Lecture 8

Solid Solutions and Phase Equilibrium

Solid Solutions and Phase Equilibrium

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.

The point defects are 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. 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.

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.

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.

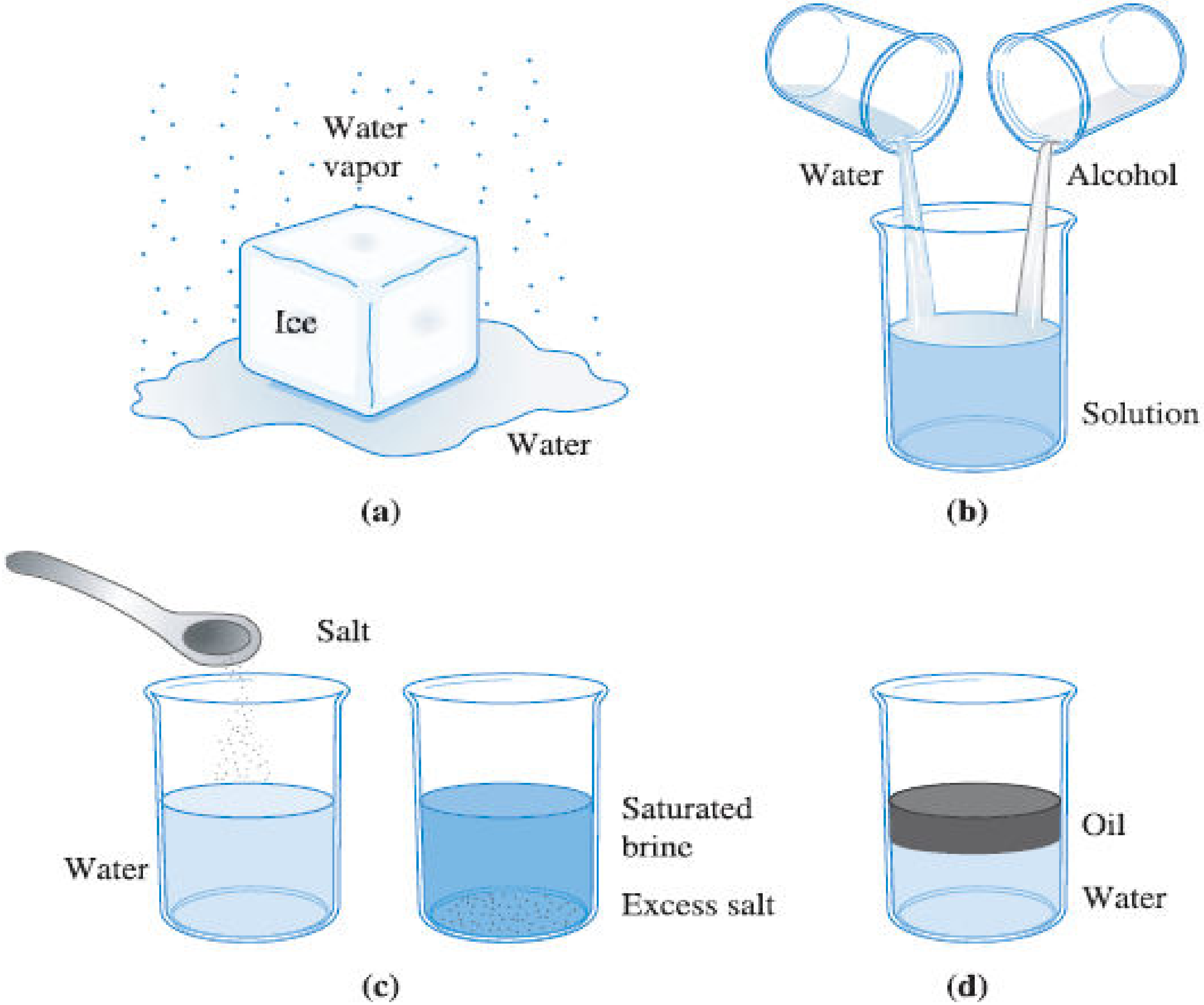


Figure 10-1 Illustration of phases and solubility: (a) The three forms of water—gas, liquid, and solid—are each a phase. (b) Water and alcohol have unlimited solubility. (c) Salt and water have limited solubility. (d) Oil and water have virtually no solubility.

Phase Rule

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:

$2 + C = F + P$ *(when temperature and pressure both can vary)* (1-10)

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.

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).

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:

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

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.

