoid (less than eutectoid) alloy. Cooling an alloy of this composition is represented by moving down the vertical line \( \gamma' \) in Figure 10.31. At about 875°C, point c, the microstructure will consist entirely of grains of the \( \gamma \) phase, as shown schematically in the figure. In cooling to point d, about 775°C, which is within the \( \alpha + \gamma \) phase region, both these phases will coexist as in the schematic microstructure. Most of the small \( \alpha \) particles will form along the original \( \gamma \) grain boundaries.
compositions of both $\alpha$ and $\gamma$ phases may be determined using the appropriate tie line; these compositions correspond, respectively, to about 0.020 and 0.40 wt% C.

While cooling an alloy through the $\alpha + \gamma$ phase region, the composition of the ferrite phase changes with temperature along the $\alpha - (\alpha + \gamma)$ phase boundary, line MN, becoming slightly richer in carbon. On the other hand, the change in composition of the austenite is more dramatic, proceeding along the $(\alpha + \gamma) - \gamma$ boundary, line MO, as the temperature is reduced.

Cooling from point d to e, just above the eutectoid but still in the $\alpha + \gamma$ region, will produce an increased fraction of the $\alpha$ phase and a microstructure similar to that also shown: the $\alpha$ particles will have grown larger. At this point, the compositions of the $\alpha$ and $\gamma$ phases are determined by constructing a tie line at the temperature $T_e$; the $\alpha$ phase will contain 0.022 wt% C, while the $\gamma$ phase will be of the eutectoid composition, 0.76 wt% C.

As the temperature is lowered just below the eutectoid, to point f, all the $\gamma$ phase that was present at temperature $T_e$ (and having the eutectoid composition) will transform to pearlite, according to the reaction in Equation 10.19. There will be virtually no change in the $\alpha$ phase that existed at point e in crossing the eutectoid temperature—it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies. The microstructure at point f will appear as the corresponding schematic inset of Figure 10.31. Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the $\alpha + \gamma$ phase region. The ferrite that is present in the pearlite is called eutectoid ferrite, whereas the other, that formed above $T_e$, is termed proeutectoid (meaning pre- or before eutectoid) ferrite, as labeled in Figure 10.31. Figure 10.32 is a photomicrograph of a 0.38 wt% C steel; large, white regions correspond to the proeutectoid

**Figure 10.31** Schematic representations of the microstructures for an iron–carbon alloy of hypoeutectoid composition $C_0$ (containing less than 0.76 wt% C) as it is cooled from within the austenite phase region to below the eutectoid temperature.
ferrite. For pearlite, the spacing between the \( \alpha \) and Fe\(_3\)C layers varies from grain to grain; some of the pearlite appears dark because the many close-spaced layers are unresolved at the magnification of the photomicrograph. The chapter-opening photograph for this chapter is a scanning electron micrograph of a hypoeutectoid (0.44 wt% C) steel in which may also be seen both pearlite and proeutectoid ferrite, only at a higher magnification. It should also be noted that two microconstituents are present in these micrographs—proeutectoid ferrite and pearlite—which will appear in all hypoeutectoid iron–carbon alloys that are slowly cooled to a temperature below the eutectoid.

The relative amounts of the proeutectoid \( \alpha \) and pearlite may be determined (in a manner similar to that described in Section 10.11 for primary and eutectic microconstituents.) We use the lever rule in conjunction with a tie line that extends from the \( \alpha - (\alpha + \text{Fe}_3\text{C}) \) phase boundary (0.022 wt% C) to the eutectoid composition (0.76 wt% C), inasmuch as pearlite is the transformation product of austenite having this composition. For example, let us consider an alloy of composition \( C_0 \) in Figure 10.33. Thus, the fraction of pearlite, \( W_p \), may be determined according to

\[
W_p = \frac{T}{T + U}
\]

\[
= \frac{C_\phi - 0.022}{0.76 - 0.022} = \frac{C_\phi - 0.022}{0.74} \quad (10.20)
\]

Furthermore, the fraction of proeutectoid \( \alpha \), \( W_\alpha \), is computed as follows:

\[
W_\alpha = \frac{U}{T + U}
\]

\[
= \frac{0.76 - C_\phi}{0.76 - 0.022} = \frac{0.76 - C_\phi}{0.74} \quad (10.21)
\]
Of course, fractions of both total $\alpha$ (eutectoid and proeutectoid) and cementite are determined using the lever rule and a tie line that extends across the entirety of the $\alpha + Fe_3C$ phase region, from 0.022 to 6.7 wt% C.

