Chapter 10

Solid Solutions and Phase Equilibrium

Have You Ever Wondered?

- *Is it possible for the solid, liquid, and gaseous forms of a material to coexist?*
- *What material is used to make red light-emitting diodes used in many modern product displays?*
- *When an alloy such as brass solidifies, which element solidifies first—copper or zinc?*

We have seen that the strength of metallic materials can be enhanced using

(a) grain size strengthening (Hall-Petch equation);
(b) cold working or strain hardening;
(c) formation of small particles of second phases; and
(d) additions of small amounts of elements.

When small amounts of elements are added, a solid material known as a solid solution may form. A **solid solution** contains two or more types of atoms or ions that are dispersed uniformly throughout the material. The impurity or **solute** atoms may occupy regular lattice sites in the crystal or interstitial sites. By controlling the amount of these point defects via the composition, the mechanical and other properties of solid solutions can be manipulated. For example, in metallic materials, the point defects created by the impurity or solute atoms disturb the atomic arrangement in the crystalline material and interfere with the movement of dislocations. The point defects cause the material to be solid-solution strengthened.

The introduction of alloying elements or impurities during processing changes the composition of the material and influences its solidification behavior. In this chapter, we will examine this effect by introducing the concept of an equilibrium phase diagram. For now, we consider a "phase" as a unique form in which a material exists.

We will define the term "phase" more precisely later in this chapter. A phase diagram depicts the stability of different phases for a set of elements (e.g., Al and Si). From the phase diagram, we can predict how a material will solidify under equilibrium conditions. We can also predict what phases will be expected to be thermodynamically stable and in what concentrations such phases should be present.

Therefore, the major objectives of this chapter are to explore

1. the formation of solid solutions;
2. the effects of solid-solution formation on the mechanical properties of metallic materials;
3. the conditions under which solid solutions can form;
4. the development of some basic ideas concerning phase diagrams; and
5. the solidification process in simple alloys.

10-1 Phases and the Phase Diagram

Pure metallic elements have engineering applications; for example, ultra-high purity copper (Cu) or aluminum (Al) is used to make microelectronic circuitry. In most applications, however, we use **alloys**. We define an "alloy" as a material that exhibits properties of a metallic material and is made from multiple elements. A *plain carbon steel* is an alloy of iron (Fe) and carbon (C). Corrosion-resistant **stainless steels** are alloys that usually contain iron (Fe), carbon (C), chromium (Cr), nickel (Ni), and some other elements. Similarly, there are alloys based on aluminum (Al), copper (Cu), cobalt (Co), nickel (Ni), titanium (Ti), zinc (Zn), and zirconium (Zr). There are two types of alloys: **single-phase alloys** and **multiple phase alloys**. In this chapter, we will examine the behavior of single-phase alloys. As a first step, let's define a "phase" and determine how the **phase rule** helps us to determine the state—solid, liquid, or gas—in which a pure material exists.

A **phase** can be defined as any portion, including the whole, of a system which is physically homogeneous within itself and bounded by a surface that separates it from any other portions. For example, water has three phases—liquid water, solid ice, and steam. A phase has the following characteristics:

1. the same structure or atomic arrangement throughout;
2. roughly the same composition and properties throughout; and
3. a definite interface between the phase and any surrounding or adjoining phases.

For example, if we enclose a block of ice in a vacuum chamber [Figure 10-1(a)], the ice begins to melt, and some of the water vaporizes. Under these conditions, we have three phases coexisting: solid H_2O, liquid H_2O, and gaseous H_2O. Each of these forms of H_2O is a distinct phase; each has a unique atomic arrangement, unique properties, and a definite boundary between each form. In this case, the phases have identical compositions.

Phase Rule

Josiah Willard Gibbs (1839–1903) was a brilliant American physicist and mathematician who conducted some of the most important pioneering work related to thermodynamic equilibrium.

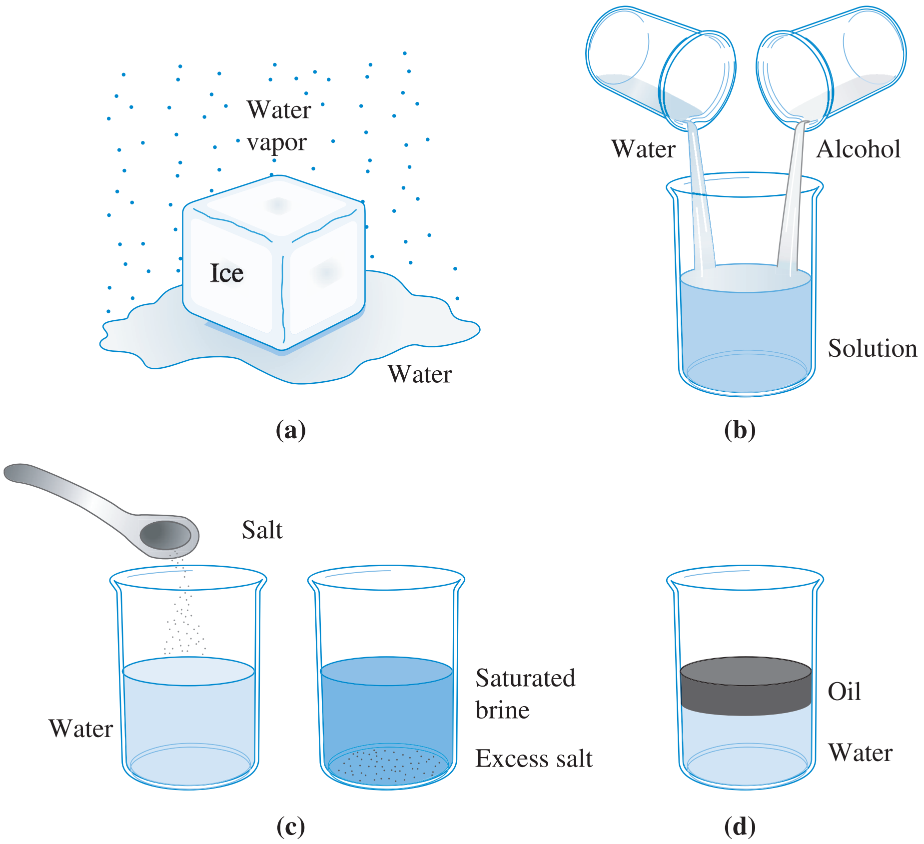

Figure 10-1 Illustration of phases and solubility: (a) The three forms of water—gas, liquid, and solid—are each a phase. (b) Water and alcohol have unlimited solubility. (c) Salt and water have limited solubility. (d) Oil and water have virtually no solubility.

Gibbs developed the **phase rule** in 1875–1876. It describes the relationship between the number of components and the number of phases for a given system and the conditions that may be allowed to change (e.g., temperature, pressure, etc.). It has the general form:

$$2 + C = F + P \text{ (when temperature and pressure both can vary)} \qquad (10\text{-}1)$$

A useful mnemonic (something that will help you remember) for the Gibbs phase rule is to start with a numeric and follow with the rest of the terms alphabetically (i.e., C, F, and P) using all positive signs. In the phase rule, C is the number of chemically independent components, usually elements or compounds, in the system; F is the number of degrees of freedom, or the number of variables (such as temperature, pressure, or composition), that are allowed to change independently without changing the number of phases in equilibrium; and P is the number of phases present (please do not confuse P with “pressure”). The constant “2” in Equation 10-1 implies that both the temperature and pressure are allowed to change. The term “chemically independent” refers to the number of different elements or compounds needed to specify a system. For example, water (H_2O) is considered as a one component system, since the concentrations of H and O in H_2O cannot be independently varied.

It is important to note that the Gibbs phase rule assumes thermodynamic equilibrium and, more often than not in materials processing, we encounter conditions in which equilibrium is *not* maintained. Therefore, you should not be surprised to see that the number and compositions of phases seen in practice are dramatically different from those predicted by the Gibbs phase rule.

Another point to note is that phases do not always have to be solid, liquid, and gaseous forms of a material. An element, such as iron (Fe), can exist in FCC and BCC crystal structures. These two solid forms of iron are two different phases of iron that will be stable at different temperatures and pressure conditions. Similarly, ice, itself, can exist in several crystal structures. Carbon can exist in many forms (e.g., graphite or diamond). These are only two of the many possible phases of carbon as we saw in Chapter 2.

As an example of the use of the phase rule, let's consider the case of pure magnesium (Mg). Figure 10-2 shows a **unary** ($C = 1$) **phase diagram** in which the lines divide the liquid, solid, and vapor phases. This unary phase diagram is also called a pressure-temperature or **P-T diagram**. In the unary phase diagram, there is only one component; in this case, magnesium (Mg). Depending on the temperature and pressure, however, there may be one, two, or even three *phases* present at any one time: solid magnesium, liquid magnesium, and magnesium vapor. Note that at atmospheric pressure (one atmosphere, given by the dashed line), the intersection of the lines in the phase diagram give the usual melting and boiling temperatures for magnesium. At very low pressures, a solid such as magnesium (Mg) can *sublime*, or go directly to a vapor form without melting, when it is heated.

Suppose we have a pressure and temperature that put us at point A in the phase diagram (Figure 10-2). At this point, magnesium is all liquid. The number of phases is one (liquid). The phase rule tells us that there are two degrees of freedom. From Equation 10-1:

$$2 + C = F + P, \quad \text{therefore, } 2 + 1 = F + 1 \text{ (i.e., } F = 2)$$

What does this mean? Within limits, as seen in Figure 10-2, we can change the pressure, the temperature, or both, and still be in an all-liquid portion of the diagram. Put another way, we must fix both the temperature and the pressure to know precisely where we are in the liquid portion of the diagram.

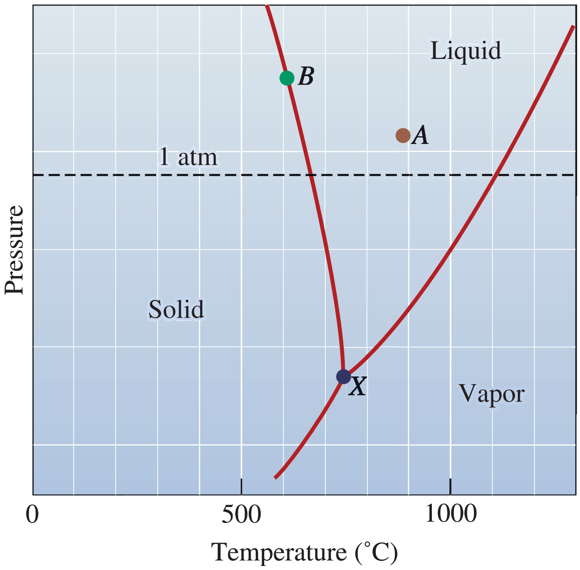

Figure 10-2
Schematic unary phase diagram for magnesium, showing the melting and boiling temperatures at one atmosphere pressure. On this diagram, point X is the triple point.

Consider point B, the boundary between the solid and liquid portions of the diagram. The number of components, C, is still one, but at point B, the solid and liquid coexist, or the number of phases P is two. From the phase rule Equation 10-1,

$$2 + C = F + P, \quad \text{therefore, } 2 + 1 = F + 2 \text{ (i.e, } F = 1)$$

or there is only one degree of freedom. For example, if we change the temperature, the pressure must also be adjusted if we are to stay on the boundary where the liquid and solid coexist. On the other hand, if we fix the pressure, the phase diagram tells us the temperature that we must have if solid and liquid are to coexist.

Finally, at point X, solid, liquid, and vapor coexist. While the number of components is still one, there are three phases. The number of degrees of freedom is zero:

$$2 + C = F + P, \quad \text{therefore, } 2 + 1 = F + 3 \text{ (i.e., } F = 0)$$

Now we have no degrees of freedom; all three phases coexist only if both the temperature and the pressure are fixed. A point on the phase diagram at which the solid, liquid, and gaseous phases coexist under equilibrium conditions is the **triple point** (Figure 10-2). In the following two examples, we see how some of these ideas underlying the Gibbs phase rule can be applied.

Example 10-1 *Design of an Aerospace Component*

Because magnesium (Mg) is a low-density material ($\rho_{Mg} = 1.738\ \text{g/cm}^3$), it has been suggested for use in an aerospace vehicle intended to enter outer space. Is this a good design?

SOLUTION

The pressure is very low in space. Even at relatively low temperatures, solid magnesium can begin to transform to a vapor, causing metal loss that could damage a space vehicle. In addition, solar radiation could cause the vehicle to heat, increasing the rate of magnesium loss.

A low-density material with a higher boiling point (and, therefore, lower vapor pressure at any given temperature) might be a better choice. At atmospheric pressure, aluminum boils at 2494°C and beryllium (Be) boils at 2770°C, compared with the boiling temperature of 1107°C for magnesium. Although aluminum and beryllium are somewhat denser than magnesium, either might be a better choice. Given the toxic effects of Be and many of its compounds when in powder form, we may want to consider aluminum first.

There are other factors to consider. In load-bearing applications, we should not only look for density but also for relative strength. Therefore, the ratio of Young's modulus to density or yield strength to density could be a better parameter to compare different materials. In this comparison, we will have to be aware that yield strength, for example, depends strongly on microstructure and that the strength of aluminum can be enhanced using aluminum alloys, while keeping the density about the same. Other factors such as oxidation during reentry into Earth's atmosphere may be applicable and will also have to be considered.

10-2 Solubility and Solid Solutions

Often, it is beneficial to know how much of each material or component we can combine without producing an additional phase. When we begin to combine different components or materials, as when we add alloying elements to a metal, solid or liquid solutions can form. For example, when we add sugar to water, we form a sugar solution. When we diffuse a small number of phosphorus (P) atoms into single crystal silicon (Si), we produce a solid solution of P in Si (Chapter 5). In other words, we are interested in the **solubility** of one material in another (e.g., sugar in water, copper in nickel, phosphorus in silicon, etc.).

Unlimited Solubility

Suppose we begin with a glass of water and a glass of alcohol. The water is one phase, and the alcohol is a second phase. If we pour the water into the alcohol and stir, only one phase is produced [Figure 10-1(b)]. The glass contains a solution of water and alcohol that has unique properties and composition. Water and alcohol are soluble in each other. Furthermore, they display **unlimited solubility**. Regardless of the ratio of water and alcohol, only one phase is produced when they are mixed together.

Similarly, if we were to mix any amounts of liquid copper and liquid nickel, only one liquid phase would be produced. This liquid alloy has the same composition and properties everywhere [Figure 10-3(a)] because nickel and copper have unlimited liquid solubility.

If the liquid copper-nickel alloy solidifies and cools to room temperature while maintaining thermal equilibrium, only one solid phase is produced. After solidification, the copper and nickel atoms do not separate but, instead, are randomly located within the FCC crystal structure. Within the solid phase, the structure, properties, and composition are uniform and no interface exists between the copper and nickel atoms. Therefore, copper and nickel also have unlimited solid solubility. The solid phase is a solid solution of copper and nickel [Figure 10-3(b)].