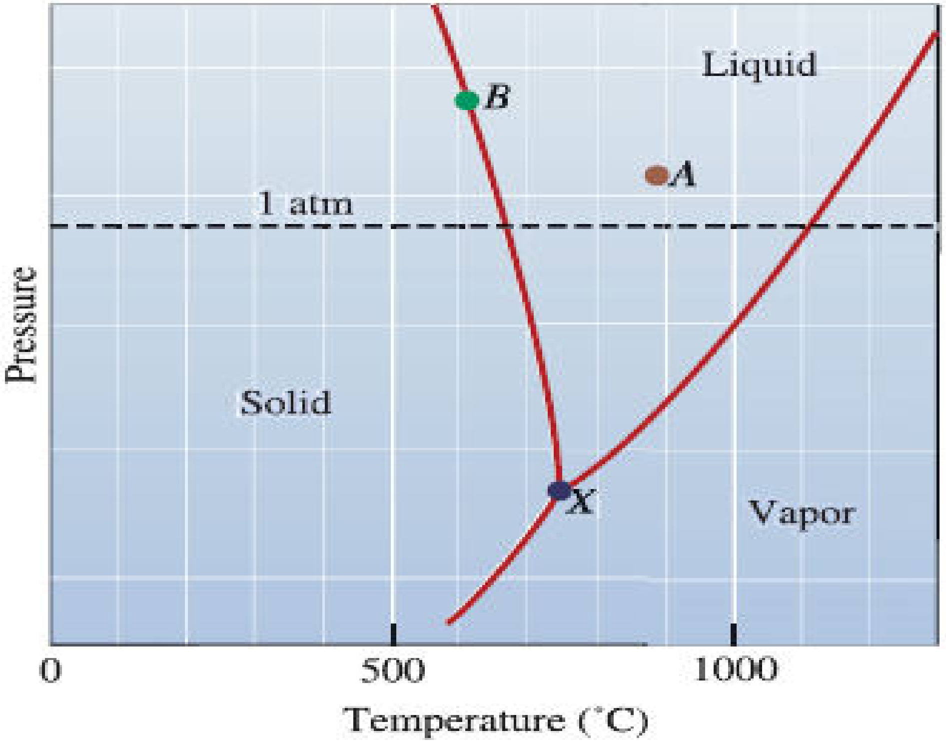


Figure 10-2
Schematic unary phase diagram for magnesium, showing the melting and boiling temperatures at one atmosphere pressure. On this diagram, point *X* is the triple point.

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).

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.

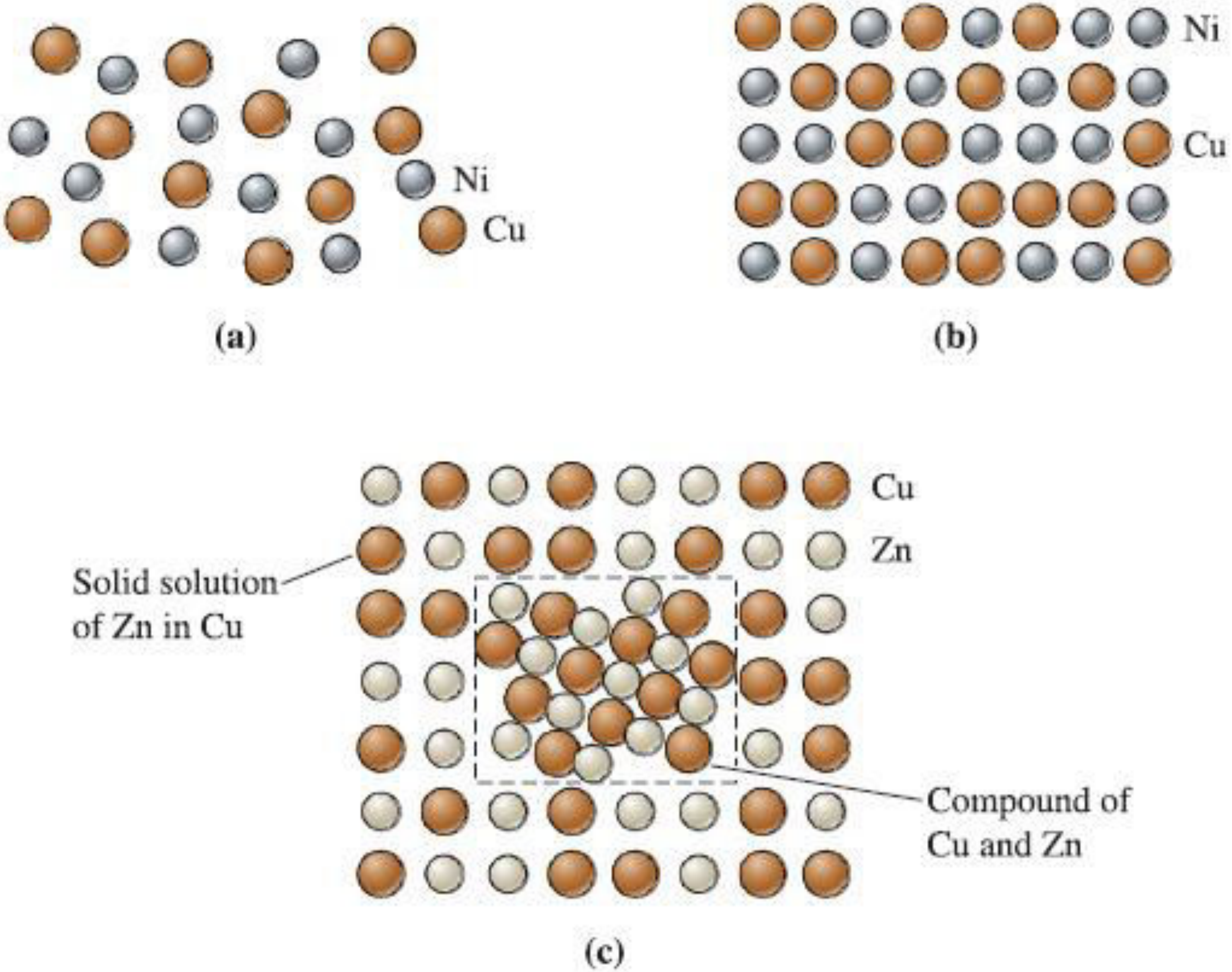


Figure 10-3 (a) Liquid copper and liquid nickel are completely soluble in each other. (b) Solid copper-nickel alloys display complete solid solubility with copper and nickel atoms occupying random lattice sites. (c) In copper-zinc alloys containing more than 30% Zn, a second phase forms because of the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

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.

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 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.