**HYPEREUTECTOID ALLOYS**

Analogous transformations and microstructures result for hypereutectoid alloys, those containing between 0.76 and 2.14 wt% C, which are cooled from temperatures within the $\gamma$ phase field. Consider an alloy of composition $C_1$ in Figure 10.34 which, upon cooling, moves down the line $zz'$. At point $g$ only the $\gamma$ phase will be present with a composition of $C_1$; the microstructure will appear as shown, having only $\gamma$ grains. Upon cooling into the $\gamma + Fe_3C$ phase field, say, to point $h$, the cementite phase will begin to form along the initial $\gamma$ grain boundaries, similar to the $\alpha$ phase in Figure 10.31, point $d$. This cementite is called proeutectoid cementite—that which forms before the eutectoid reaction. Of course, the cementite composition remains constant (6.70 wt% C) as the temperature changes. However, the composition of the austenite phase will move along line PO toward the eutectoid. As the temperature is lowered through the eutectoid to point $i$, all remaining austenite of eutectoid composition is converted into pearlite; thus, the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents (Figure 10.34). In the photomicrograph of a 1.4 wt% C steel (Figure 10.35), note that the proeutectoid cementite appears light. Since it has much the same appearance as proeutectoid ferrite (Figure 10.32), there is some difficulty in distinguishing between hypoeutectoid and hypereutectoid steels on the basis of microstructure.

Relative amounts of both pearlite and proeutectoid $Fe_3C$ microconstituents may be computed for hypereutectoid steel alloys in a manner analogous to that for hypoeutectoid materials; the appropriate tie line extends between 0.76 and 6.70 wt% C. Thus, for an alloy having composition $C_1$ in Figure 10.33, fractions of pearlite $W_p$ and proeutectoid cementite $W_{Fe_3C}$ are determined from the following lever rule expressions:

$$W_p = \frac{X}{V + X} = \frac{6.70 - C_1}{6.70 - 0.76} = \frac{6.70 - C_1}{5.94}$$

(10.22)
10.19 Development of Microstructures in Iron–Carbon Alloys

FIGURE 10.34 Schematic representations of the microstructures for an iron–carbon alloy of hypereutectoid composition $C_1$ (containing between 0.76 and 2.14 wt% C), as it is cooled from within the austenite phase region to below the eutectoid temperature.

FIGURE 10.35 Photomicrograph of a 1.4 wt% C steel having a microstructure consisting of a white proeutectoid cementite network surrounding the pearlite colonies. 1000x. (Copyright 1971 by United States Steel Corporation.)
EXAMPLE PROBLEM 10.4

For a 99.65 wt% Fe–0.35 wt% C alloy at a temperature just below the eutectoid, determine the following:

(a) The fractions of total ferrite and cementite phases.
(b) The fractions of the proeutectoid ferrite and pearlite.
(c) The fraction of eutectoid ferrite.

SOLUTION

(a) This part of the problem is solved by application of the lever rule expressions employing a tie line that extends all the way across the \( \alpha + \text{Fe}_3\text{C} \) phase field. Thus, \( C_\delta \) is 0.35 wt% C, and

\[
W_\alpha = \frac{6.70 - 0.35}{6.70 - 0.022} = 0.95
\]

and

\[
W_{\text{Fe}_3\text{C}} = \frac{0.35 - 0.022}{6.70 - 0.022} = 0.05
\]

(b) The fractions of proeutectoid ferrite and pearlite are determined by using the lever rule, and a tie line that extends only to the eutectoid composition (i.e., Equations 10.20 and 10.21). Or

\[
W_p = \frac{0.35 - 0.022}{0.76 - 0.022} = 0.44
\]

and

\[
W_{\text{Fe}_3\text{C}} = \frac{0.76 - 0.35}{0.76 - 0.022} = 0.56
\]

(c) All ferrite is either as proeutectoid or eutectoid (in the pearlite). Therefore, the sum of these two ferrite fractions will equal the fraction of total ferrite, that is,

\[
W_\alpha + W_{\text{Fe}_3\text{C}} = W_\alpha
\]

where \( W_{\text{Fe}_3\text{C}} \) denotes the fraction of the total alloy that is eutectoid ferrite. Values for \( W_\alpha \) and \( W_{\text{Fe}_3\text{C}} \) were determined in parts (a) and (b) as 0.95 and 0.56, respectively. Therefore,

\[
W_{\text{Fe}_3\text{C}} = W_\alpha - W_{\text{Fe}_3\text{C}} = 0.95 - 0.56 = 0.39
\]