A solid solution is *not* a mixture. A mixture contains more than one type of phase, and the characteristics of each phase are retained when the mixture is formed. In contrast to this, the components of a solid solution completely dissolve in one another and do not retain their individual characteristics.

Another example of a system forming a solid solution is that of barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$), which are compounds found in the $BaO–TiO_2–SrO$ ternary system. We use solid solutions of $BaTiO_3$ with $SrTiO_3$ and other oxides to make electronic components such as capacitors. Millions of multilayer capacitors are made each year using such materials (Chapter 19).

Many compound semiconductors that share the same crystal structure readily form solid solutions with 100% solubility. For example, we can form solid solutions of gallium arsenide (GaAs) and aluminum arsenide (AlAs). The most commonly used red LEDs for in displays are made using solid solutions based on the GaAs-GaP system. Solid solutions can be formed using more than two compounds or elements.

Limited Solubility

When we add a small quantity of salt (one phase) to a glass of water (a second phase) and stir, the salt dissolves completely in the water. Only one phase—salty water or brine—is found. If we add too much salt to the water, the excess salt sinks to the bottom of the glass [Figure 10-1(c)]. Now we have two phases—water that is saturated with salt plus excess solid salt. We find that salt has a **limited solubility** in water.

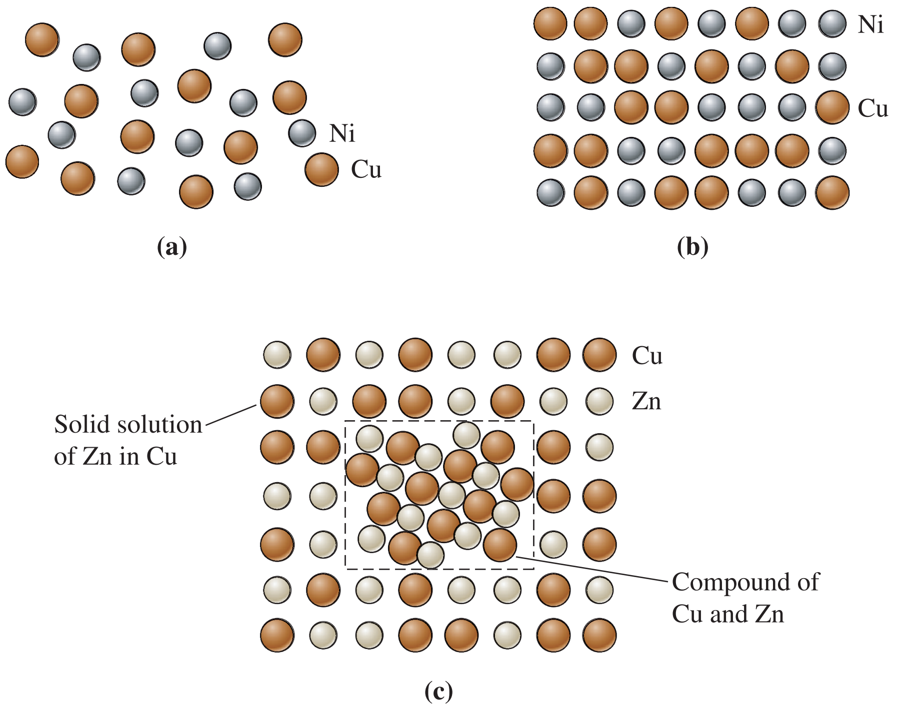

Figure 10-3 (a) Liquid copper and liquid nickel are completely soluble in each other. (b) Solid copper-nickel alloys display complete solid solubility with copper and nickel atoms occupying random lattice sites. (c) In copper-zinc alloys containing more than 30% Zn, a second phase forms because of the limited solubility of zinc in copper.

If we add a small amount of liquid zinc to liquid copper, a single liquid solution is produced. When that copper-zinc solution cools and solidifies, a single solid solution having an FCC structure results, with copper and zinc atoms randomly located at the normal lattice points. If the liquid solution contains more than about 30% Zn, some of the excess zinc atoms combine with some of the copper atoms to form a CuZn compound [Figure 10-3(c)]. Two solid phases now coexist: a solid solution of copper saturated with about 30% Zn plus a CuZn compound. The solubility of zinc in copper is limited. Figure 10-4 shows a portion of the Cu-Zn phase diagram illustrating the solubility of zinc in copper at low temperatures. The solubility increases with increasing temperature. This is similar to how we can dissolve more sugar or salt in water by increasing the temperature.

In Chapter 5, we examined how silicon (Si) can be doped with phosphorous (P), boron (B), or arsenic (As). All of these dopant elements exhibit limited solubility in Si (i.e., at small concentrations they form a solid solution with Si). Thus, solid solutions are produced even if there is limited solubility. We do not need 100% solid solubility to form solid solutions. Note that solid solutions may form either by substitutional or interstitial mechanisms. The guest atoms or ions may enter the host crystal structure at regular crystallographic positions or the interstices.

In the extreme case, there may be almost no solubility of one material in another. This is true for oil and water [Figure 10-1(d)] or for copper-lead (Cu-Pb) alloys. Note that even though materials do not dissolve into one another, they can be dispersed into one another. For example, oil-like phases and aqueous liquids can be mixed, often using surfactants (soap-like molecules), to form emulsions. Immiscibility, or lack of solubility, is seen in many molten and solid ceramic and metallic materials.

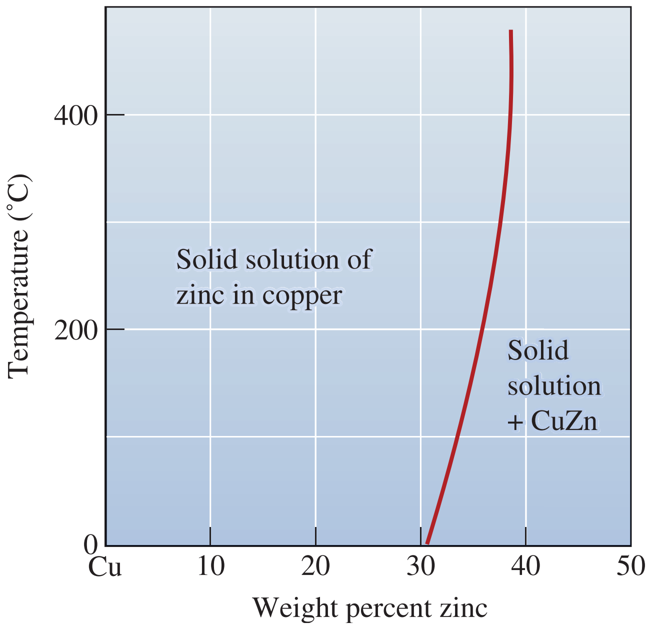

Figure 10-4 The solubility of zinc in copper. The solid line represents the solubility limit; when excess zinc is added, the solubility limit is exceeded and two phases coexist.

Polymeric Systems We can process polymeric materials to enhance their usefulness by employing a concept similar to the formation of solid solutions in metallic and ceramic systems. We can form materials that are known as **copolymers** that consist of different monomers. For example, acrylonitrile (A), butadiene (B), and styrene (S) monomers can be made to react to form a copolymer known as ABS. This resultant copolymer is similar to a solid solution in that it has the functionalities of the three monomers from which it is derived, blending their properties. Similar to the Cu-Ni or $BaTiO_3$-$SrTiO_3$ solid solutions, we will not be able to separate out the acrylonitrile, butadiene, or styrene from an ABS plastic. Injection molding is used to convert ABS into telephones, helmets, steering wheels, and small appliance cases. Figure 10-5 illustrates the properties of different copolymers in the ABS system. Note that this is *not* a phase diagram. Dylark™ is another example of a copolymer. It is formed using maleic anhydride and a styrene monomer. The Dylark™ copolymer, with carbon black for UV protection, reinforced with fiberglass, and toughened with rubber, has been used for instrument panels in many automobiles (Chapter 16).

10-3 Conditions for Unlimited Solid Solubility

In order for an alloy system, such as copper-nickel to have unlimited solid solubility, certain conditions must be satisfied. These conditions, the **Hume-Rothery** rules, are as follows:

1. *Size factor*: The atoms or ions must be of similar size, with no more than a 15% difference in atomic radius, in order to minimize the lattice strain (i.e., to minimize, at an atomic level, the deviations caused in interatomic spacing).
2. *Crystal structure*: The materials must have the same crystal structure; otherwise, there is some point at which a transition occurs from one phase to a second phase with a different structure.
3. *Valence*: The ions must have the same valence; otherwise, the valence electron difference encourages the formation of compounds rather than solutions.

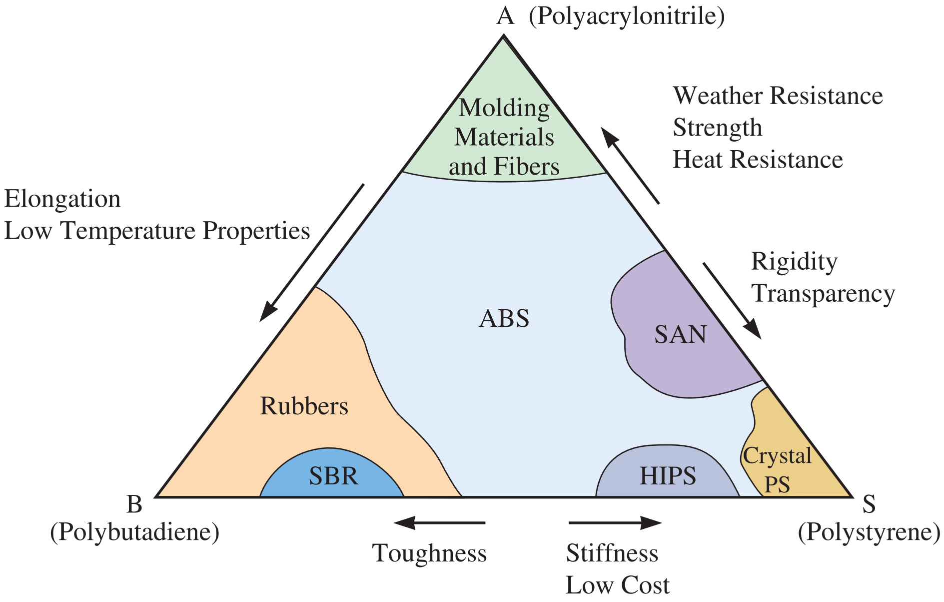

Figure 10-5 Diagram showing how the properties of copolymers formed in the ABS system vary. This is not a phase diagram. *(From* STRONG, A. BRENT, PLASTICS: MATERIALS AND PROCESSING, 2nd, ©2000*.* Electronically reproduced by permission of Pearson Education, Inc., Upper Saddle River, New Jersery.*)*

4. *Electronegativity*: The atoms must have approximately the same electronegativity. Electronegativity is the affinity for electrons (Chapter 2). If the electronegativities differ significantly, compounds form—as when sodium and chloride ions combine to form sodium chloride.

Hume-Rothery's conditions must be met, but they are not necessarily sufficient, for two metals (e.g., Cu and Ni) or compounds (e.g., $BaTiO_3$-$SrTiO_3$) to have unlimited solid solubility.

Figure 10-6 shows schematically the two-dimensional structures of MgO and NiO. The Mg^{+2} and Ni^{+2} ions are similar in size and valence and, consequently, can

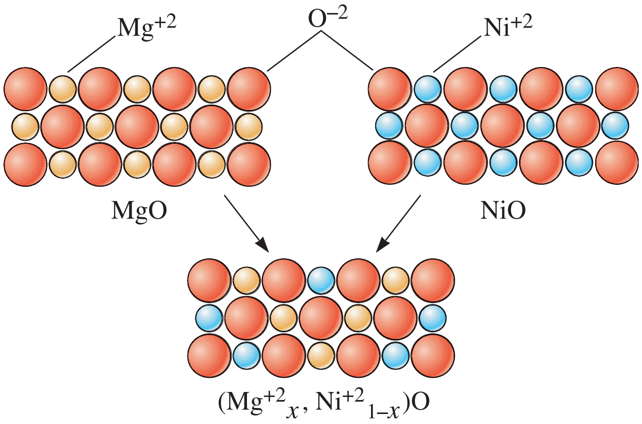

Figure 10-6 MgO and NiO have similar crystal structures, ionic radii, and valences; thus the two ceramic materials can form solid solutions.

replace one another in a sodium chloride (NaCl) crystal structure (Chapter 3), forming a complete series of solid solutions of the form ($Mg_x^{+2}Ni_{1-x}^{+2}$)O, where x = the mole fraction of Mg^{+2} or MgO.

The solubility of interstitial atoms is always limited. Interstitial atoms are much smaller than the atoms of the host element, thereby violating the first of Hume-Rothery's conditions.

Example 10-2 *Ceramic Solid Solutions of MgO*

NiO can be added to MgO to produce a solid solution. What other ceramic systems are likely to exhibit 100% solid solubility with MgO?

SOLUTION

In this case, we must consider oxide additives that have metal cations with the same valence and ionic radius as the magnesium cations. The valence of the magnesium ion is +2, and its ionic radius is 0.66 Å. From Appendix B, some other possibilities in which the cation has a valence of +2 include the following:

	r(Å)	$\left[\frac{r_{ion} - r_{Mg^{+2}}}{r_{Mg^{+2}}}\right] \times 100\%$	Crystal Structure
Cd^{+2} in CdO	$r_{Cd^{+2}} = 0.97$	47	NaCl
Ca^{+2} in CaO	$r_{Ca^{+2}} = 0.99$	50	NaCl
Co^{+2} in CoO	$r_{Co^{+2}} = 0.72$	9	NaCl
Fe^{+2} in FeO	$r_{Fe^{+2}} = 0.74$	12	NaCl
Sr^{+2} in SrO	$r_{Sr^{+2}} = 1.12$	70	NaCl
Zn^{+2} in ZnO	$r_{Zn^{+2}} = 0.74$	12	NaCl

The percent difference in ionic radii and the crystal structures are also shown and suggest that the FeO-MgO system will probably display unlimited solid solubility. The CoO and ZnO systems also have appropriate radius ratios and crystal structures.

10-4 Solid-Solution Strengthening

In metallic materials, one of the important effects of solid-solution formation is the resultant **solid-solution strengthening** (Figure 10-7). This strengthening, via solid-solution formation, is caused by increased resistance to dislocation motion. This is one of the important reasons why brass (Cu-Zn alloy) is stronger than pure copper. We will learn later that carbon also plays another role in the strengthening of steels by forming iron carbide (Fe_3C) and other phases (Chapter 12). Jewelry could be made out from pure gold or silver; however, pure gold and pure silver are extremely soft and malleable. Jewelers add copper to gold and silver so that the jewelry will retain its shape.