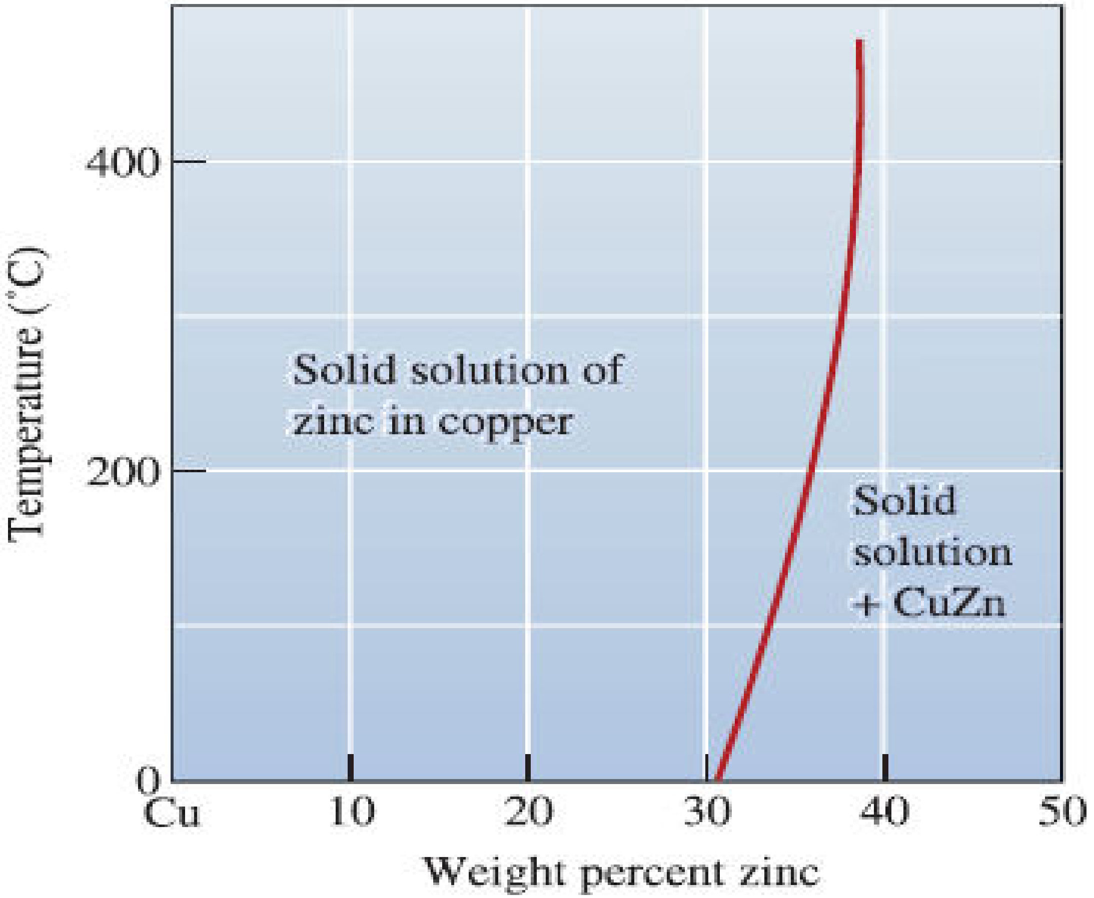
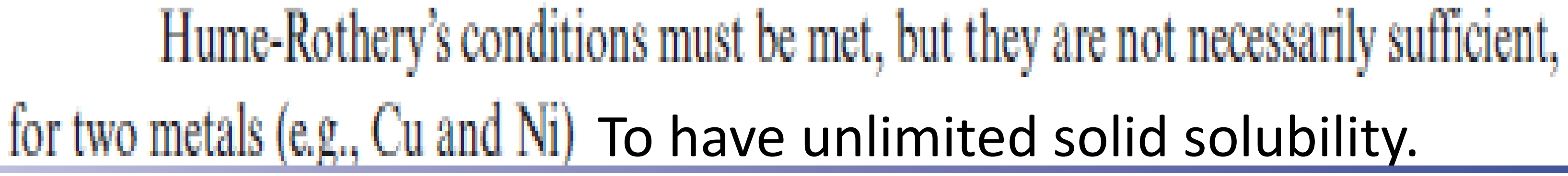


Figure 10-4
The solubility of zinc in copper. The solid line represents the solubility limit; when excess zinc is added, the solubility limit is exceeded and two phases coexist.