NONEQUILIBRIUM COOLING

In this discussion on the microstructural development of iron–carbon alloys it has been assumed that, upon cooling, conditions of metastable equilibrium\(^1\) have been

---

\(^1\) The term “metastable equilibrium” is used in this discussion inasmuch as \( \text{Fe}_3\text{C} \) is only a metastable compound.
continuously maintained; that is, sufficient time has been allowed at each new temperature for any necessary adjustment in phase compositions and relative amounts as predicted from the Fe–Fe₃C phase diagram. In most situations these cooling rates are impractically slow and really unnecessary; in fact, on many occasions nonequilibrium conditions are desirable. Two nonequilibrium effects of practical importance are (1) the occurrence of phase changes or transformations at temperatures other than those predicted by phase boundary lines on the phase diagram, and (2) the existence at room temperature of nonequilibrium phases that do not appear on the phase diagram. Both are discussed in the next chapter.

10.20 The Influence of Other Alloying Elements (CD-ROM)

**SUMMARY**

Equilibrium phase diagrams are a convenient and concise way of representing the most stable relationships between phases in alloy systems. This discussion considered binary phase diagrams for which temperature and composition are variables. A reas, or phase regions, are defined on these temperature-versus-composition plots within which either one or two phases exist. For an alloy of specified composition and at a known temperature, the phases present, their compositions, and relative amounts under equilibrium conditions may be determined. Within two-phase regions, tie lines and the lever rule must be used for phase composition and mass fraction computations, respectively.

Several different kinds of phase diagram were discussed for metallic systems. Isomorphous diagrams are those for which there is complete solubility in the solid phase; the copper–nickel system displays this behavior. Also discussed for alloys belonging to isomorphous systems were the development of microstructure for both cases of equilibrium and nonequilibrium cooling and the dependence of mechanical characteristics on composition.

In a eutectic reaction, as found in some alloy systems, a liquid phase transforms isothermally to two different solid phases upon cooling. Such a reaction is noted on the copper–silver and lead–tin phase diagrams. Complete solid solubility for all compositions does not exist; instead, solid solutions are terminal—there is only a limited solubility of each component in the other. Four different kinds of microstructures that may develop for the equilibrium cooling of alloys belonging to eutectic systems were discussed.

Other equilibrium phase diagrams are more complex, having intermediate compounds and/or phases, possibly more than a single eutectic, and other reactions including eutectoid, peritectic, and congruent phase transformations. These are found for copper–zinc and magnesium–lead systems.

{Phase diagrams for the Al₂O₃-Cr₂O₃, MgO-Al₂O₃, ZrO₂-CaO, and SiO₂-Al₂O₃ systems were discussed. These diagrams are especially useful in assessing the high-temperature performance of ceramic materials.)

{The Gibbs phase rule was introduced; it is a simple equation that relates the number of phases present in a system at equilibrium with the number of degrees of freedom, the number of components, and the number of noncompositional variables.)
Considerable attention was given to the iron–carbon system, and specifically, the iron–iron carbide phase diagram, which technologically is one of the most important. The development of microstructure in many iron–carbon alloys and steels depends on the eutectoid reaction in which the FCC austenite phase of composition 0.76 wt% C transforms isothermally to the BCC α ferrite phase (0.022 wt% C) and the intermetallic compound, cementite (Fe₃C). The microstructural product of an iron–carbon alloy of eutectoid composition is pearlite, a microconstituent consisting of alternating layers of ferrite and cementite. The microstructures of alloys having carbon contents less than the eutectoid (hypoeutectoid) are comprised of a proeutectoid ferrite phase in addition to pearlite. On the other hand, pearlite and proeutectoid cementite constitute the microconstituents for hypereutectoid alloys—those with carbon contents in excess of the eutectoid composition.

**Important Terms and Concepts**

- Austenite
- Cementite
- Component
- Congruent transformation
- Equilibrium
- Eutectic phase
- Eutectic reaction
- Eutectic structure
- Eutectoid reaction
- Ferrite
- Free energy
- Gibbs phase rule
- Hypereutectoid alloy
- Hypoeutectoid alloy
- Intermediate solid solution
- Invariant point
- Liquidus line
- Metastable
- Microconstituent
- Pearlite
- Peritectic reaction
- Phase
- Phase diagram
- Phase equilibrium
- Primary phase
- Proeutectoid cementite
- Proeutectoid ferrite
- Solidus line
- Solubility limit
- Solvus line
- System
- Terminal solid solution
- Tie line

**References**

- Petzow, G., and G. Effenberg, Ternary Alloys, A
Questions and Problems

Note: To solve those problems having an asterisk (*) by their numbers, consultation of supplementary topics [appearing only on the CD-ROM (and not in print)] will probably be necessary.