In the copper-nickel (Cu-Ni) system, we intentionally introduce a solid substitutional atom (nickel) into the original crystal structure (copper). The copper-nickel alloy is stronger than pure copper. Similarly, if less than 30% Zn is added to copper, the zinc

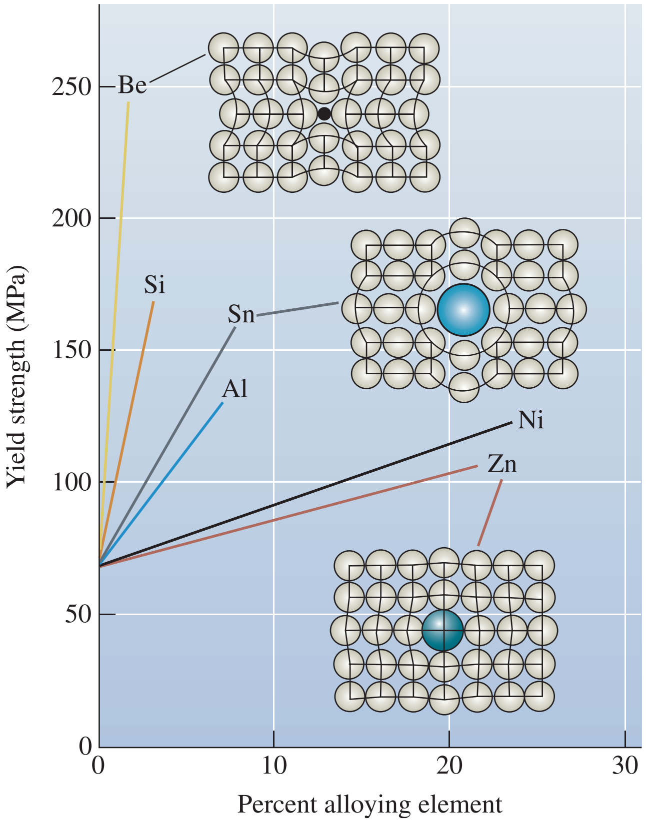

Figure 10-7
The effects of several alloying elements on the yield strength of copper. Nickel and zinc atoms are about the same size as copper atoms, but beryllium and tin atoms are much different from copper atoms. Increasing both the atomic size difference and the amount of alloying element increases solid-solution strengthening.

behaves as a substitutional atom that strengthens the copper-zinc alloy, as compared with pure copper.

Recall from Chapter 7 that the strength of ceramics is mainly dictated by the distribution of flaws; solid-solution formation does not have a strong effect on their mechanical properties. This is similar to why strain hardening was not much of a factor in enhancing the strength of ceramics or semiconductors such as silicon (Chapter 8). As discussed before, solid-solution formation in ceramics and semiconductors (such as Si, GaAs, etc.) has considerable influence on their magnetic, optical, and dielectric properties. The following discussion related to mechanical properties, therefore, applies mainly to metals.

Degree of Solid-Solution Strengthening

The degree of solid-solution strengthening depends on two factors. First, a large difference in atomic size between the original (host or solvent) atom and the added (guest or solute) atom increases the strengthening effect. A larger size difference produces a greater disruption of the initial crystal structure, making slip more difficult (Figure 10-7).

Second, the greater the amount of alloying element added, the greater the strengthening effect (Figure 10-7). A Cu-20% Ni alloy is stronger than a Cu-10% Ni alloy. Of course, if too much of a large or small atom is added, the solubility limit may be exceeded and a different strengthening mechanism, **dispersion strengthening**, is produced. In dispersion strengthening, the interface between the host phase and guest phase resists dislocation motion and contributes to strengthening. This mechanism is discussed further in Chapter 11.

Example 10-3 *Solid-Solution Strengthening*

From the atomic radii, show whether the size difference between copper atoms and alloying atoms accurately predicts the amount of strengthening found in Figure 10-7.

SOLUTION

The atomic radii and percent size difference are shown below.

Metal	Atomic Radius (Å)	$\left[\frac{r_{atom} - r_{Cu}}{r_{Cu}}\right] \times 100\%$
Cu	1.278	0
Zn	1.332	+4.2
Sn	1.405	+9.9
Al	1.432	+12.1
Ni	1.243	−2.7
Si	1.176	−8.0
Be	1.143	−10.6

For atoms larger than copper—namely, zinc, tin, and aluminum—increasing the size difference generally increases the strengthening effect. Likewise for smaller atoms, increasing the size difference increases strengthening.

Effect of Solid-Solution Strengthening on Properties

The effects of solid-solution strengthening on the properties of a metal include the following (Figure 10-8):

1. The yield strength, tensile strength, and hardness of the alloy are greater than those of the pure metals. This is one reason why we most often use alloys rather than pure

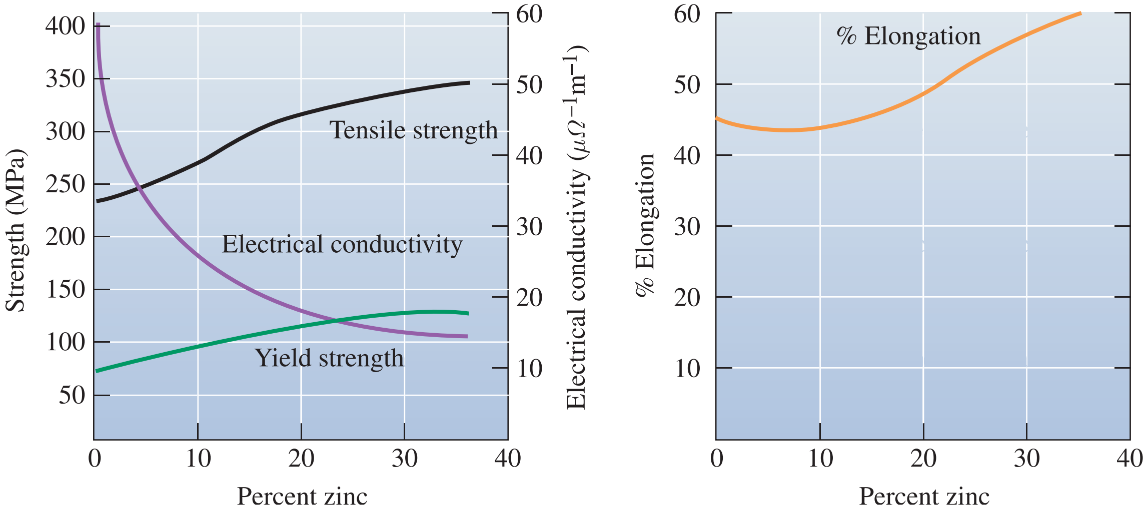

Figure 10-8
The effect of additions of zinc to copper on the properties of the solid-solution-strengthened alloy. The increase in % elongation with increasing zinc content is *not* typical of solid-solution strengthening.

metals. For example, small concentrations of Mg are added to aluminum to provide higher strength to the aluminum alloys used in making aluminum beverage cans.

2. Almost always, the ductility of the alloy is less than that of the pure metal. Only rarely, as in copper-zinc alloys, does solid-solution strengthening increase both strength and ductility.
3. Electrical conductivity of the alloy is much lower than that of the pure metal (Chapter 19). This is because electrons are scattered by the atoms of the alloying elements more so than the host atoms. Solid-solution strengthening of copper or aluminum wires used for transmission of electrical power is not recommended because of this pronounced effect. Electrical conductivity of many alloys, although lower than pure metals, is often more stable as a function of temperature.
4. The resistance to creep and strength at elevated temperatures is improved by solid-solution strengthening. Many high-temperature alloys, such as those used for jet engines, rely partly on extensive solid-solution strengthening.

10-5 Isomorphous Phase Diagrams

A **phase diagram** shows the phases and their compositions at any combination of temperature and alloy composition. When only two elements or two compounds are present in a material, a **binary phase diagram** can be constructed. **Isomorphous phase diagrams** are found in a number of metallic and ceramic systems. In the isomorphous systems, which include the copper-nickel and NiO-MgO systems [Figure 10-9(a) and (b)], only one solid phase forms; the two components in the system display complete solid solubility. As shown in the phase diagrams for the $CaO \cdot SiO_2 \cdot SrO$ and thallium-lead (Tl-Pb) systems, it is possible to have phase diagrams show a minimum or maximum point, respectively [Figure 10-9(c) and (d)]. Notice the horizontal scale can represent either mole% or weight% of one of the components. We can also plot atomic% or mole fraction of one of the components. Also, notice that the $CaO \cdot SiO_2$ and $SrO \cdot SiO_2$ diagram could be plotted as a *ternary phase diagram*. A ternary phase diagram is a phase diagram for systems consisting of three components. Here, we represent it as a *pseudo-binary diagram* (i.e., we assume that this is a diagram that represents phase equilibria between $CaO \cdot SiO_2$ and $SrO \cdot SiO_2$). In a pseudo-binary diagram, we represent equilibria between three or more components using two compounds. Ternary phase diagrams are often encountered in ceramic and metallic systems.

More recently, considerable developments have been made in phase diagrams using computer databases containing thermodynamic properties of different elements and compounds. There are several valuable pieces of information to be obtained from phase diagrams, as follows.

Liquidus and Solidus Temperatures

We define the **liquidus temperature** as the temperature above which a material is completely liquid. The upper curve in Figure 10-9(a), known as the **liquidus**, represents the liquidus temperatures for copper-nickel alloys of different compositions. We must heat a copper-nickel alloy above the liquidus temperature to produce a completely liquid alloy that can then be cast into a useful shape. The liquid alloy begins to solidify when the temperature cools to the liquidus temperature. For the Cu-40% Ni alloy in Figure 10-9(a), the liquidus temperature is 1280°C.

The **solidus temperature** is the temperature below which the alloy is 100% solid. The lower curve in Figure 10-9(a), known as the **solidus**, represents the solidus temperatures for Cu-Ni alloys of different compositions. A copper-nickel alloy is not completely solid

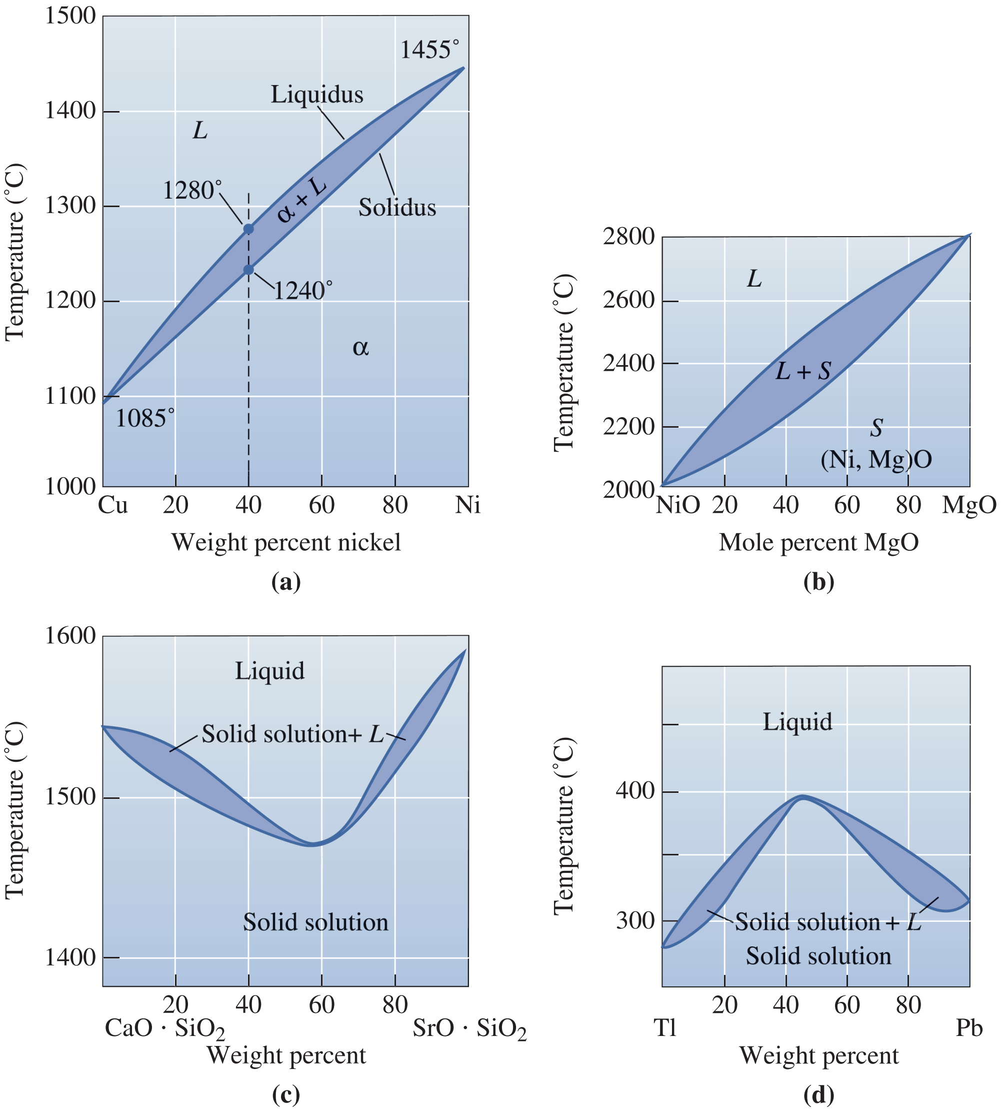

Figure 10-9 (a) and (b) The equilibrium phase diagrams for the Cu-Ni and NiO-MgO systems. The liquidus and solidus temperatures are shown for a Cu-40% Ni alloy. (c) and (d) Systems with solid-solution maxima and minima. *(Adapted from* Introduction to Phase Equilibria, *by C.G. Bergeron, and S.H. Risbud. Copyright © 1984 American Ceramic Society. Adapted by permission.)*

until the material cools below the solidus temperature. If we use a copper-nickel alloy at high temperatures, we must be sure that the service temperature is below the solidus so that no melting occurs. For the Cu-40% Ni alloy in Figure 10-9(a), the solidus temperature is 1240°C.

Copper-nickel alloys melt and freeze over a range of temperatures between the liquidus and the solidus. The temperature difference between the liquidus and the solidus is the **freezing range** of the alloy. Within the freezing range, two phases coexist: a liquid and a solid. The solid is a solution of copper and nickel atoms and is designated as the α phase. For the Cu-40% Ni alloy (α phase) in Figure 10-9(a), the freezing range is $1280 - 1240 = 40$°C. Note that pure metals solidify at a fixed temperature (i.e., the freezing range is zero degrees).

Phases Present Often we are interested in which phases are present in an alloy at a particular temperature. If we plan to make a casting, we must be sure that the metal is initially all liquid; if we plan to heat treat an alloy component, we must be sure that no liquid forms during the process. Different solid phases have different properties. For example, BCC Fe (indicated as the α phase on the iron-carbon phase diagram) is ferromagnetic; however, FCC iron (indicated as the γ phase on the Fe-C diagram) is not.

The phase diagram can be treated as a road map; if we know the coordinates—temperature and alloy composition—we can determine the phases present, assuming we know that thermodynamic equilibrium exists. There are many examples of technologically important situations in which we do not want equilibrium phases to form. For example, in the formation of silicate glass, we want an amorphous glass and not crystalline SiO_2 to form. When we harden steels by quenching them from a high temperature, the hardening occurs because of the formation of nonequilibrium phases. In such cases, phase diagrams will **not** provide all of the information we need. In these cases, we need to use special diagrams that take into account the effect of time (i.e., kinetics) on phase transformations. We will examine the use of such diagrams in later chapters.