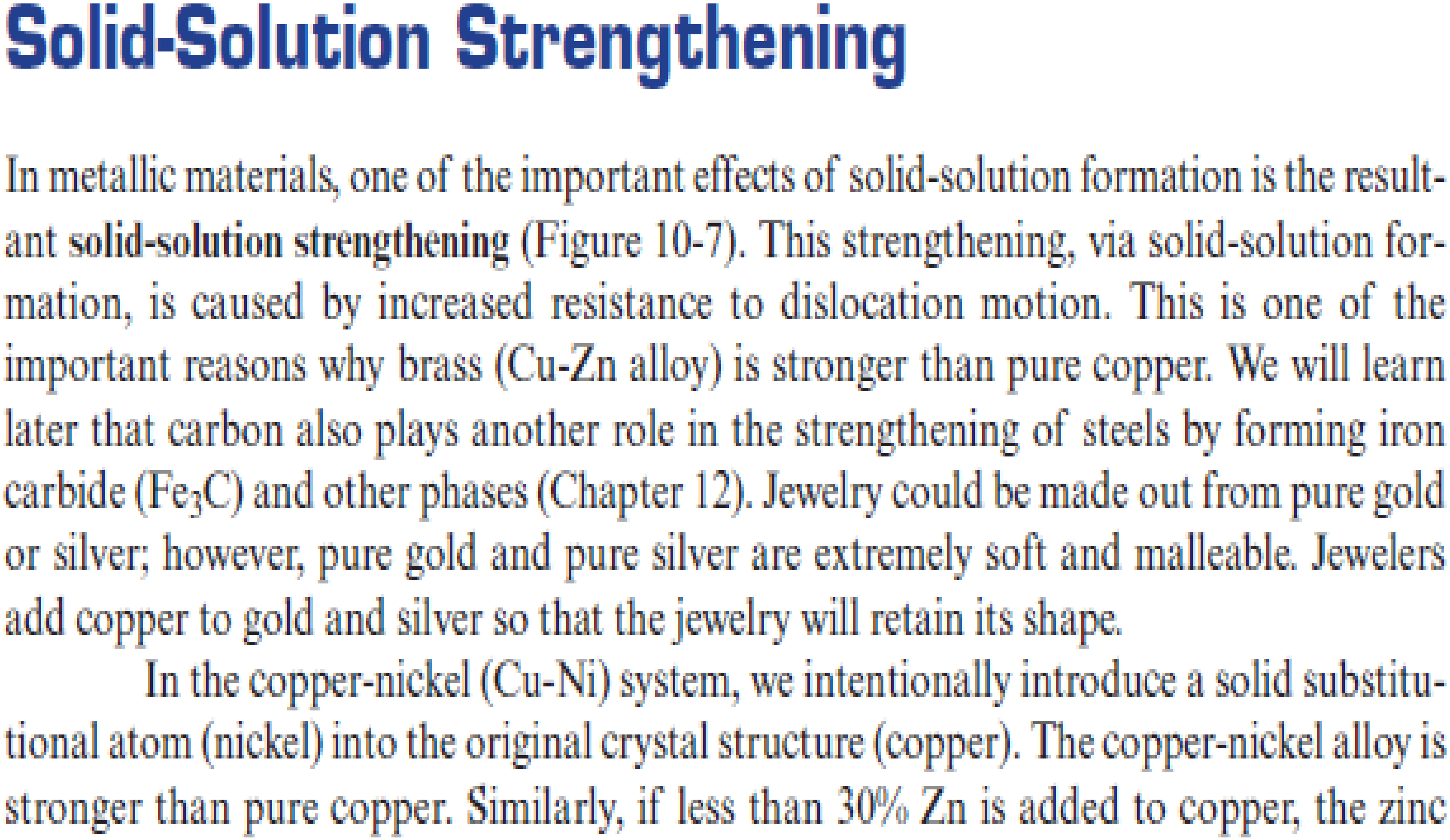
Conditions for Unlimited Solid Solubility

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.
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) To have unlimited solid solubility.



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

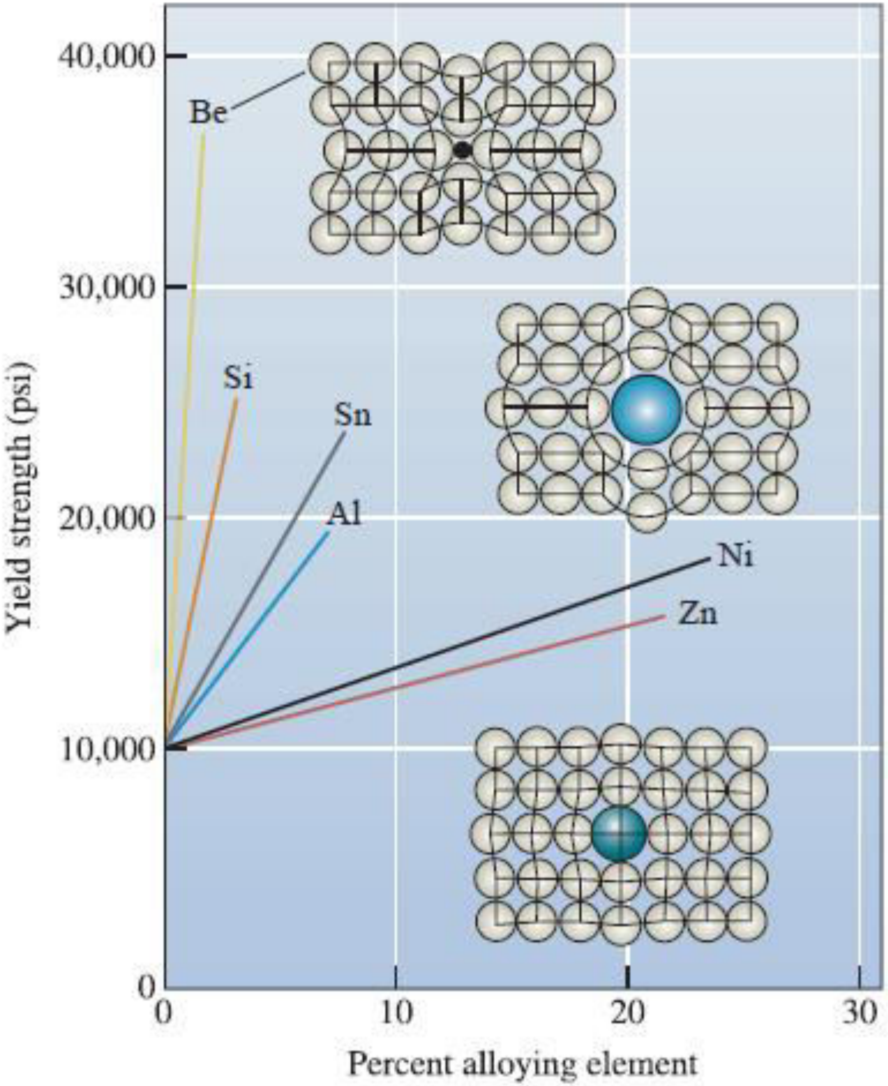


Figure 10-7
The effects of several alloying elements on the yield strength of copper. Nickel and zinc atoms are about the same size as copper atoms, but beryllium and tin atoms are much different from copper atoms. Increasing both the atomic size difference and the amount of alloying element increases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

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.