10.1 Cite three variables that determine the microstructure of an alloy.

10.2 What thermodynamic condition must be met for a state of equilibrium to exist?

10.3 For metal alloys, the development of microstructure depends on the phenomenon of diffusion (Figures 10.13 and 10.30). It was noted in Section 6.3 that the driving force for steady-state diffusion is a concentration gradient. However, concentration gradients are normally absent in regions where diffusion is occurring, as represented in Figures 10.13 and 10.30; for these situations, what is the driving force?

10.4 What is the difference between the states of phase equilibrium and metastability?

10.5 Cite the phases that are present and the phase compositions for the following alloys:
(a) 90 wt% Zn–10 wt% Cu at 400°C (750°F).
(b) 75 wt% Sn–25 wt% Pb at 175°C (345°F).
(c) 55 wt% Ag–45 wt% Cu at 900°C (1650°F).
(d) 30 wt% Pb–70 wt% Mg at 425°C (795°F).
(e) 2.12 kg Zn and 1.88 kg Cu at 500°C (930°F).
(f) 37 lb_m Pb and 6.5 lb_m Mg at 400°C (750°F).
(g) 8.2 mol Ni and 4.3 mol Cu at 1250°C (2280°F).
(h) 4.5 mol Sn and 0.45 mol Pb at 200°C (390°F).

10.6 For an alloy of composition 74 wt% Zn–26 wt% Cu, cite the phases present and their compositions at the following temperatures: 850°C, 750°C, 680°C, 600°C, and 500°C.

10.7 Determine the relative amounts (in terms of mass fractions) of the phases for the alloys and temperatures given in Problem 10.5.

10.8 Derive Equations 10.6a and 10.7a, which may be used to convert mass fraction to volume fraction, and vice versa.

10.9 Determine the relative amounts (in terms of volume fractions) of the phases for the alloys and temperatures given in Problem 10.5a, b, and c. Below are given the approximate densities of the various metals at the alloy temperatures:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temperature (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>900</td>
<td>9.97</td>
</tr>
<tr>
<td>Cu</td>
<td>400</td>
<td>8.77</td>
</tr>
<tr>
<td>Cu</td>
<td>900</td>
<td>8.56</td>
</tr>
<tr>
<td>Pb</td>
<td>175</td>
<td>11.20</td>
</tr>
<tr>
<td>Sn</td>
<td>175</td>
<td>7.22</td>
</tr>
<tr>
<td>Zn</td>
<td>400</td>
<td>6.83</td>
</tr>
</tbody>
</table>

10.10 Below is a portion of the H₂O–NaCl phase diagram:
(a) Using this diagram, briefly explain how spreading salt on ice that is at a temperature below 0°C (32°F) can cause the ice to melt.

(b) What concentration of salt is necessary to have a 50% ice-50% liquid brine at −10°C (14°F)?

10.11 A 1.5-kg specimen of a 90 wt% Pb–10 wt% Sn alloy is heated to 250°C (480°F), at which temperature it is entirely an α-phase solid solution (Figure 10.7). The alloy is to be melted to the extent that 50% of the specimen is liquid, the remainder being the α phase. This may be accomplished either by heating the alloy or changing its composition while holding the temperature constant.

(a) To what temperature must the specimen be heated?

(b) How much tin must be added to the 1.5-kg specimen at 250°C to achieve this state?

10.12 Consider the sugar-water phase diagram of Figure 10.1.

(a) How much sugar will dissolve in 1500 g water at 90°C (194°F)?

(b) If the saturated liquid solution in part (a) is cooled to 20°C (68°F), some of the sugar will precipitate out as a solid. What will be the composition of the saturated liquid solution (in wt% sugar) at 20°C?

(c) How much of the solid sugar will come out of solution upon cooling to 20°C?

10.13 Consider a specimen of ice I which is at −10°C and 1 atm pressure. Using Figure 10.38, the pressure-temperature phase diagram for H₂O, determine the pressure to which the specimen must be raised or lowered to cause it (a) to melt, and (b) to sublime.