The following two examples illustrate the applications of some of these concepts.

Example 10-4 *NiO-MgO Isomorphous System*

From the phase diagram for the NiO-MgO binary system [Figure 10-9(b)], describe a composition that can melt at 2600°C but will not melt when placed into service at 2300°C.

SOLUTION

The material must have a liquidus temperature below 2600°C, but a solidus temperature above 2300°C. The NiO-MgO phase diagram [Figure 10-9(b)] permits us to choose an appropriate composition.

To identify a composition with a liquidus temperature below 2600°C, there must be less than 60 mol% MgO in the refractory. To identify a composition with a solidus temperature above 2300°C, there must be at least 50 mol% MgO present. Consequently, we can use any composition between 50 mol% MgO and 60 mol% MgO.

Example 10-5 *Design of a Composite Material*

One method to improve the fracture toughness of a ceramic material (Chapter 7) is to reinforce the ceramic matrix with ceramic fibers. A materials designer has suggested that Al_2O_3 could be reinforced with 25% Cr_2O_3 fibers, which would interfere with the propagation of any cracks in the alumina. The resulting composite is expected to operate under load at 2000°C for several months.

Criticize the appropriateness of this design.

SOLUTION

Since the composite will operate at high temperatures for a substantial period of time, the two phases—the Cr_2O_3 fibers and the Al_2O_3 matrix—must not react with

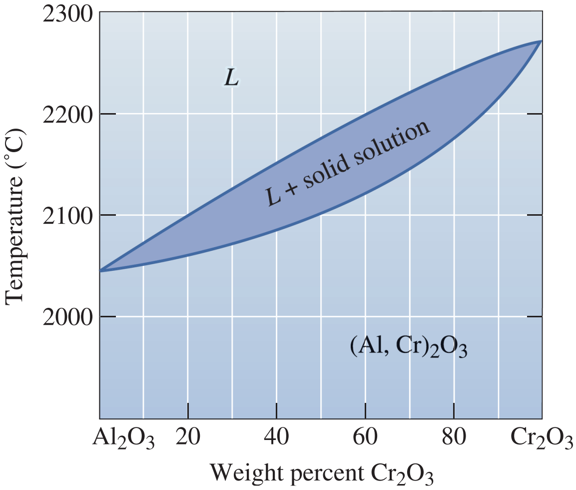

Figure 10-10
The Al_2O_3-Cr_2O_3 phase diagram (for Example 10-5).

one another. In addition, the composite must remain solid to at least 2000°C. The phase diagram in Figure 10-10 permits us to consider this choice for a composite.

Pure Cr_2O_3, pure Al_2O_3, and Al_2O_3-25% Cr_2O_3 have solidus temperatures above 2000°C; consequently, there is no danger of melting any of the constituents; however, Cr_2O_3 and Al_2O_3 display unlimited solid solubility. At the high service temperature, 2000°C, Al^{3+} ions will diffuse from the matrix into the fibers, replacing Cr^{3+} ions in the fibers. Simultaneously, Cr^{3+} ions will replace Al^{3+} ions in the matrix. Long before several months have elapsed, these diffusion processes will cause the fibers to completely dissolve into the matrix. With no fibers remaining, the fracture toughness will again be poor.

Composition of Each Phase

For each phase, we can specify a composition, expressed as the percentage of each element in the phase. Usually the composition is expressed in weight percent (wt%). When only one phase is present in the alloy or a ceramic solid solution, the composition of the phase equals the overall composition of the material. If the original composition of a single phase alloy or ceramic material changes, then the composition of the phase must also change.

When two phases, such as liquid and solid, coexist, their compositions differ from one another and also differ from the original overall composition. In this case, if the original composition changes slightly, the composition of the two phases is unaffected, provided that the temperature remains constant.

This difference is explained by the Gibbs phase rule. In this case, unlike the example of pure magnesium (Mg) described earlier, we keep the pressure fixed at one atmosphere, which is normal for binary phase diagrams. The phase rule given by Equation 10-1 can be rewritten as

$$1 + C = F + P \quad \text{(for constant pressure)} \qquad (10\text{-}2)$$

where, again, C is the number of independent chemical components, P is the number of phases (*not pressure*), and F is the number of degrees of freedom. We now use the number 1 instead of the number 2 because we are holding the pressure constant. This reduces the number of degrees of freedom by one. The pressure is typically, although not necessarily, one atmosphere. In a binary system, the number of components C is two; the degrees of freedom that we have include changing the temperature and changing the composition of the phases present. We can apply this form of the phase rule to the Cu-Ni system, as shown in Example 10-6.

Example 10-6 *Gibbs Rule for an Isomorphous Phase Diagram*

Determine the degrees of freedom in a Cu-40% Ni alloy at (a) 1300°C, (b) 1250°C, and (c) 1200°C. Use Figure 10-9(a).

SOLUTION

This is a binary system ($C = 2$). The two components are Cu and Ni. We will assume constant pressure. Therefore, Equation 10-2 ($1 + C = F + P$) can be used as follows.

(a) At 1300°C, $P = 1$, since only one phase (liquid) is present; $C = 2$, since both copper and nickel atoms are present. Thus,

$$1 + C = F + P \quad \therefore 1 + 2 = F + 1 \text{ or } F = 2$$

We must fix both the temperature and the composition of the liquid phase to completely describe the state of the copper-nickel alloy in the liquid region.

(b) At 1250°C, $P = 2$, since both liquid and solid are present; $C = 2$, since copper and nickel atoms are present. Now,

$$1 + C = F + P \quad \therefore 1 + 2 = F + 2 \text{ or } F = 1$$

If we fix the temperature in the two-phase region, the compositions of the two phases are also fixed. Alternately, if the composition of one phase is fixed, the temperature and composition of the second phase are automatically fixed.

(c) At 1200°C, $P = 1$, since only one phase (solid) is present; $C = 2$, since both copper and nickel atoms are present. Again,

$$1 + C = F + P \quad \therefore 1 + 2 = F + 1 \text{ or } F = 2$$

and we must fix both temperature and composition to completely describe the state of the solid.

Because there is only one degree of freedom in a two-phase region of a binary phase diagram, the compositions of the two phases are always fixed when we specify the temperature. This is true even if the overall composition of the alloy changes. Therefore, we can use a tie line to determine the composition of the two phases. **A tie line** is a horizontal line within a two-phase region drawn at the temperature of interest (Figure 10-11). In an isomorphous system, the tie line connects the liquidus and solidus points at the specified temperature. The ends of the tie line represent the compositions of the two phases in equilibrium. Tie lines are not used in single-phase regions because we do not have two phases to "tie" in.

For any alloy with an overall or bulk composition lying between c_L and c_S, the composition of the liquid is c_L and the composition of the solid α is c_S.

The following example illustrates how the concept of a tie line is used to determine the composition of different phases in equilibrium.

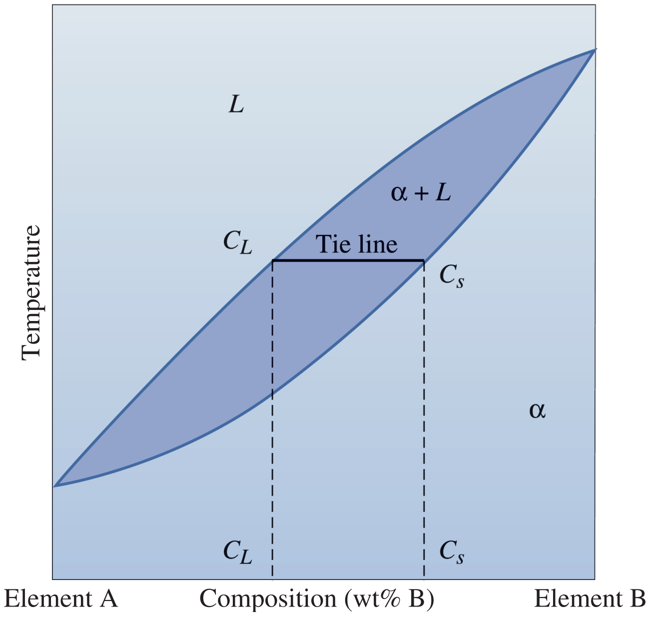

Figure 10-11
A hypothetical binary phase diagram between two elements A and B. When an alloy is present in a two-phase region, a tie line at the temperature of interest fixes the composition of the two phases. This is a consequence of the Gibbs phase rule, which provides only one degree of freedom in the two-phase region.

Example 10-7 *Compositions of Phases in the Cu-Ni Phase Diagram*

Determine the composition of each phase in a Cu-40% Ni alloy at 1300°C, 1270°C, 1250°C, and 1200°C. (See Figure 10-12.)

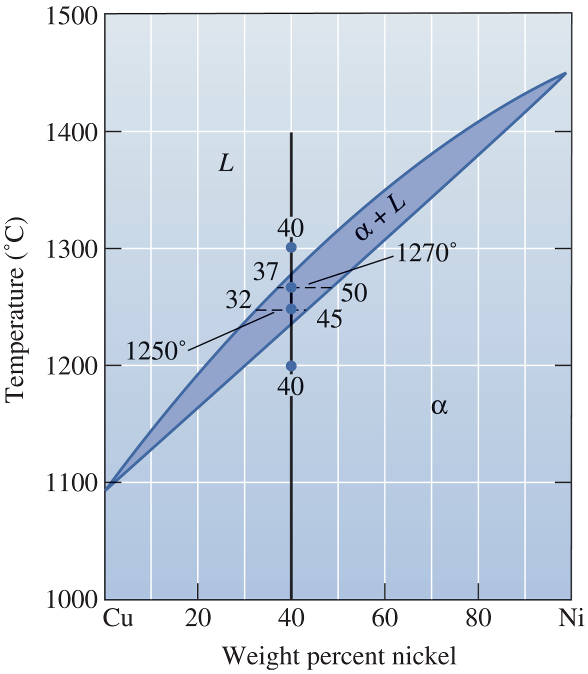

Figure 10-12
Tie lines and phase compositions for a Cu-40% Ni alloy at several temperatures (for Example 10-7).

SOLUTION

The vertical line at 40% Ni represents the overall composition of the alloy.

- **1300°C**: Only liquid is present. The liquid must contain 40% Ni, the overall composition of the alloy.
- **1270°C**: Two phases are present. A horizontal line within the $\alpha + L$ field is drawn. The endpoint at the liquidus, which is in contact with the liquid region, is at 37% Ni. The endpoint at the solidus, which is in contact with the α region, is at 50% Ni. Therefore, the liquid contains 37% Ni, and the solid contains 50% Ni.
- **1250°C**: Again two phases are present. The tie line drawn at this temperature shows that the liquid contains 32% Ni, and the solid contains 45% Ni.
- **1200°C**: Only solid α is present, so the solid must contain 40% Ni.

In Example 10-7, we find that, in the two-phase region, solid α contains more nickel and the liquid L contains more copper than the overall composition of the alloy. Generally, the higher melting point element (in this case, nickel) is concentrated in the first solid that forms.

Amount of Each Phase (the Lever Rule)

Lastly, we are interested in the relative amounts of each phase present in the alloy. These amounts are normally expressed as weight percent (wt%). We express absolute amounts of different phases in units of mass or weight (grams, kilograms, etc.). The following example illustrates the rationale for the **lever rule**.

Example 10-8 *Application of the Lever Rule*

Calculate the amounts of α and L at 1250°C in the Cu-40% Ni alloy shown in Figure 10-13.

SOLUTION

Let's say that x = mass fraction of the alloy that is solid α. Since we have only two phases, the balance of the alloy must be in the liquid phase (L). Thus, the mass fraction of liquid will be $1 - x$. Consider 100 grams of the alloy. This alloy will

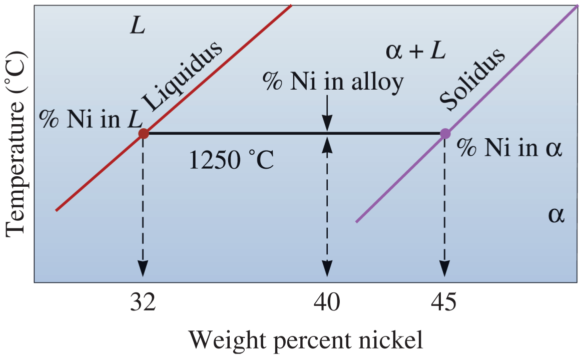

Figure 10-13 A tie line at 1250°C in the copper-nickel system that is used in Example 10-8 to find the amount of each phase.

consist of 40 grams of nickel at all temperatures. At 1250°C, let us write an equation that will represent the mass balance for nickel. At 1250°C, we have $100x$ grams of the α phase. We have $100(1 - x)$ grams of liquid.

$$\text{Total mass of nickel in 100 grams of the alloy} = \text{mass of nickel in liquid} + \text{mass of nickel in } \alpha$$

$$\therefore\ 100 \times (\text{\% Ni in alloy}) = [(100)(1 - x)](\text{\% Ni in } L) + (100)(x)(\text{\% Ni in } \alpha)$$

$$\therefore\ (\text{\% Ni in alloy}) = (\text{\% Ni in } L)(1 - x) + (\text{\% Ni in } \alpha)(x)$$

By multiplying and rearranging,

$$x = \frac{(\text{\% Ni in alloy}) - (\text{\% Ni in } L)}{(\text{\% Ni in } \alpha) - (\text{\% Ni in } L)}$$

From the phase diagram at 1250°C:

$$x = \frac{40 - 32}{45 - 32} = \frac{8}{13} = 0.62$$

If we convert from mass fraction to mass percent, the alloy at 1250°C contains 62% α and 38% L. Note that the concentration of nickel in the α phase (at 1250°C) is 45%, and the concentration of nickel in the liquid phase (at 1250°C) is 32%.

To calculate the amounts of liquid and solid, we construct a lever on our tie line, with the fulcrum of our lever being the original composition of the alloy. The leg of the lever *opposite* to the composition of the phase, the amount of which we are calculating, is divided by the total length of the lever to give the amount of that phase. In Example 10-8, note that the denominator represents the total length of the tie line and the numerator is the portion of the lever that is *opposite* the composition of the solid we are trying to calculate.

The lever rule in general can be written as

$$\text{Phase percent} = \frac{\text{opposite arm of lever}}{\text{total length of tie line}} \times 100 \qquad (10\text{-}3)$$

We can work the lever rule in any two-phase region of a binary phase diagram. The lever rule calculation is not used in single-phase regions because the answer is trivial (there is 100% of that phase present). The lever rule is used to calculate the relative fraction or % of a phase in a two-phase mixture. The end points of the tie line we use give us the composition (i.e., the chemical concentration of different components) of each phase.

The following example reinforces the application of the lever rule for calculating the amounts of phases for an alloy at different temperatures. This is one way to track the solidification behavior of alloys, something we did not see in Chapter 9.