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)	$\left[\dfrac{r_{atom} - r_{Cu}}{r_{Cu}}\right] \times 100\%$
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 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.

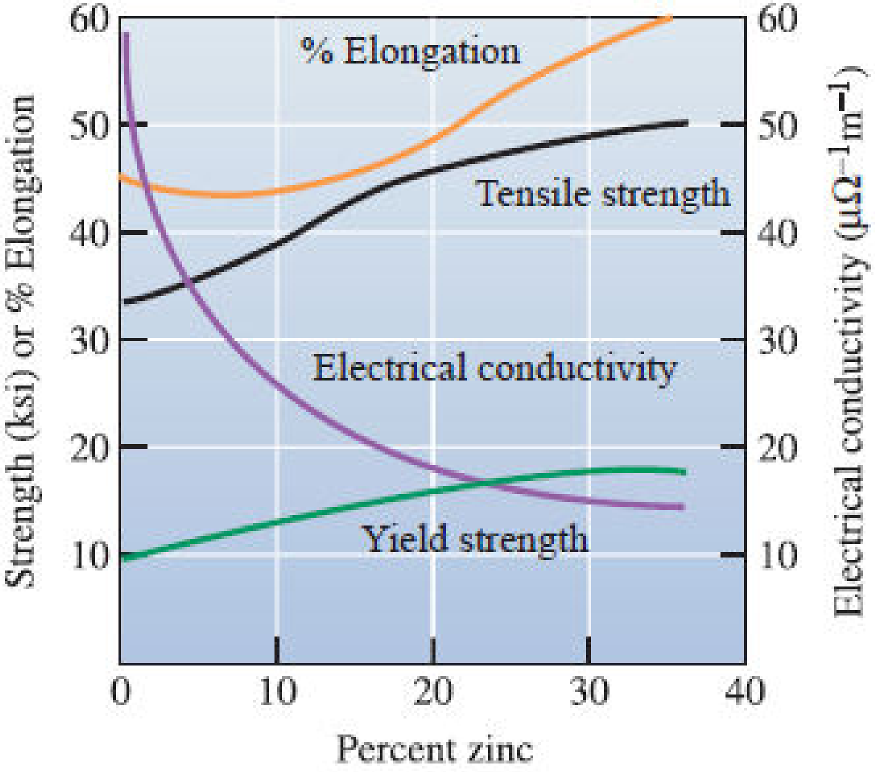


Figure 10-8
The effect of additions of zinc to copper on the properties of the solid-solution-strengthened alloy. The increase in % elongation with increasing zinc content is *not* typical of solid-solution strengthening.

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 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.

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 [Figure 10-9(a), only one solid phase forms; the two components in the system display complete solid solubility. As shown in the phase diagrams for thallium-lead (Tl-Pb) systems, it is possible to have phase diagrams show a minimum or maximum point, respectively [Figure 10-9(b)].

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.