10.14 At a pressure of 0.01 atm, determine (a) the melting temperature for ice I, and (b) the boiling temperature for water.

10.15 A magnesium–lead alloy of mass 5.5 kg consists of a solid α phase that has a composition that is just slightly below the solubility limit at 200°C (390°F).

(a) What mass of lead is in the alloy?

(b) If the alloy is heated to 350°C (660°F), how much more lead may be dissolved in the α phase without exceeding the solubility limit of this phase?

10.16* (a) Briefly describe the phenomenon of coring and why it occurs.

(b) Cite one undesirable consequence of coring.

10.17 It is desired to produce a copper–nickel alloy that has a minimum noncold-worked tensile strength of 350 MPa (50,750 psi) and a ductility of at least 48% EL. Is such an alloy possible? If so, what must be its composition? If this is not possible, then explain why.

10.18 Is it possible to have a copper–silver alloy that, at equilibrium, consists of a β phase
Questions and Problems

10.19 Is it possible to have a copper–zinc alloy that, at equilibrium, consists of an \( \alpha \) phase of composition 80 wt% Zn–20 wt% Cu, and also a liquid phase of composition 95 wt% Zn–5 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.

10.20 A copper–nickel alloy of composition 70 wt% Ni–30 wt% Cu is slowly heated from a temperature of 1300°C (2370°F).
(a) At what temperature does the first liquid phase form?
(b) What is the composition of this liquid phase?
(c) At what temperature does complete melting of the alloy occur?
(d) What is the composition of the last solid remaining prior to complete melting?

10.21 A 50 wt% Pb–50 wt% Mg alloy is slowly cooled from 700°C (1290°F) to 400°C (750°F).
(a) At what temperature does the first solid phase form?
(b) What is the composition of this solid phase?
(c) At what temperature does the liquid solidify?
(d) What is the composition of this last remaining solid phase?

10.22 A 90 wt% Ag–10 wt% Cu alloy is heated to a temperature within the \( \beta \) liquid phase region. If the composition of the liquid phase is 85 wt% Ag, determine (a) the temperature of the alloy, (b) the composition of the \( \beta \) phase, and (c) the mass fractions of both phases.

10.23 Below are given the solidus and liquidus temperatures for the germanium–silicon system. Construct the phase diagram for this system and label each region.

<table>
<thead>
<tr>
<th>Composition (wt% Si)</th>
<th>Solidus Temperature (°C)</th>
<th>Liquidus Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>938</td>
<td>938</td>
</tr>
<tr>
<td>10</td>
<td>1005</td>
<td>1147</td>
</tr>
<tr>
<td>20</td>
<td>1065</td>
<td>1226</td>
</tr>
<tr>
<td>30</td>
<td>1123</td>
<td>1278</td>
</tr>
<tr>
<td>40</td>
<td>1178</td>
<td>1315</td>
</tr>
<tr>
<td>50</td>
<td>1232</td>
<td>1346</td>
</tr>
<tr>
<td>60</td>
<td>1282</td>
<td>1367</td>
</tr>
<tr>
<td>70</td>
<td>1326</td>
<td>1385</td>
</tr>
<tr>
<td>80</td>
<td>1359</td>
<td>1397</td>
</tr>
<tr>
<td>90</td>
<td>1390</td>
<td>1408</td>
</tr>
<tr>
<td>100</td>
<td>1414</td>
<td>1414</td>
</tr>
</tbody>
</table>

10.24 A 30 wt% Sn–70 wt% Pb alloy is heated to a temperature within the \( \alpha \) + liquid phase region. If the mass fraction of each phase is 0.5, estimate (a) the temperature of the alloy, and (b) the compositions of the two phases.

10.25* When kaolinite clay [Al\(_2\)(Si\(_2\)O\(_5\))(OH)\(_4\)] is heated to a sufficiently high temperature, chemical water is driven off.
(a) Under these circumstances what is the composition of the remaining product?
(b) What are the liquidus and solidus temperatures of this material?

10.26 For alloys of two hypothetical metals A and B, there exist an \( \alpha \)-rich phase and a \( \beta \)-rich phase. From the mass fractions of both phases for two different alloys, which are at the same temperature, determine the composition of the phase boundary (or solubility limit) for both \( \alpha \) and \( \beta \) phases at this temperature.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Fraction ( \alpha ) Phase</th>
<th>Fraction ( \beta ) Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 wt% A–40 wt% B</td>
<td>0.57</td>
<td>0.43</td>
</tr>
<tr>
<td>30 wt% A–70 wt% B</td>
<td>0.14</td>
<td>0.86</td>
</tr>
</tbody>
</table>

10.27 A hypothetical A–B alloy of composition 55 wt% B–45 wt% A at some temperature is found to consist of mass fractions of 0.5 for both \( \alpha \) and \( \beta \) phases. If the composition of the \( \beta \) phase is 90 wt% B–10 wt% A, what is the composition of the \( \alpha \) phase?