Example 10-9 *Solidification of a Cu-40% Ni Alloy*

Determine the amount of each phase in the Cu-40% Ni alloy shown in Figure 10-12 at 1300°C, 1270°C, 1250°C, and 1200°C.

SOLUTION

- **1300°C**: There is only one phase, so 100% L.
- **1270°C**: $\% L = \dfrac{50 - 40}{50 - 37} \times 100 = 77\%$

  $\% \alpha = \dfrac{40 - 37}{50 - 37} \times 100 = 23\%$
- **1250°C**: $\% L = \dfrac{45 - 40}{45 - 32} \times 100 = 38\%$

  $\% \alpha = \dfrac{40 - 32}{45 - 32} \times 100 = 62\%$
- **1200°C**: There is only one phase, so 100% α.

Note that at each temperature, we can determine the composition of the phases in equilibrium from the ends of the tie line drawn at that temperature.

This may seem a little odd at first. How does the α phase change its composition? The liquid phase also changes its composition, and the amounts of each phase change with temperature as the alloy cools from the liquidus to the solidus.

Sometimes we wish to express composition as atomic percent (at%) rather than weight percent (wt%). For a Cu-Ni alloy, where M_{Cu} and M_{Ni} are the molecular weights, the following equations provide examples for making these conversions:

$$\text{at\% Ni} = \left(\frac{\dfrac{\text{wt\% Ni}}{M_{\mathrm{Ni}}}}{\dfrac{\text{wt\% Ni}}{M_{\mathrm{Ni}}} + \dfrac{\text{wt\% Cu}}{M_{\mathrm{Cu}}}} \right) \times 100 \qquad (10\text{-}4)$$

$$\text{wt\% Ni} = \left(\frac{(\text{at\% Ni}) \times (M_{\mathrm{Ni}})}{\text{at\% Ni} \times M_{\mathrm{Ni}} + \text{at\% Cu} \times M_{\mathrm{Cu}}} \right) \times 100 \qquad (10\text{-}5)$$

10-6 Relationship Between Properties and the Phase Diagram

We have previously mentioned that a copper-nickel alloy will be stronger than either pure copper or pure nickel because of solid solution strengthening. The mechanical properties of a series of copper-nickel alloys can be related to the phase diagram as shown in Figure 10-14.

The strength of copper increases by solid-solution strengthening until about 67% Ni is added. Pure nickel is solid-solution strengthened by the addition of copper until

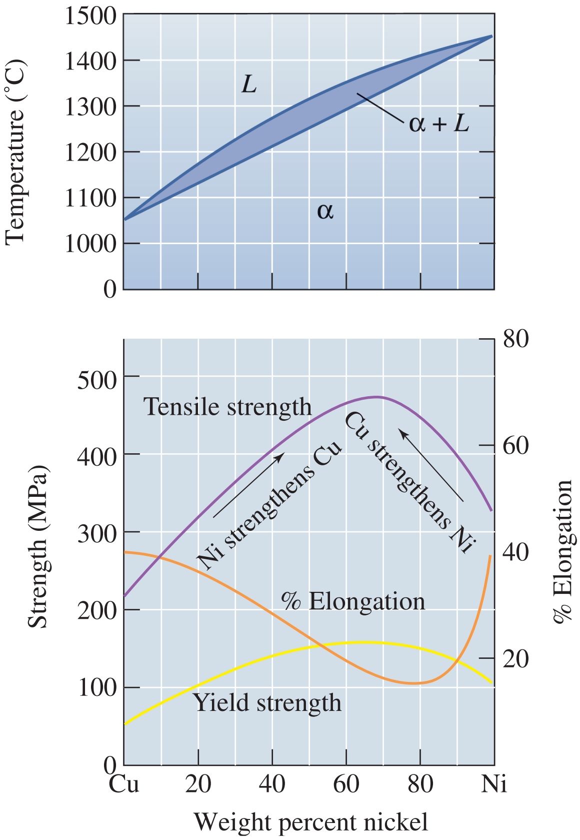

Figure 10-14
The mechanical properties of copper-nickel alloys. Copper is strengthened by up to 67% Ni, and nickel is strengthened by up to 33% Cu.

33% Cu is added. The maximum strength is obtained for a Cu 67% Ni alloy, known as *Monel*. The maximum is closer to the pure nickel side of the phase diagram because pure nickel is stronger than pure copper.

Example 10-10 *Design of a Melting Procedure for a Casting*

You need to produce a Cu-Ni alloy having a minimum yield strength of 138 MPa, a minimum tensile strength of 414 MPa, and a minimum % elongation of 20%. You have in your inventory a Cu-20% Ni alloy and pure nickel. Design a method for producing castings having the required properties.

SOLUTION

From Figure 10-14, we determine the required composition of the alloy. To meet the required yield strength, the alloy must contain between 40 and 90% Ni; for the tensile strength, 40 to 88% Ni is required. The required % elongation can be obtained for alloys containing less than 60% Ni or more than 90% Ni. To satisfy all of these conditions, we could use Cu-40% to 60% Ni.

We prefer to select a low nickel content, since nickel is more expensive than copper. In addition, the lower nickel alloys have a lower liquidus, permitting castings to be made with less energy. Therefore, a reasonable alloy is Cu-40% Ni.

To produce this composition from the available melting stock, we must blend some of the pure nickel with the Cu-20% Ni ingot. Assume we wish to produce 10 kg of the alloy. Let x be the mass of Cu-20% Ni alloy we will need. The mass of pure nickel needed will be $10 - x$. Since the final alloy consists of 40% Ni, the total mass of nickel needed will be

$$(10\,\text{kg})\left(\frac{40\%\ \text{Ni}}{100\%}\right) = 4\,\text{kg Ni}$$

Now let's write a mass balance for nickel. The sum of the nickel from the Cu-20% Ni alloy and the pure nickel must be equal to the total nickel in the Cu-40% Ni alloy being produced:

$$(x\ \text{kg})\left(\frac{20\%\ \text{Ni}}{100\%}\right) + (10 - x\ \text{kg})\left(\frac{100\%\ \text{Ni}}{100\%}\right) = 4\ \text{kg Ni}$$

$$0.2x + 10 - x = 4$$

$$6 = 0.8x$$

$$x = 7.5\ \text{kg}$$

Therefore, we need to melt 7.5 kg of Cu-20% Ni with 2.5 kg of pure nickel to produce the required alloy. We would then heat the alloy above the liquidus temperature, which is 1280°C for the Cu-40% Ni alloy, before pouring the liquid metal into the appropriate mold.

We need to conduct such calculations for many practical situations dealing with the processing of alloys, because when we make them, we typically use new and recycled materials.

10-7 Solidification of a Solid-Solution Alloy

When an alloy such as Cu-40% Ni is melted and cooled, solidification requires both nucleation and growth. Heterogeneous nucleation permits little or no undercooling, so solidification begins when the liquid reaches the liquidus temperature (Chapter 9). The phase diagram (Figure 10-15), with a tie line drawn at the liquidus temperature, indicates that the *first solid to form* has a composition of Cu-52% Ni.

Two conditions are required for growth of the solid α. First, growth requires that the latent heat of fusion (ΔH_f), which evolves as the liquid solidifies, be removed from the solid–liquid interface. Second, unlike the case of pure metals, diffusion must occur so that the compositions of the solid and liquid phases follow the solidus and liquidus curves during cooling. The latent heat of fusion (ΔH_f) is removed over a range of temperatures so that the cooling curve shows a change in slope, rather than a flat plateau (Figure 10-16). Thus, as we mentioned before in Chapter 9, the solidification of alloys is different from that of pure metals.

At the start of freezing, the liquid contains Cu-40% Ni, and the first solid contains Cu-52% Ni. Nickel atoms must have diffused to and concentrated at the first solid to form. After cooling to 1250°C, solidification has advanced, and the phase diagram tells us that now all of the liquid must contain 32% Ni and all of the solid must contain 45% Ni. On cooling from the liquidus to 1250°C, some nickel atoms must diffuse from the first solid to the new solid, reducing the nickel in the first solid. Additional nickel atoms diffuse from the solidifying liquid to the new solid. Meanwhile, copper atoms have concentrated—by diffusion—into the remaining liquid. This process must continue until we reach the solidus temperature, where the last liquid to freeze, which contains Cu-28% Ni, solidifies and forms a solid containing Cu-40% Ni. Just below the solidus, all of the solid must contain a uniform concentration of 40% Ni throughout.

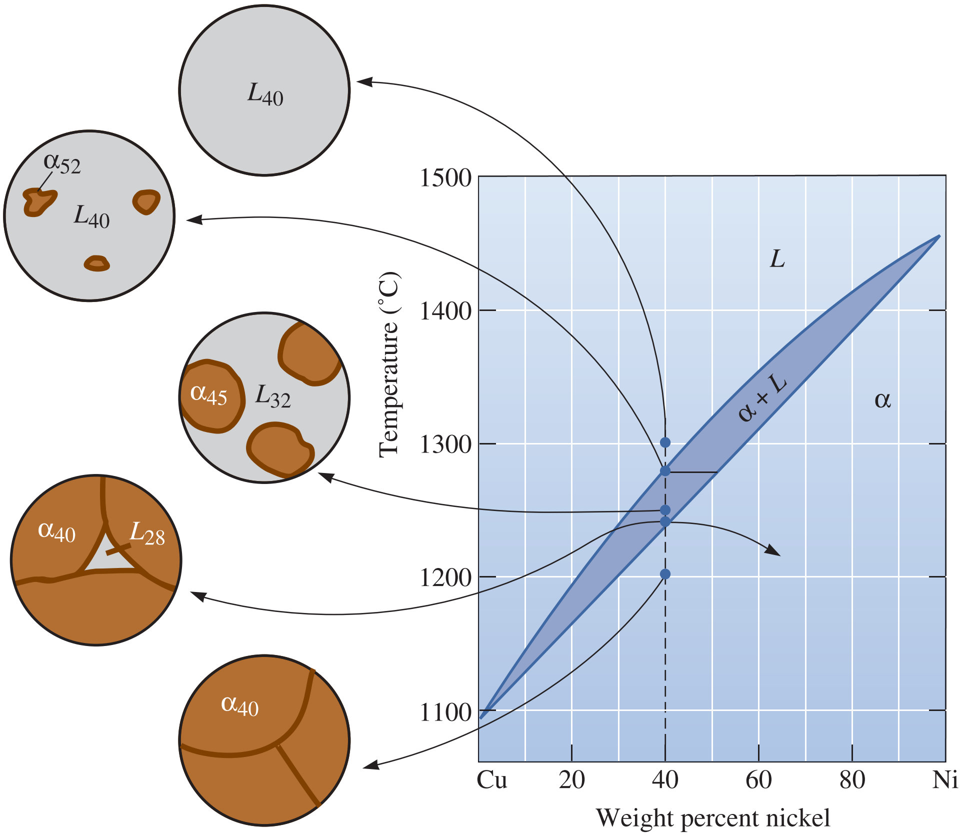

Figure 10-15 The change in structure of a Cu-40% Ni alloy during equilibrium solidification. The nickel and copper atoms must diffuse during cooling in order to satisfy the phase diagram and produce a uniform equilibrium structure.

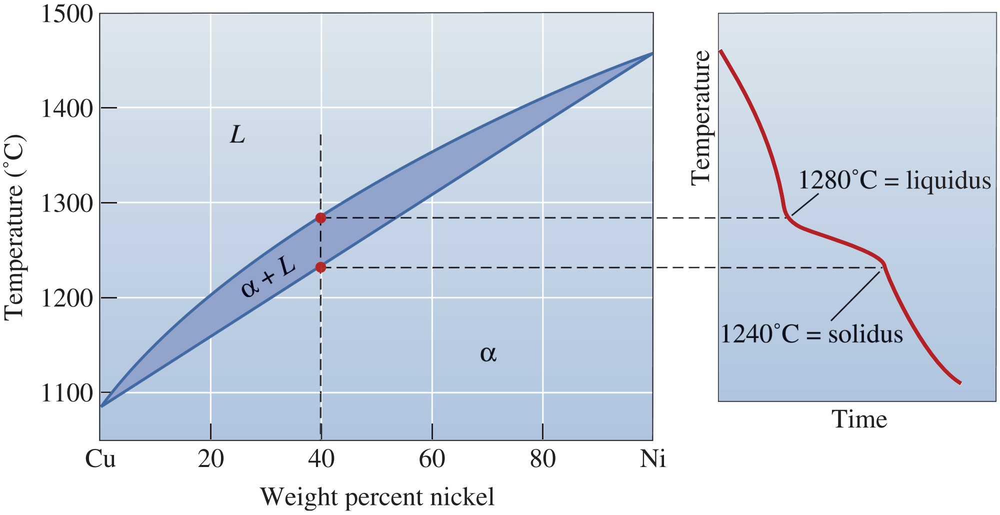

Figure 10-16 The cooling curve for an isomorphous alloy during solidification. We assume that cooling rates are low so that thermal equilibrium is maintained at each temperature. The changes in slope of the cooling curve indicate the liquidus and solidus temperatures, in this case, for a Cu-40% Ni alloy.

In order to achieve this equilibrium final structure, the cooling rate must be extremely slow. Sufficient time must be permitted for the copper and nickel atoms to diffuse and produce the compositions given by the phase diagram. In many practical casting situations, the cooling rate is too rapid to permit equilibrium. Therefore, in most castings made from alloys, we expect chemical segregation. We saw in Chapter 9 that porosity is a defect that can be present in many cast products. Another such defect often present in cast products is chemical **segregation**. This is discussed in detail in the next section.

10-8 Nonequilibrium Solidification and Segregation

In Chapter 5, we examined the thermodynamic and kinetic driving forces for diffusion. We know that diffusion occurs fastest in gases, followed by liquids, and then solids. We also saw that increasing the temperature enhances diffusion rates. When cooling is too rapid for atoms to diffuse and produce equilibrium conditions, nonequilibrium structures are produced in the casting. Let's see what happens to our Cu-40% Ni alloy on rapid cooling.