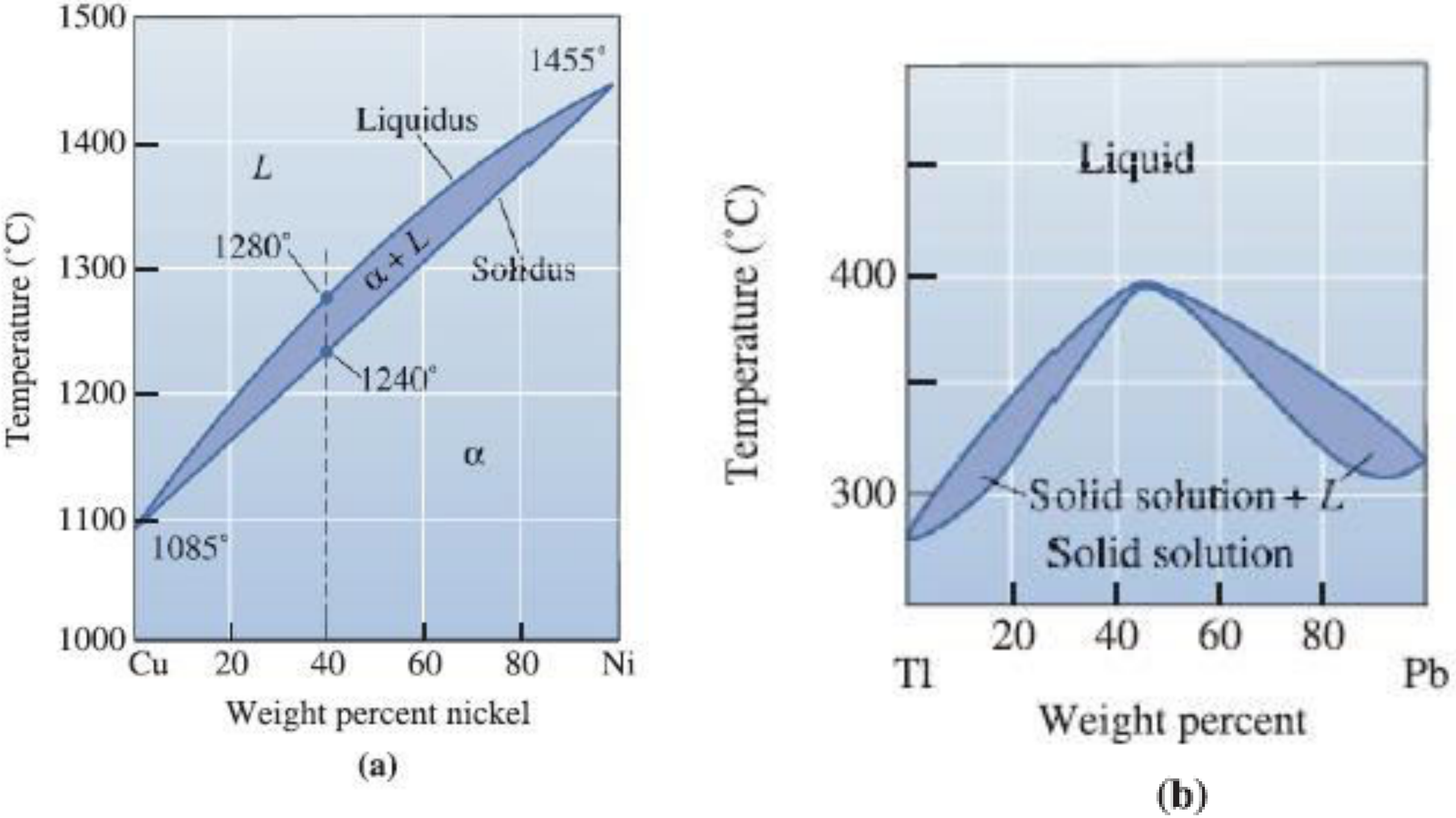


Figure 10-9 (a) and (b) The equilibrium phase diagrams for the Cu-Ni The liquidus and solidus temperatures are shown for a Cu-40% Ni alloy. (b) Systems with solid-solution maxima and minima. (Adapted from Introduction to Phase Equilibria, by C.G. Bergeron, and S.H. Risbud. Copyright © 1984 American Ceramic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

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 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 phase on the iron-carbon phase diagram) is ferromagnetic; however, FCC iron (indicated as the 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. 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.

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

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

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

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.

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.

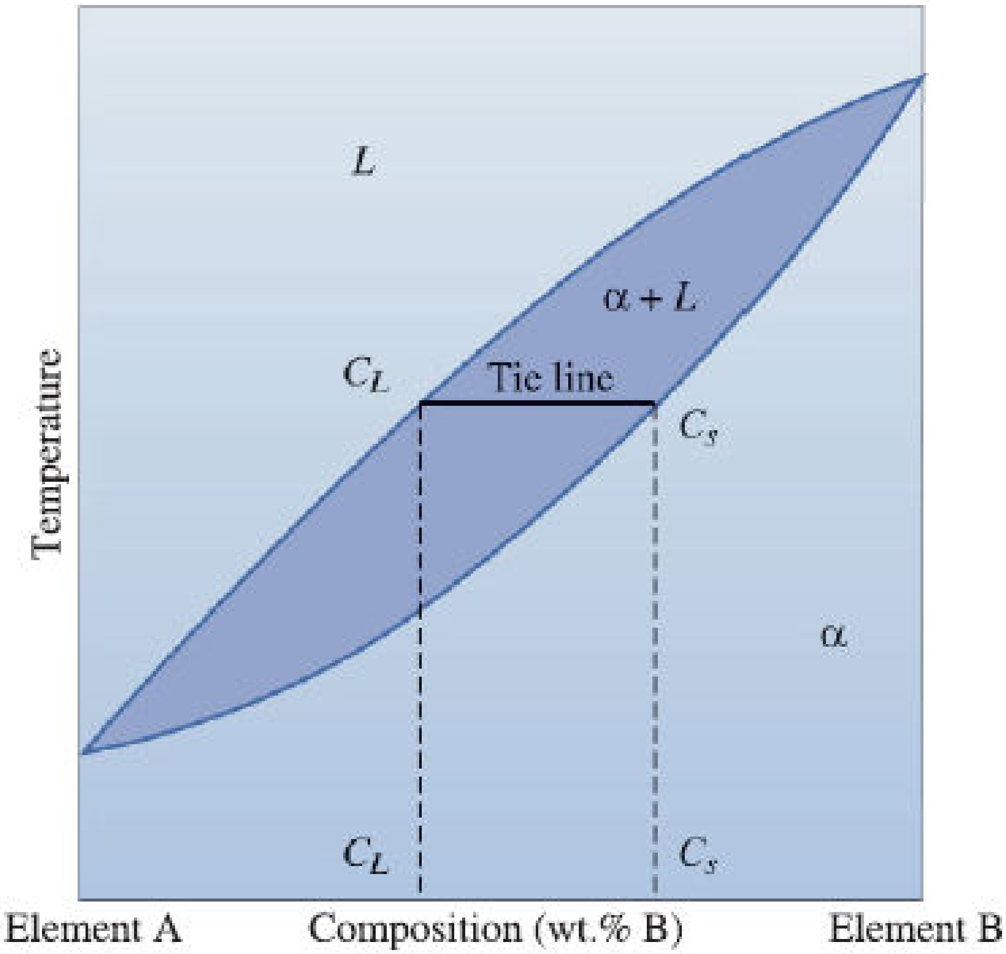


Figure 10-11
A hypothetical binary phase diagram between two elements A and B. When an alloy is present in a two-phase region, a tie line at the temperature of interest fixes the composition of the two phases. This is a consequence of the Gibbs phase rule, which provides only one degree of freedom in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