10.28 Is it possible to have a copper–silver alloy of composition 50 wt% Ag–50 wt% Cu, of composition 92 wt% Ag–8 wt% Cu, and also a liquid phase of composition 76 wt% Ag–24 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.
which, at equilibrium, consists of \( \alpha \) and \( \beta \) phases having mass fractions \( W_\alpha = 0.60 \) and \( W_\beta = 0.40 \)? If so, what will be the approximate temperature of the alloy? If such an alloy is not possible, explain why.

10.29 For 11.20 kg of a magnesium-lead alloy of composition 30 wt% Pb - 70 wt% Mg, is it possible, at equilibrium, to have \( \alpha \) and Mg Pb phases having respective masses of 7.39 kg and 3.81 kg? If so, what will be the approximate temperature of the alloy? If such an alloy is not possible, explain why.

10.30 At 700°C (1290°F), what is the maximum solubility (a) of Cu in A g? (b) Of A g in Cu?

10.31* A 45 wt% Pb - 55 wt% Mg alloy is rapidly quenched to room temperature from an elevated temperature in such a way that the high-temperature microstructure is preserved. This microstructure is found to consist of the \( \alpha \) phase and Mg Pb, having respective mass fractions of 0.65 and 0.35. Determine the approximate temperature from which the alloy was quenched.

10.32* Is it possible to have a copper-silver alloy in which the mass fractions of primary \( \beta \) and total \( \beta \) are 0.68 and 0.925, respectively, at 775°C (1425°F)? Why or why not?

10.33* For 6.70 kg of a magnesium-lead alloy, is it possible to have the masses of primary \( \alpha \) and total \( \alpha \) of 4.23 kg and 6.00 kg, respectively, at 460°C (860°F)? Why or why not?

10.34* For a copper-silver alloy of composition 25 wt% A g - 75 wt% Cu and at 775°C (1425°F) do the following:
   (a) Determine the mass fractions of the \( \alpha \) and \( \beta \) phases.
   (b) Determine the mass fractions of primary \( \alpha \) and eutectic microconstituents.
   (c) Determine the mass fraction of eutectic \( \alpha \).

10.35* The microstructure of a lead-tin alloy at 180°C (355°F) consists of primary \( \beta \) and eutectic structures. If the mass fractions of these two microconstituents are 0.57 and 0.43, respectively, determine the composition of the alloy.

10.36* Consider the hypothetical eutectic phase diagram for metals A and B, which is similar to that for the lead-tin system, Figure 10.7. Assume that (1) \( \alpha \) and \( \beta \) phases exist at the A and B extremities of the phase diagram, respectively; (2) the eutectic composition is 47 wt% B - 53 wt% A; and (3) the composition of the \( \beta \) phase at the eutectic temperature is 92.6 wt% B - 7.4 wt% A. Determine the composition of an alloy that will yield primary \( \alpha \) and total \( \alpha \) mass fractions of 0.356 and 0.693, respectively.

10.37* Briefly explain why, upon solidification, an alloy of eutectic composition forms a microstructure consisting of alternating layers of the two solid phases.

10.38* For an 85 wt% Pb - 15 wt% Mg alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 600°C (1110°F), 500°C (930°F), 270°C (520°F), and 200°C (390°F). Label all phases and indicate their approximate compositions.

10.39* For a 68 wt% Zn - 32 wt% Cu alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1000°C (1830°F), 760°C (1400°F), 600°C (1110°F), and 400°C (750°F). Label all phases and indicate their approximate compositions.

10.40* For a 30 wt% Zn - 70 wt% Cu alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1100°C (2010°F), 950°C (1740°F), 900°C (1650°F), and 700°C (1290°F). Label all phases and indicate their approximate compositions.