Again, the first solid, containing 52% Ni, forms on reaching the liquidus temperature (Figure 10-17). On cooling to 1260°C, the tie line tells us that the liquid contains 34% Ni and the solid that forms at that temperature contains 46% Ni. Since diffusion occurs

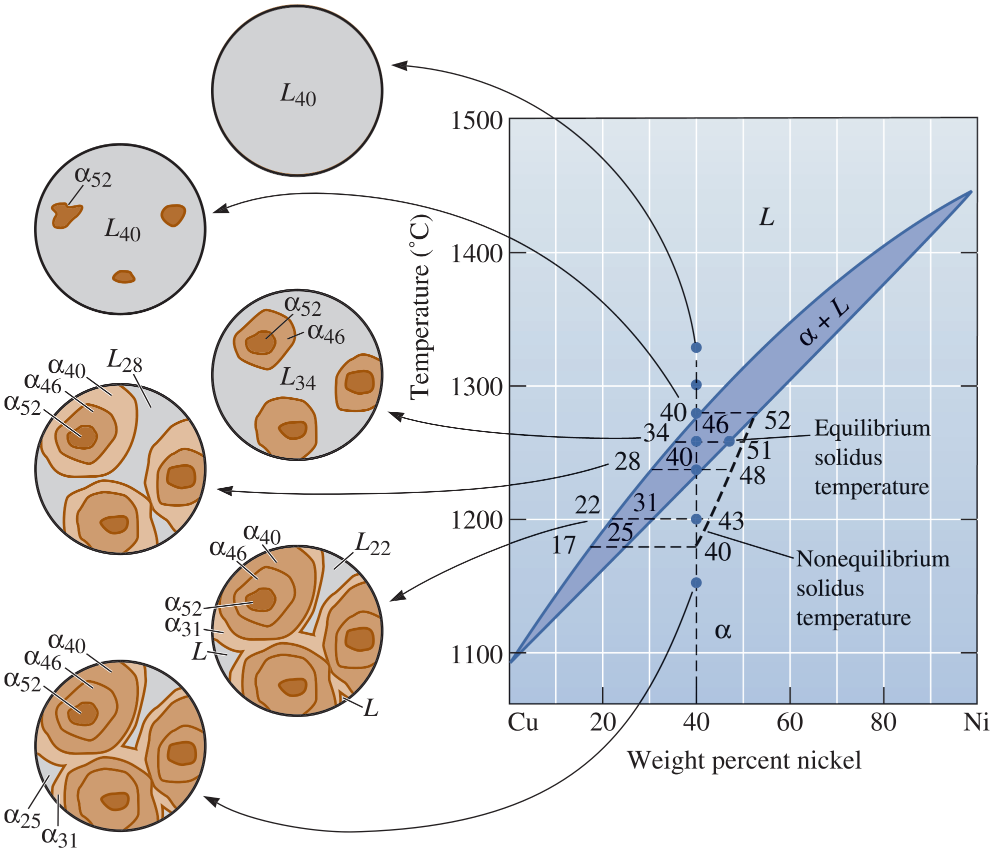

Figure 10-17 The change in structure of a Cu-40% Ni alloy during nonequilibrium solidification. Insufficient time for diffusion in the solid produces a segregated structure. Notice the nonequilibrium solidus curve.

rapidly in liquids, we expect the tie line to predict the liquid composition accurately; however, diffusion in solids is comparatively slow. The first solid that forms still has about 52% Ni, but the new solid contains only 46% Ni. We might find that the average composition of the solid is 51% Ni. This gives a different nonequilibrium solidus than that given by the phase diagram. As solidification continues, the nonequilibrium solidus line continues to separate from the equilibrium solidus.

When the temperature reaches 1240°C (the equilibrium solidus), a significant amount of liquid remains. The liquid will not completely solidify until we cool to 1180°C, where the nonequilibrium solidus intersects the original composition of 40% Ni. At that temperature, liquid containing 17% Ni solidifies, giving solid containing 25% Ni. The last liquid to freeze therefore contains 17% Ni, and the last solid to form contains 25% Ni. The average composition of the solid is 40% Ni, but the composition is not uniform.

The actual location of the nonequilibrium solidus line and the final nonequilibrium solidus temperature depend on the cooling rate. Faster cooling rates cause greater departures from equilibrium. The following example illustrates how we can account for the changes in composition under nonequilibrium conditions.

Example 10-11 *Nonequilibrium Solidification of Cu-Ni Alloys*

Calculate the composition and amount of each phase in a Cu-40% Ni alloy that is present under the nonequilibrium conditions shown in Figure 10-17 at 1300°C, 1280°C, 1260°C, 1240°C, 1200°C, and 1150°C. Compare with the equilibrium compositions and amounts of each phase.

SOLUTION

We use the tie line to the equilibrium solidus temperature to curve to calculate compositions and percentages of phases as per the lever rule. Similarly, the nonequilibrium solidus temperature curve is used to calculate percentages and concentrations of different phases formed under nonequilibrium conditions.

Temperature	Equilibrium	Nonequilibrium
1300°C	L: 40% Ni 100% L	L: 40% Ni 100% L
1280°C	L: 40% Ni 100% L	L: 40% Ni 100% L
1260°C	L: 34% Ni $\frac{46 - 40}{46 - 34} = 50\%\ L$	L: 34% Ni $\frac{51 - 40}{51 - 34} = 65\%\ L$
	α: 46% Ni $\frac{40 - 34}{46 - 34} = 50\%\ \alpha$	α: 51% Ni $\frac{40 - 34}{51 - 34} = 35\%\ \alpha$
1240°C	L: 28% Ni ~ 0% L	L: 28% Ni $\frac{48 - 40}{48 - 28} = 40\%\ L$
	α: 40% Ni 100% α	α: 48% Ni $\frac{40 - 28}{48 - 28} = 60\%\ \alpha$
1200°C	α: 40% Ni 100% α	L: 22% Ni $\frac{43 - 40}{43 - 22} = 14\%\ L$
		α: 43% Ni $\frac{40 - 22}{43 - 22} = 86\%\ \alpha$
1150°C	α: 40% Ni 100% α	α: 40% Ni 100% α

Microsegregation The nonuniform composition produced by nonequilibrium solidification is known as segregation. **Microsegregation**, also known as **interdendritic segregation** and **coring**, occurs over short distances, often between small dendrite arms. The centers of the dendrites, which represent the first solid to freeze, are rich in the higher melting point element in the alloy. The regions between the dendrites are rich in the lower melting point element, since these regions represent the last liquid to freeze. The composition and properties of the α phase (in the case of Cu-Ni alloys) differ from one region to the next, and we expect the casting to have poorer properties as a result.

Microsegregation can cause **hot shortness**, or melting of the lower melting point interdendritic material at temperatures below the equilibrium solidus. When we heat the Cu-40% Ni alloy to 1225°C, below the equilibrium solidus but above the nonequilibrium solidus, the low nickel regions between the dendrites melt.

Homogenization We can reduce the interdendritic segregation and problems with hot shortness by means of a **homogenization heat treatment**. If we heat the casting to a temperature below the nonequilibrium solidus, the nickel atoms in the centers of the dendrites diffuse to the interdendritic regions; copper atoms diffuse in the opposite direction [Figure 10-18(a)]. Since the diffusion distances are relatively short, only a few hours are required to eliminate most of the composition differences. The homogenization time is related to

$$t = \mathrm{c}\,\frac{(\mathrm{SDAS})^2}{D_s} \tag{10-6}$$

where SDAS is the secondary dendrite arm spacing, D_s is the rate of diffusion of the solute in the matrix, and c is a constant. A small SDAS reduces the diffusion distance and permits short homogenization times.

Macrosegregation There exists another type of segregation, known as **macrosegregation**, which occurs over a large distance, between the surface and the center of the casting, with the surface (which freezes first) containing slightly more than the average amount of the higher melting point metal. We cannot eliminate macrosegregation by a homogenization treatment, because the diffusion distances are too great. Macrosegregation can be reduced by hot working, which was discussed in Chapter 8. This is because in hot working, we are basically breaking down the cast macrostructure.

Rapidly Solidified Powders In applications in which porosity, microsegregation, and macrosegregation must be minimized, powders of complex alloys are prepared using **spray atomization** [Figure 10-18(b)]. In spray atomization, homogeneous melts of complex compositions are prepared and sprayed through a ceramic nozzle. The melt stream is broken into finer droplets and quenched using argon (Ar) or nitrogen (N_2) gases (gas atomization) or water (water atomization). The molten droplets solidify rapidly, generating powder particles ranging from ~10–100 μm in size. Since the solidification of droplets occurs very quickly, there is very little time for diffusion, and therefore, chemical segregation does not occur. Many complex nickel- and cobalt-based superalloys and stainless steel powders are examples of materials prepared using this technique. The spray atomized powders are blended and formed into desired shapes. The techniques used in processing such powders include sintering (Chapter 5), **hot pressing** (HP) and **hot isostatic pressing** (HIP). In HIP, sintering is conducted under an isostatic pressure (~ 170 MPa) using, for example, argon gas. Very large (~ up to 6 cm diameter, several meters long) and smaller components can be

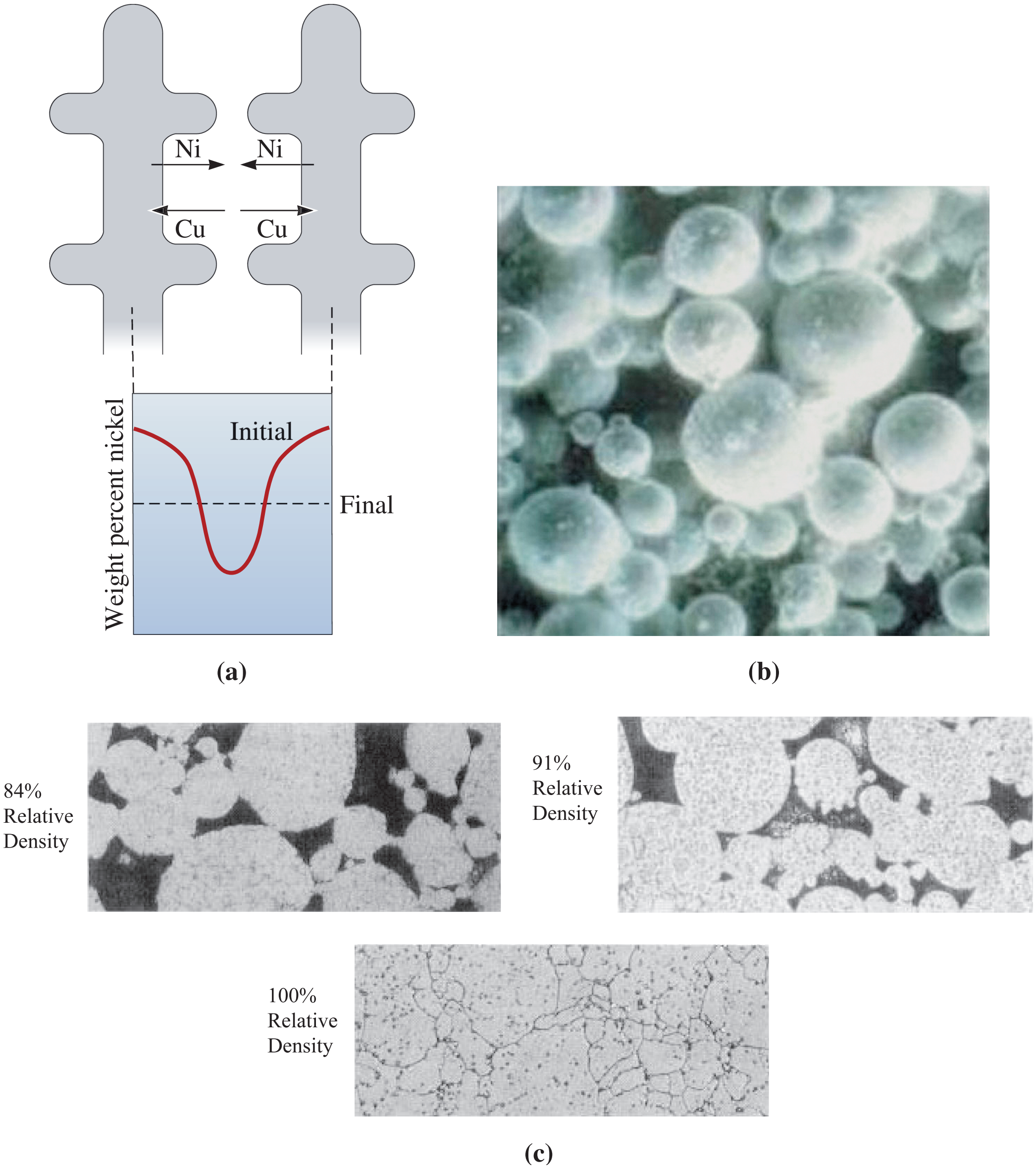

Figure 10-18 (a) Microsegregation between dendrites can be reduced by a homogenization heat treatment. Counterdiffusion of nickel and copper atoms may eventually eliminate the composition gradients and produce a homogeneous composition. (b) Spray atomized powders of superalloys. (c) Progression of densification in low carbon Astroalloy sample processed using HIP. *(Micrographs courtesy of J. Staite, Hann, B. and Rizzo, F., Crucible Compaction Metals.)*

processed using HIP. Smaller components such as disks that hold turbine blades can be machined from these. The progression of densification in a low carbon Astroalloy sample processed using spray atomized powders is shown in Figure 10-18(c).

Hot pressing is sintering under a uniaxial pressure and is used in the production of smaller components of materials that are difficult to sinter otherwise (Chapter 15). The HIP and hot pressing techniques are used for both metallic and ceramic powder materials.

Summary

- A phase is any portion, including the whole, of a system that is physically homogeneous within it and bounded by a surface that separates it from any other portions.
- A phase diagram typically shows phases that are expected to be present in a system under thermodynamic equilibrium conditions. Sometimes metastable phases may also be shown.
- Solid solutions in metallic or ceramic materials exist when elements or compounds with similar crystal structures form a single phase that is chemically homogeneous.
- Solid-solution strengthening is accomplished in metallic materials by the formation of solid solutions. The point defects created restrict dislocation motion and cause strengthening.
- The degree of solid-solution strengthening increases when (1) the amount of the alloying element increases and (2) the atomic size difference between the host material and the alloying element increases.
- The amount of alloying element (or compound) that we can add to produce solid-solution strengthening is limited by the solubility of the alloying element or compound in the host material. The solubility is limited when (1) the atomic size difference is more than about 15%, (2) the alloying element (or compound) has a different crystal structure than the host element (or compound), and (3) the valence and electronegativity of the alloying element or constituent ions are different from those of the host element (or compound).
- In addition to increasing strength and hardness, solid-solution strengthening typically decreases ductility and electrical conductivity of metallic materials. An important function of solid-solution strengthening is to provide good high-temperature properties to the alloy.
- A phase diagram in which constituents exhibit complete solid solubility is known as an isomorphous phase diagram.
- As a result of solid-solution formation, solidification begins at the liquidus temperature and is completed at the solidus temperature; the temperature difference over which solidification occurs is the freezing range.
- In two-phase regions of the phase diagram, the ends of a tie line fix the composition of each phase, and the lever rule permits the amount of each phase to be calculated.
- Microsegregation and macrosegregation occur during solidification. Microsegregation, or coring, occurs over small distances, often between dendrites. The centers of the dendrites are rich in the higher melting point element, whereas interdendritic regions, which solidify last, are rich in the lower melting point element.
- Homogenization can reduce microsegregation.
- Macrosegregation describes differences in composition over long distances, such as between the surface and center of a casting. Hot working may reduce macrosegregation.

Glossary

Alloy A material made from multiple elements that exhibits properties of a metallic material.

Binary phase diagram A phase diagram for a system with two components.

Copolymer A polymer that is formed by combining two or more different types of monomers, usually with the idea of blending the properties affiliated with individual polymers.