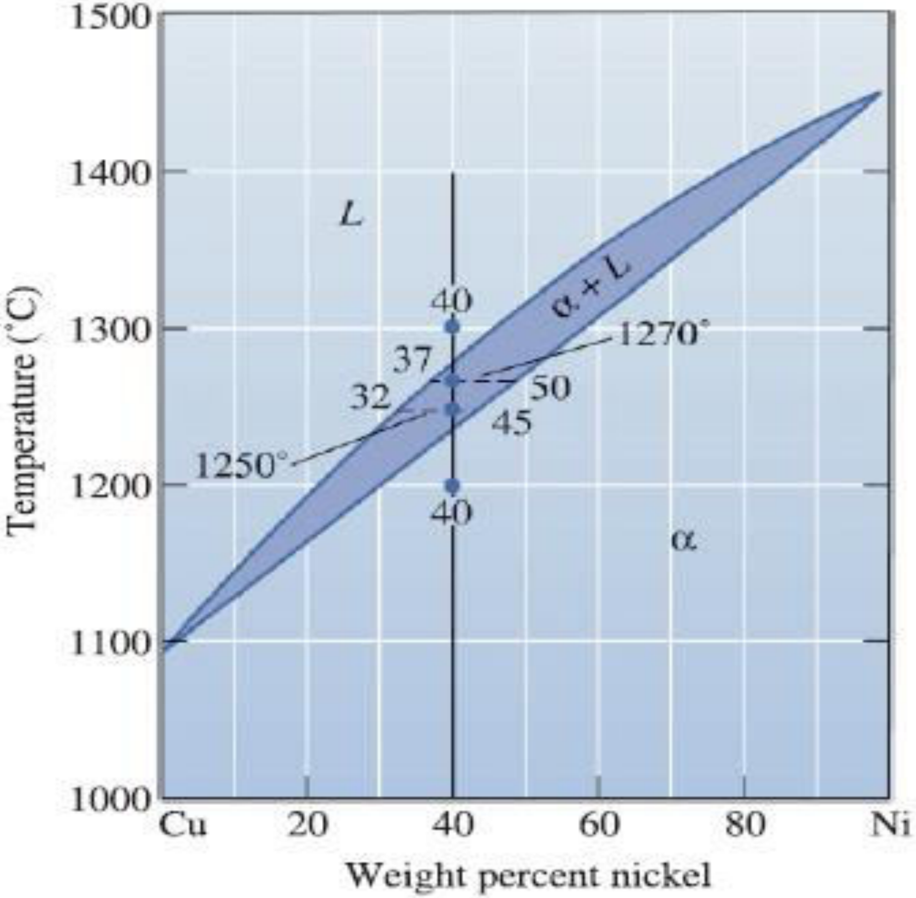


Figure 10-12
Tie lines and phase compositions for a Cu-40% Ni alloy at several temperatures (for Example 10-7).

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, pounds, 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

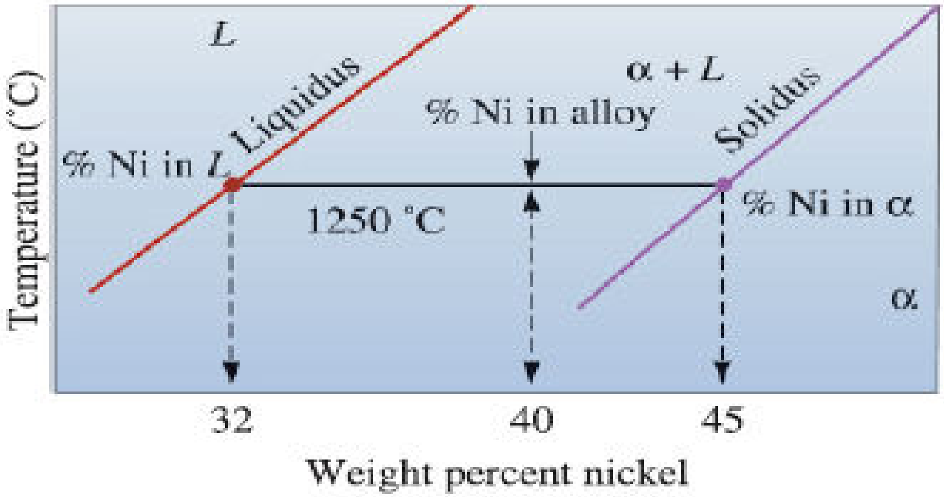


Figure 10-13
A tie line at 1250°C in the copper-nickel system that is used in Example 10-8 to find the amount of each phase.

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.

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

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

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

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

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

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.

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.

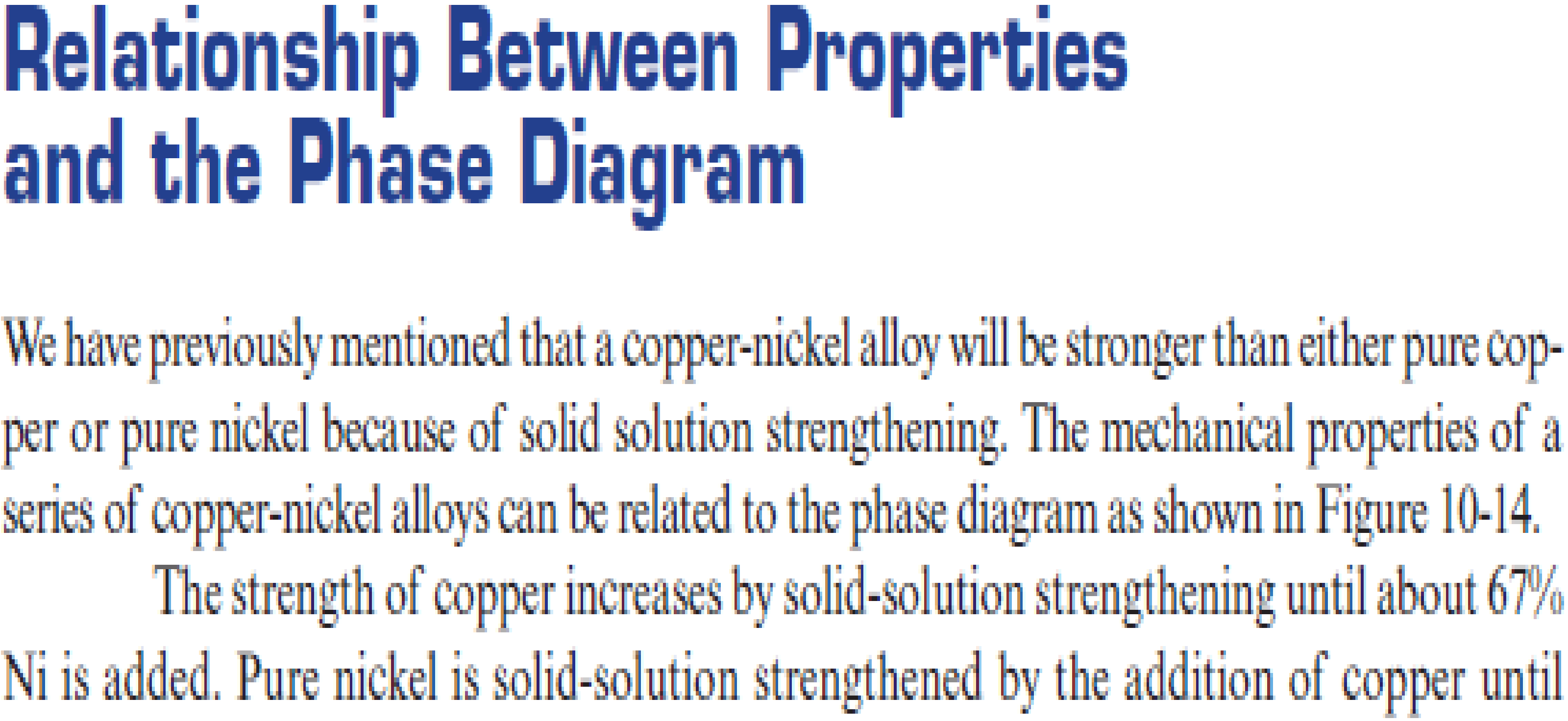
Note that at each temperature, we can determine the composition of the phases in equilibrium from the ends of the tie line drawn at that temperature.