10.41 What is the principal difference between congruent and incongruent phase transformations?

10.42 Figure 10.39 is the aluminum-neodymium phase diagram, for which only single-phase regions are labeled. Specify temperature-composition points at which all eutectics, eutectoids, peritectics, and congruent phase transformations occur. Also, for each, write the reaction upon cooling.
10.43 Figure 10.40 is a portion of the titanium–copper phase diagram for which only single-phase regions are labeled. Specify all temperature–composition points at which eutectics, eutectoids, peritectics, and congruent phase transformations occur. Also, for each, write the reaction upon cooling.

10.44* For the ZrO₂–CaO system (Figure 10.23), write all eutectic and eutectoid reactions for cooling.

10.45* From Figure 10.22, the phase diagram for the MgO–Al₂O₃ system, it may be noted that the spinel solid solution exists over a range of compositions, which means that it is nonstoichiometric at compositions other than 50 mol% MgO – 50 mol% Al₂O₃. The maximum nonstoichiometry on the Al₂O₃-rich side of the spinel phase field exists at about 2000°C (3630°F) corresponding to approximately 82 mol% (92 wt%) Al₂O₃.
Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.

(b) The maximum nonstoichiometry on the MgO-rich side of the spinel phase field exists at about 2000°C (3630°F) corresponding to approximately 39 mol% (62 wt%) \( A_2O_3 \). Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.

10.46* For a ternary system, three components are present; temperature is also a variable. Compute the maximum number of phases that may be present for a ternary system, assuming that pressure is held constant.

10.47* In Figure 10.38 is shown the pressure-temperature phase diagram for H\(_2\)O. Apply the Gibbs phase rule at points \( A \), \( B \), and \( C \); that is, specify the number of degrees of freedom at each of the points, that is, the number of externally controllable variables that need be specified to completely define the system.

10.48 Construct the hypothetical phase diagram for metals \( A \) and \( B \) between temperatures of 600°C and 1000°C given the following information:

- The melting temperature of metal \( A \) is 940°C.
- The solubility of \( B \) in \( A \) is negligible at all temperatures.
- The melting temperature of metal \( B \) is 830°C.
- The maximum solubility of \( A \) in \( B \) is 12 wt% \( A \), which occurs at 700°C.
- At 600°C, the solubility of \( A \) in \( B \) is 8 wt% \( A \).
- One eutectic occurs at 700°C and 75 wt% \( B \) – 25 wt% \( A \).
- A second eutectic occurs at 730°C and 60 wt% \( B \) – 40 wt% \( A \).
- A third eutectic occurs at 755°C and 40 wt% \( B \) – 60 wt% \( A \).
- One congruent melting point occurs at 780°C and 51 wt% \( B \) – 49 wt% \( A \).
- A second congruent melting point occurs at 755°C and 67 wt% \( B \) – 33 wt% \( A \).
- The intermetallic compound \( A\)\(B_2 \) exists at 51 wt% \( B \) – 49 wt% \( A \).

10.49* Two intermetallic compounds, \( A\)\(B \) and \( A\)\(B_2 \), exist for elements \( A \) and \( B \). If the compositions for \( A\)\(B \) and \( A\)\(B_2 \) are 34.3 wt% \( A \) – 65.7 wt% \( B \) and 20.7 wt% \( A \) – 79.3 wt% \( B \), respectively, and element \( A \) is potassium, identify element \( B \).

10.50 Compute the mass fractions of \( \alpha \) ferrite and cementite in pearlite.

10.51 What is the difference between a phase and a microconstituent?

10.52 (a) What is the distinction between hypo-eutectoid and hypereutectoid steels?

(b) In a hypoeutectoid steel, both eutectoid and proeutectoid ferrite exist. Explain the difference between them. What will be the carbon concentration in each?

10.53 Briefly explain why a proeutectoid phase forms along austenite grain boundaries. Hint: Consult Section 5.8.

10.54 What is the carbon concentration of an iron–carbon alloy for which the fraction of total ferrite is 0.94?

10.55 What is the proeutectoid phase for an iron–carbon alloy in which the mass fractions of total ferrite and total cementite are 0.92 and 0.08, respectively? Why?

10.56 Consider 1.0 kg of austenite containing 1.15 wt% \( C \), cooled to below 727°C (1341°F).

(a) What is the proeutectoid phase?

(b) How many kilograms each of total ferrite and cementite form?

(c) How many kilograms each of pearlite and the proeutectoid phase form?

(d) Schematically sketch and label the resulting microstructure.

10.57 Consider 2.5 kg of austenite containing 0.65 wt% \( C \), cooled to below 727°C (1341°F).

(a) What is the proeutectoid phase?

(b) How many kilograms each of total ferrite and cementite form?