Coring Chemical segregation in cast products, also known as microsegregation or interdendritic segregation. The centers of the dendrites are rich in the higher melting point element, whereas interdendritic regions, which solidify last, are rich in the lower melting point element.

Dispersion strengthening Strengthening, typically used in metallic materials, by the formation of ultra-fine dispersions of a second phase. The interface between the newly formed phase and the parent phase provides additional resistance to dislocation motion, thereby causing strengthening of metallic materials (Chapter 11).

Freezing range The temperature difference between the liquidus and solidus temperatures.

Gibbs phase rule Describes the number of degrees of freedom, or the number of variables that must be fixed to specify the temperature and composition of a phase ($2 + C = F + P$, where pressure and temperature can change, $1 + C = F + P$, where pressure or temperature is constant).

Homogenization heat treatment The heat treatment used to reduce the microsegregation caused by nonequilibrium solidification. This heat treatment cannot eliminate macrosegregation.

Hot isostatic pressing (HIP) Sintering of metallic or ceramic powders, conducted under an isostatic pressure.

Hot pressing (HP) Sintering of metal or ceramic powders under a uniaxial pressure; used for production of smaller components of materials that are difficult to sinter otherwise.

Hot shortness Melting of the lower melting point nonequilibrium material that forms due to segregation, even though the temperature is below the equilibrium solidus temperature.

Hume-Rothery rules The conditions that an alloy or ceramic system must meet if the system is to display unlimited solid solubility. The Hume-Rothery rules are necessary but are not sufficient for materials to show unlimited solid solubility.

Interdendritic segregation See "Coring."

Isomorphous phase diagram A phase diagram in which the components display unlimited solid solubility.

Lever rule A technique for determining the amount of each phase in a two-phase system.

Limited solubility When only a certain amount of a solute material can be dissolved in a solvent material.

Liquidus Curves on phase diagrams that describe the liquidus temperatures of all possible alloys.

Liquidus temperature The temperature at which the first solid begins to form during solidification.

Macrosegregation The presence of composition differences in a material over large distances caused by nonequilibrium solidification. The only way to remove this type of segregation is to break down the cast structure by hot working.

Microsegregation See "Coring."

Multiple-phase alloy An alloy that consists of two or more phases.

Phase Any portion, including the whole of a system, which is physically homogeneous within it and bounded by a surface so that it is separate from any other portions.

Phase diagrams Diagrams showing phases present under equilibrium conditions and the phase compositions at each combination of temperature and overall composition. Sometimes phase diagrams also indicate metastable phases.

Phase rule See Gibbs phase rule.

P-T diagram A diagram describing thermodynamic stability of phases under different temperature and pressure conditions (same as a unary phase diagram).

Segregation The presence of composition differences in a material, often caused by insufficient time for diffusion during solidification.

Single-phase alloy An alloy consisting of one phase.

Solid solution A solid phase formed by combining multiple elements or compounds such that the overall phase has a uniform composition and properties that are different from those of the elements or compounds forming it.

Solid-solution strengthening Increasing the strength of a metallic material via the formation of a solid solution.

Solidus Curves on phase diagrams that describe the solidus temperature of all possible alloys.

Solidus temperature The temperature below which all liquid has completely solidified.

Solubility The amount of one material that will completely dissolve in a second material without creating a second phase.

Spray atomization A process in which molten alloys or metals are sprayed using a ceramic nozzle. The molten material stream is broken using a gas (e.g., Ar, N_2) or water. This leads to fine droplets that solidify rapidly, forming metal or alloy powders with $\sim$ 10–100 μm particle size range.

Tie line A horizontal line drawn in a two-phase region of a phase diagram to assist in determining the compositions of the two phases.

Triple point A pressure and temperature at which three phases of a single material are in equilibrium.

Unary phase diagram A phase diagram in which there is only one component.

Unlimited solubility When the amount of one material that will dissolve in a second material without creating a second phase is unlimited.

10-1 Explain the principle of grain-size strengthening. Does this mechanism work at high temperatures? Explain.

10-2 Explain the principle of strain hardening. Does this mechanism work at high temperatures? Explain.

10-3 What is the principle of solid-solution strengthening? Does this mechanism work at high temperatures? Explain.

10-4 What is the principle of dispersion strengthening?

Section 10-1 Phases and Phase Diagrams

10-5 What does the term “phase” mean?

10-6 What are the different phases of water?

10-7 Ice has been known to exist in different polymorphs. Are these different phases of water?

10-8 Write down the Gibbs phase rule, assuming temperature and pressure are allowed to change. Explain clearly the meaning of each term.

10-9 What is a phase diagram?

10-10 The unary phase diagram for SiO_2 is shown in Figure 10-19. Locate the triple point where solid, liquid, and vapor coexist and give the temperature and the type of solid present. What do the other “triple” points indicate?

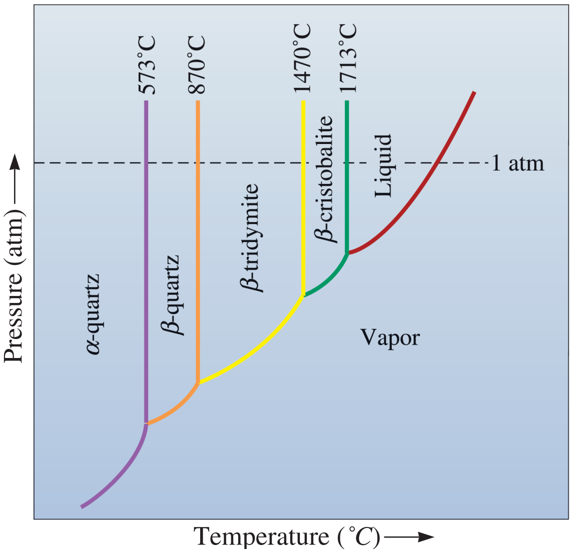

Figure 10-19 Pressure-temperature diagram for SiO_2. The dotted line shows one atmosphere pressure. (For Problem 10-10.)

10-11 Figure 10-20 shows the unary phase diagram for carbon. Based on this diagram, under what conditions can carbon in the form of graphite be converted into diamond?

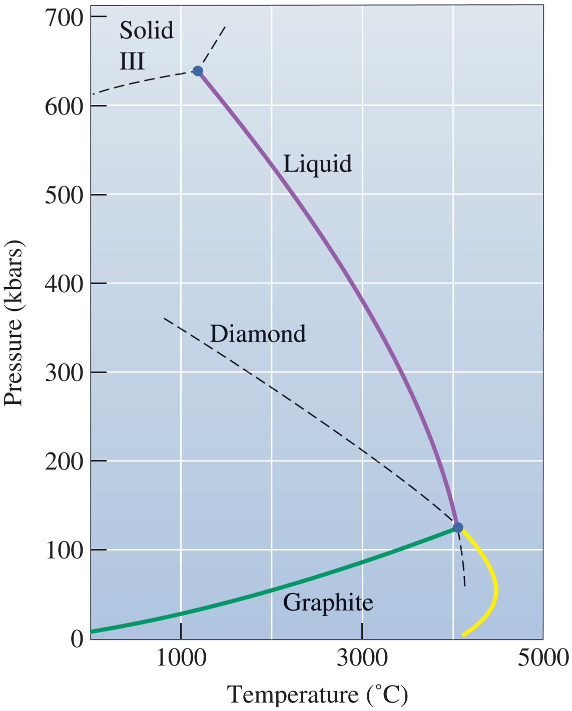

Figure 10-20 Unary phase diagram for carbon. Region for diamond formation is shown with a dotted line (for Problem 10-11). *(Adapted from* Introduction to Phase Equilibria, *by C.G. Bergeron and S.H. Risbud, Fig. 2-11. Copyright © 1984 American Ceramic Society. Adapted by permission.)*

10-12 Natural diamond is formed approximately 120 to 200 km below the earth's surface under high pressure and high temperature conditions. Assuming that the average density of the earth is 5500 kg/m^3, use this information and the unary phase diagram for C (Figure 10–20) to calculate the range of the earth's geothermal gradient (rate of increase of temperature with depth). Estimate the pressure below the earth's surface as $\rho g h$ where ρ is density, g is gravity, and h is depth. Note that 10 kbar = 10^9 Pa.

Section 10-2 Solubility and Solid Solutions

10-13 What is a solid solution?

10-14 How can solid solutions form in ceramic systems?

10-15 Do we need 100% solid solubility to form a solid solution of one material in another?

10-16 Small concentrations of lead zirconate ($PbZrO_3$) are added to lead titanate ($PbTiO_3$). Draw a schematic of the resultant solid-solution crystal structure that is expected to form. This material, known as lead zirconium titanate (better known as PZT), has many applications ranging from spark igniters to ultrasound imaging. See Section 3-7 for information on the perovskite crystal structure.

10-17 Can solid solutions be formed between three elements or three compounds?

10-18 What is a copolymer? What is the advantage to forming copolymers?

10-19 Is copolymer formation similar to solid-solution formation?

10-20 What is the ABS copolymer? State some of the applications of this material.

Section 10-3 Conditions for Unlimited Solid Solubility

10-21 Briefly state the Hume-Rothery rules and explain the rationale.

10-22 Can the Hume-Rothery rules apply to ceramic systems? Explain.

10-23 Based on Hume-Rothery's conditions, which of the following systems would be expected to display unlimited solid solubility? Explain.

(a) Au-Ag; (b) Al-Cu; (c) Al-Au; (d) U-W; (e) Mo-Ta; (f) Nb-W; (g) Mg-Zn; and (h) Mg-Cd.

10-24 Identify which of the following oxides when added to $BaTiO_3$ are likely to exhibit 100% solid solubility: (a) $SrTiO_3$; (b) $CaTiO_3$; (c) $ZnTiO_3$; and (d) $BaZrO_3$. All of these oxides have a perovskite crystal structure.

Section 10-4 Solid-Solution Strengthening

10-25 Suppose 1 at% of the following elements is added to copper (forming a separate alloy with each element) without exceeding the solubility limit. Which one would be expected to give the higher strength alloy? Are any of the alloying elements expected to have unlimited solid solubility in copper? (a) Au; (b) Mn; (c) Sr; (d) Si; and (e) Co.

10-26 Suppose 1 at% of the following elements is added to aluminum (forming a separate alloy with each element) without exceeding the solubility limit. Which one would be expected to give the smallest reduction in electrical conductivity? Are any of the alloy elements expected to have unlimited solid solubility in aluminum? (a) Li; (b) Ba; (c) Be; (d) Cd; and (e) Ga.

10-27 Which of the following oxides is expected to have the largest solid solubility in Al_2O_3? (a) Y_2O_3; (b) Cr_2O_3; and (c) Fe_2O_3.

10-28 What is the role of small concentrations of Mg in aluminum alloys used to make beverage cans?

10-29 Why do jewelers add small amounts of copper to gold and silver?

10-30 Why is it not a good idea to use solid–solution strengthening as a mechanism to increase the strength of copper for electrical applications?

10-31 Determine the degrees of freedom under the following conditions:

(a) Tl-20 wt% Pb at 325°C and 400°C;

(b) Tl-40 wt% Pb at 325°C and 400°C;

(c) Tl-90 wt% Pb at 325°C and 400°C.

Refer to the phase diagram in Figure 10-9(d).

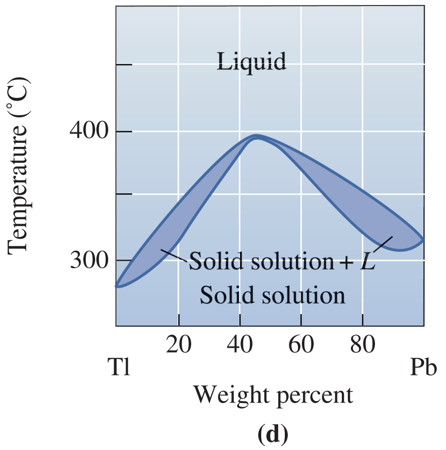

Figure 10-9(d) (Repeated for Problems 10-31 and 10-32.) The Tl-Pb phase diagram.

Section 10-5 Isomorphous Phase Diagrams

10-32 Determine the composition range in which the Tl-Pb alloy at 350°C is (a) fully liquid; (b) fully solid; and (c) partly liquid and partly solid.

Refer to Figure 10-9(d) for the Tl-Pb phase diagram. Further, determine the amount of liquid and solid solution for Tl-25 wt% Pb and Tl-75 wt% Pb at 350°C and also the wt% Pb in the liquid and solid solution for both of the alloy compositions.

10-33 Determine the liquidus temperature, solidus temperature, and freezing range for the following NiO-MgO ceramic compositions: (a) NiO-30 mol% MgO; (b) NiO-45 mol% MgO; (c) NiO-60 mol% MgO; and (d) NiO-85 mol% MgO. [See Figure 10-9(b).]

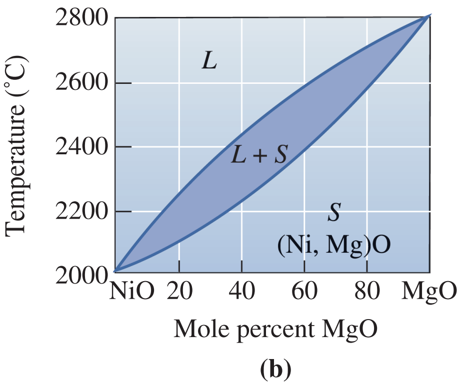

Figure 10-9(b) (Repeated for Problems 10-33, 10-35, 10-38, 10-42, 10-43 and 10-45.) The equilibrium phase diagram for the NiO-MgO system.

10-34 Determine the liquidus temperature, solidus temperature, and freezing range for the following MgO-FeO ceramic compositions:

(a) MgO-25 wt% FeO;
(b) MgO-45 wt% FeO;
(c) MgO-65 wt% FeO; and
(d) MgO-80 wt% FeO.
(See Figure 10-21.)

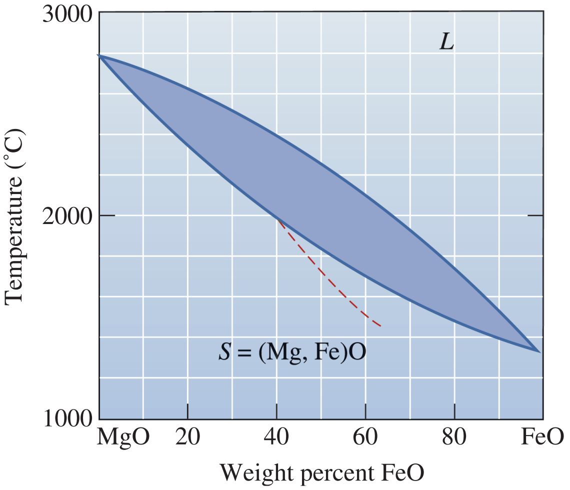

Figure 10-21 The equilibrium phase diagram for the MgO-FeO system. The dotted curve shows the nonequilibrium solidus. (For Problems 10-34, 10-36, 10-44, 10-45, 10-53, 10-57, and 10-63.)