(c) How many kilograms each of pearlite and the proeutectoid phase form?

(d) Schematically sketch and label the resulting microstructure.
10.58 Compute the mass fractions of proeutectoid ferrite and pearlite that form in an iron–carbon alloy containing 0.25 wt% C.

10.59 The microstructure of an iron–carbon alloy consists of proeutectoid ferrite and pearlite; the mass fractions of these two microconstituents are 0.286 and 0.714, respectively. Determine the concentration of carbon in this alloy.

10.60 The mass fractions of total ferrite and total cementite in an iron–carbon alloy are 0.88 and 0.12, respectively. Is this a hypoeutectoid or hypereutectoid alloy? Why?

10.61 The microstructure of an iron–carbon alloy consists of proeutectoid ferrite and pearlite; the mass fractions of these microconstituents are 0.20 and 0.80, respectively. Determine the concentration of carbon in this alloy.

10.62 Consider 2.0 kg of a 99.6 wt% Fe–0.4 wt% C alloy that is cooled to a temperature just below the eutectoid.
(a) How many kilograms of proeutectoid ferrite form?
(b) How many kilograms of eutectoid ferrite form?
(c) How many kilograms of cementite form?

10.63 Compute the maximum mass fraction of proeutectoid cementite possible for a hypereutectoid iron–carbon alloy.

10.64 Is it possible to have an iron–carbon alloy for which the mass fractions of total ferrite and proeutectoid cementite are 0.846 and 0.049, respectively? Why or why not?

10.65 Is it possible to have an iron–carbon alloy for which the mass fractions of total cementite and pearlite are 0.039 and 0.417, respectively? Why or why not?

10.66 Compute the mass fraction of eutectoid ferrite in an iron–carbon alloy that contains 0.43 wt% C.

10.67 The mass fraction of eutectoid cementite in an iron–carbon alloy is 0.104. On the basis of this information, is it possible to determine the composition of the alloy? If so, what is its composition? If this is not possible, explain why.

10.68 The mass fraction of eutectoid ferrite in an iron–carbon alloy is 0.82. On the basis of this information, is it possible to determine the composition of the alloy? If so, what is its composition? If this is not possible, explain why.

10.69 For an iron–carbon alloy of composition 5 wt% C–95 wt% Fe, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1175°C (2150°F), 1145°C (2095°F), and 700°C (1290°F). Label the phases and indicate their compositions (approximate).

10.70 Often, the properties of multiphase alloys may be approximated by the relationship

\[ E_{\text{alloy}} = E_{\alpha}V_{\alpha} + E_{\beta}V_{\beta} \]

where \( E \) represents a specific property (modulus of elasticity, hardness, etc.), and \( V \) is the volume fraction. The subscripts \( \alpha \) and \( \beta \) denote the existing phases or microconstituents. Employ the relationship above to determine the approximate Brinell hardness of a 99.80 wt% Fe–0.20 wt% C alloy. Assume Brinell hardnesses of 80 and 280 for ferrite and pearlite, respectively, and that volume fractions may be approximated by mass fractions.

10.71* On the basis of the photomicrograph (i.e., the relative amounts of the microconstituents) for the lead–tin alloy shown in Figure 10.15 and the Pb–Sn phase diagram (Figure 10.7), estimate the composition of the alloy, and then compare this estimate with the composition given in the figure legend of Figure 10.15. Make the following assumptions: (1) the area fraction of each phase and microconstituent in the photomicrograph is equal to its volume fraction; (2) the densities of the \( \alpha \) and \( \beta \) phases as well as the eutectic structure are 11.2, 7.3, and 8.7 g/cm³, respectively; and (3) this photomicrograph represents the equilibrium microstructure at 180°C (356°F).

10.72* A steel alloy contains 97.5 wt% Fe, 2.0 wt% Mo, and 0.5 wt% C.
(a) What is the eutectoid temperature of this alloy?
(b) What is the eutectoid composition?
(c) What is the proeutectoid phase?
Assume that there are no changes in the positions of other phase boundaries with the addition of Mo.

10.73* A steel alloy is known to contain 93.8 wt% Fe, 6.0 wt% Ni, and 0.2 wt% C.
(a) What is the approximate eutectoid temperature of this alloy?
(b) What is the proeutectoid phase when this alloy is cooled to a temperature just below the eutectoid?
(c) Compute the relative amounts of the proeutectoid phase and pearlite. Assume that there are no alterations in the positions of other phase boundaries with the addition of Ni.