10-35 Determine the phases present, the compositions of each phase, and the amount of each phase in mol% for the following NiO-MgO ceramics at 2400°C: (a) NiO-30 mol% MgO; (b) NiO-45 mol% MgO; (c) NiO-60 mol% MgO; and (d) NiO-85 mol% MgO. [See Figure 10-9(b).]

10-36 Determine the phases present, the compositions of each phase, and the amount of each phase in wt% for the following MgO-FeO ceramics at 2000°C: (i) MgO-25 wt% FeO; (ii) MgO-45 wt% FeO; (iii) MgO-60 wt% FeO; and (iv) MgO-80 wt% FeO. (See Figure 10-21.)

10-37 Consider a ceramic composed of 30 mol% MgO and 70 mol% FeO. Calculate the composition of the ceramic in wt%.

10-38 A NiO-20 mol% MgO ceramic is heated to 2200°C. Determine (a) the composition of the solid and liquid phases in both mol% and wt%; (b) the amount of each phase in mol% and wt%; and (c) assuming that the density of the solid is 6.32 g/cm^3 and that of the liquid is 7.14 g/cm^3, determine the amount of each phase in vol%. [See Figure 10-9(b).]

10-39 A Nb-60 wt% W alloy is heated to 2800°C. Determine (a) the composition of the solid and liquid phases in both wt% and at%; (b) the amount of each phase in both wt% and at%; and (c) assuming that the density of the solid is 16.05 g/cm^3 and that of the liquid is 13.91 g/cm^3, determine the amount of each phase in vol%. (See Figure 10-22.)

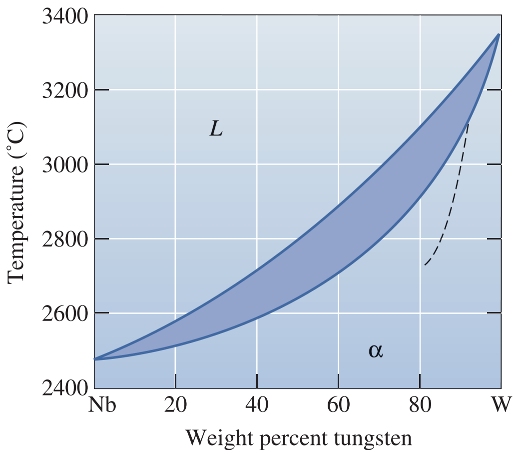

Figure 10-22 The equilibrium phase diagram for the Nb-W system. The dotted curve shows nonequilibrium solidus. (Repeated for Problems 10-39, 10-46, 10-47, 10-48, 10-49, 10-54, 10-56, 10-59, and 10-64.)

10-40 How many grams of nickel must be added to 500 grams of copper to produce an alloy that has a liquidus temperature of 1350°C? What is the ratio of the number of nickel atoms to copper atoms in this alloy? [See Figure 10-9(a).]

10-41 How many grams of nickel must be added to 500 grams of copper to produce an alloy that contains 50 wt% α at 1300°C? [See Figure 10-9(a).]

10-42 How many grams of MgO must be added to 1 kg of NiO to produce a ceramic that has a solidus temperature of 2200°C? [See Figure 10-9(b).]

10-43 How many grams of MgO must be added to 1 kg of NiO to produce a ceramic that contains 25 mol% solid at 2400°C? [See Figure 10-9(b).]

10-44 We would like to produce a solid MgO-FeO ceramic that contains equal mol percentages

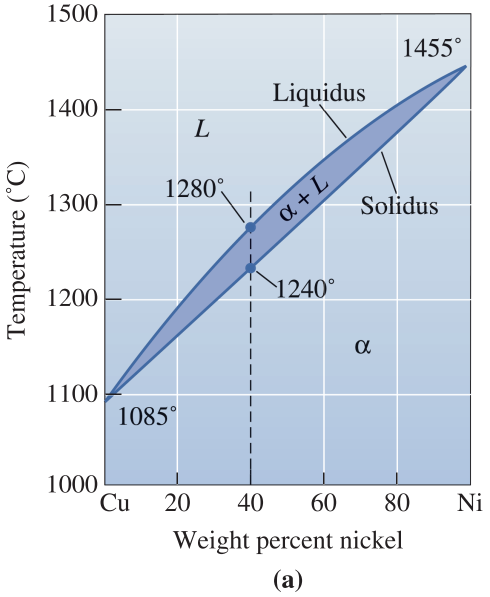

Figure 10-9(a) (Repeated for Problems 10-40 and 10-41

of MgO and FeO at 1200°C. Determine the wt% FeO in the ceramic. (See Figure 10-21.)

10-45 We would like to produce a MgO-FeO ceramic that is 30 wt% solid at 2000°C. Determine the composition of the ceramic in wt%. (See Figure 10-21.)

10-46 A Nb-W alloy held at 2800°C is partly liquid and partly solid. (a) If possible, determine the composition of each phase in the alloy, and (b) if possible, determine the amount of each phase in the alloy. (See Figure 10-22.)

10-47 A Nb-W alloy contains 55% α at 2600°C. Determine (a) the composition of each phase, and (b) the composition of the alloy. (See Figure 10-22.)

10-48 Suppose a 544-kg bath of a Nb-40 wt% W alloy is held at 2800°C. How many kilograms of tungsten can be added to the bath before any solid forms? How many kilograms of tungsten must be added to cause the entire bath to be solid? (See Figure 10-22.)

10-49 A fiber-reinforced composite material is produced, in which tungsten fibers are embedded in a Nb matrix. The composite is composed of 70 vol% tungsten. (a) Calculate the wt% of tungsten fibers in the composite, and (b) suppose the composite is heated to 2600°C and held for several years. What happens to the fibers? Explain. (See Figure 10-22.)

10-50 Suppose a crucible made of pure nickel is used to contain 500 g of liquid copper at 1150°C. Describe what happens to the system as it is held at this temperature for several hours. Explain [See Figure 10-9(a).]

Section 10-6 Relationship between Properties and the Phase Diagram

10-51 What is brass? Explain which element strengthens the matrix for this alloy.

10-52 What is the composition of the Monel alloy?

Section 10-7 Solidification of a Solid-Solution Alloy

10-53 Equal moles of MgO and FeO are combined and melted. Determine (a) the liquidus temperature, the solidus temperature, and the freezing range of the ceramic, and (b) determine the phase(s) present, their composition(s), and their amount(s) at 1800°C. (See Figure 10-21.)

10-54 Suppose 75 cm^3 of Nb and 45 cm^3 of W are combined and melted. Determine (a) the liquidus temperature, the solidus temperature, and the freezing range of the alloy, and (b) the phase(s) present, their composition(s), and their amount(s) at 2800°C. [See Figure 10-22.]

10-55 A NiO-60 mol% MgO ceramic is allowed to solidify. Determine (a) the composition of the first solid to form, and (b) the composition of the last liquid to solidify under equilibrium conditions. (See Figure 10-9(b).)

10-56 A Nb-35% W alloy is allowed to solidify. Determine (a) the composition of the first solid to form, and (b) the composition of the last liquid to solidify under equilibrium conditions. (See Figure 10-22.)

10-57 For equilibrium conditions and a MgO-65 wt% FeO ceramic, determine (a) the liquidus temperature; (b) the solidus temperature; (c) the freezing range; (d) the composition of the first solid to form during solidification; (e) the composition of the last liquid to solidify; (f) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 1800°C; and (g) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 1600°C. (See Figure 10-21.)

10-58 Figure 10-23 shows the cooling curve for a NiO-MgO ceramic. Determine (a) the liquidus temperature; (b) the solidus temperature; (c) the freezing range; (d) the pouring temperature; (e) the superheat; (f) the local solidification time; (g) the total solidification time; and (h) the composition of the ceramic.

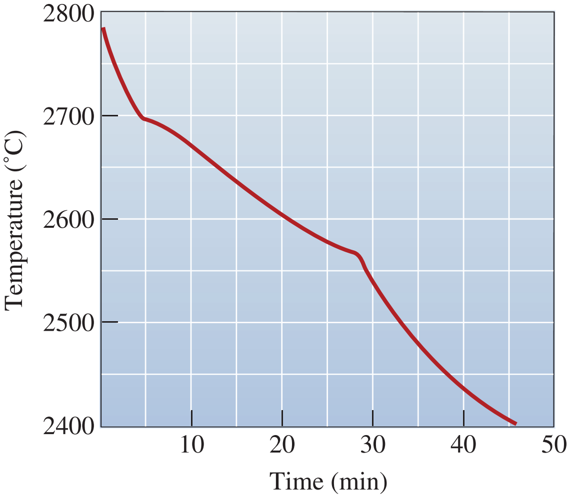

Figure 10-23 Cooling curve for a NiO-MgO ceramic (for Problem 10-58).

10-59 For equilibrium conditions and a Nb-80 wt% W alloy, determine (a) the liquidus temperature; (b) the solidus temperature; (c) the freezing range; (d) the composition of the first solid to form during solidification; (e) the composition of the last liquid to solidify; (f) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 3000°C; and (g) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 2800°C. (See Figure 10-22.)

10-60 Figure 10-24 shows the cooling curve for a Nb-W alloy. Determine (a) the liquidus temperature; (b) the solidus temperature; (c) the freezing range; (d) the pouring temperature; (e) the superheat; (f) the local solidification time; (g) the total solidification time; and (h) the composition of the alloy.

10-61 Cooling curves are shown in Figure 10-25 for several Mo-V alloys. Based on these curves, construct the Mo-V phase diagram.

Section 10-8 Nonequilibrium Solidification and Segregation

10-62 What are the origins of chemical segregation in cast products?

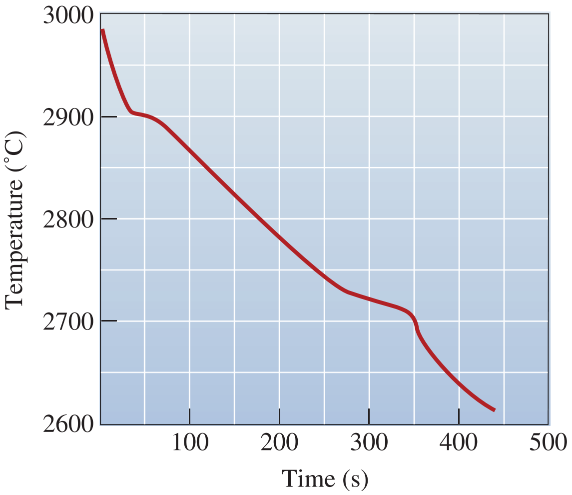

Figure 10-24 Cooling curve for a Nb-W alloy (for Problem 10-60).

10-63 For the nonequilibrium conditions shown for the MgO-65 wt% FeO ceramic, determine (a) the liquidus temperature; (b) the nonequilibrium solidus temperature; (c) the freezing range; (d) the composition of the first solid to form during solidification; (e) the composition of the last liquid to solidify; (f) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 1800°C; and (g) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 1600°C. (See Figure 10-21.)

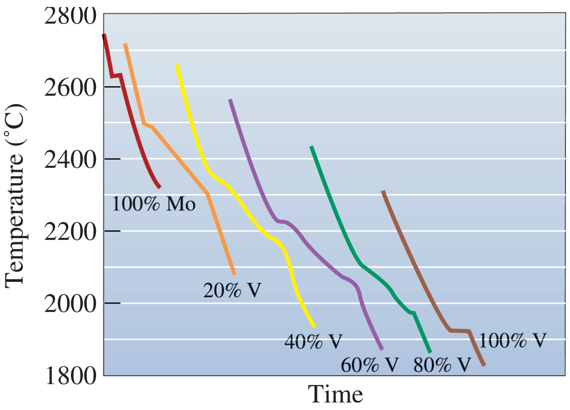

Figure 10-25 Cooling curves for a series of Mo-V alloys (for Problem 10-61).

10-64 For the nonequilibrium conditions shown for the Nb-80 wt% W alloy, determine (a) the liquidus temperature; (b) the nonequilibrium solidus temperature; (c) the freezing range; (d) the composition of the first solid to form during solidification; (e) the composition of the last liquid to solidify; (f) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 3000°C; and (g) the phase(s) present, the composition of the phase(s), and the amount of the phase(s) at 2800°C. (See Figure 10-22.)

10-65 How can microsegregation be removed?

10-66 What is macrosegregation? Is there a way to remove it without breaking up the cast structure?

10-67 What is homogenization? What type of segregation can it remove?

10-68 A copper-nickel alloy that solidifies with a secondary dendrite arm spacing (SDAS) of 0.001 cm requires 15 hours of homogenization heat treatment at 1100°C. What is the homogenization time required for the same alloy with a SDAS of 0.01 cm and 0.0001 cm? If the diffusion coefficient of Ni in Cu at 1100°C is 3×10^{-10} cm^2/s, calculate the constant c in the homogenization time equation. What assumption is made in this calculation?

10-69 What is spray atomization? Can it be used for making ceramic powders?

10-70 Suppose you are asked to manufacture a critical component based on a nickel-based superalloy. The component must not contain any porosity and it must be chemically homogeneous. What manufacturing process would you use for this application? Why?

10-71 What is hot pressing? How is it different from hot isostatic pressing?

Design Problems

10-72 Homogenization of a slowly cooled Cu-Ni alloy having a secondary dendrite arm spacing of 0.025 cm requires 8 hours at 1000°C. Design a process to produce a homogeneous structure in a more rapidly cooled Cu-Ni alloy having a SDAS of 0.005 cm.

10-73 Design a process to produce a NiO-60% MgO refractory with a structure that is 40% glassy phase at room temperature. Include all relevant temperatures.

10-74 Design a method by which glass beads (having a density of 2.3 g/cm^3) can be uniformly mixed and distributed in a Cu-20% Ni alloy (density of 8.91 g/cm^3).

10-75 Suppose that MgO contains 5 mol% NiO. Design a solidification purification method that will reduce the NiO to less than 1 mol% in the MgO.

Computer Problems

10-76 *Gibbs Phase Rule*. Write a computer program that will automate the Gibbs phase rule calculation. The program should ask the user for information on whether the pressure and temperature or only the pressure is to be held constant. The program then should use the correct equation to calculate the appropriate variable the user wants to know. The user will provide inputs for the number of components. Then, if the user wishes to provide the number of phases present, the program should calculate the degrees of freedom and vice-versa.

10-77 *Conversion of Wt% to At% for a Binary System*. Write a computer program that will allow conversion of wt% into at%. The program should ask the user to provide appropriate formula weights of the elements/compounds. (See Equations 10-4 and 10-5.)

10-78 *Hume-Rothery Rules*. Write a computer program that will predict whether or not there will likely be 100% solid solubility between two elements. The program should ask the user to provide the user with information on crystal structures of the elements or compounds, radii of different/atoms or ions involved, and valence and electronegativity values. You will have to make assumptions as to how much difference in values of electronegativity might be acceptable. The program should then use the Hume-Rothery rules and provide the user with guidance on the possibility of forming a system that shows 100% solid solubility.

Knovel® Problems

K10-1 What is the solidus temperature for a silicon-germanium system containing 30 wt% Si?