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:

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

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



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

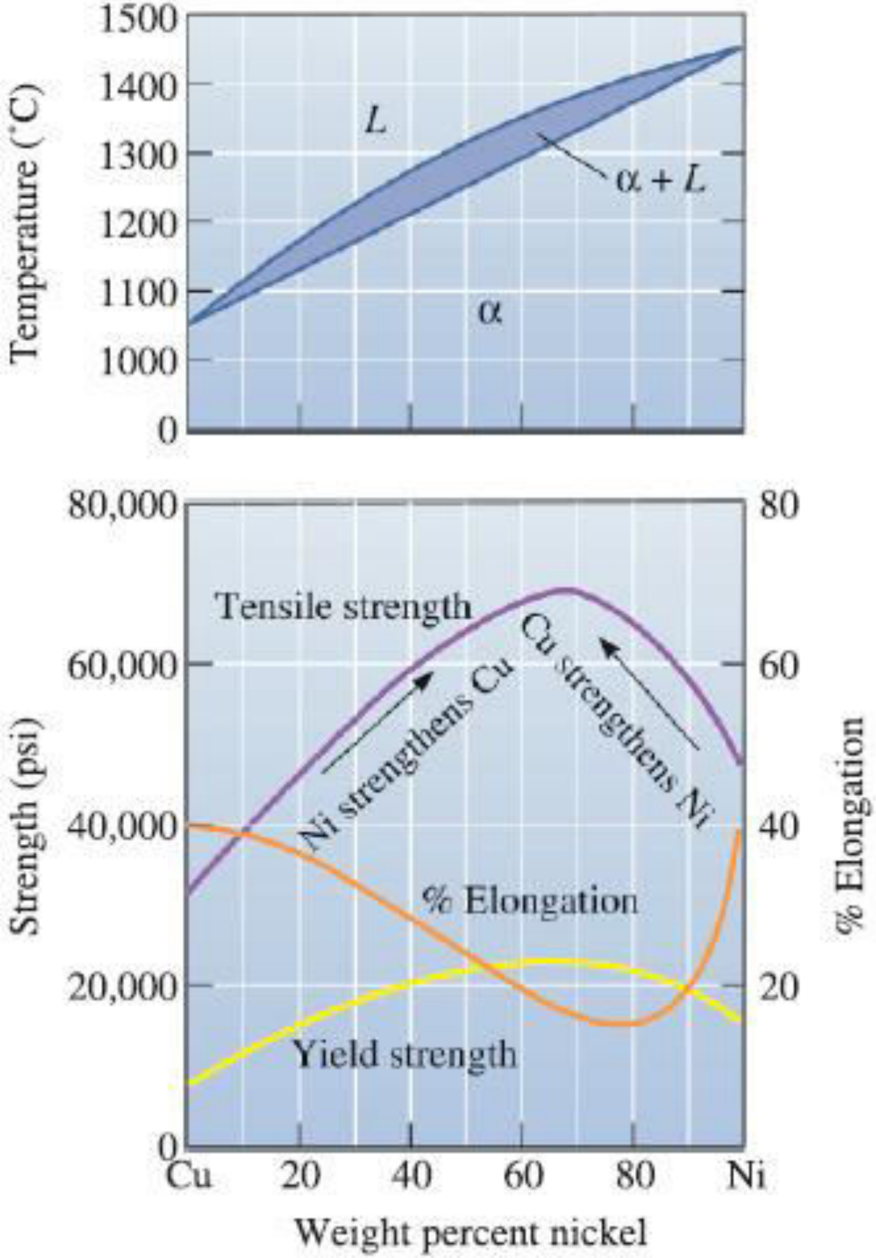


Figure 10-14
The mechanical properties of copper-nickel alloys. Copper is strengthened by up to 67% Ni, and nickel is strengthened by up to 33% Cu.

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 20,000 psi, a minimum tensile strength of 60,000 psi, 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.

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.

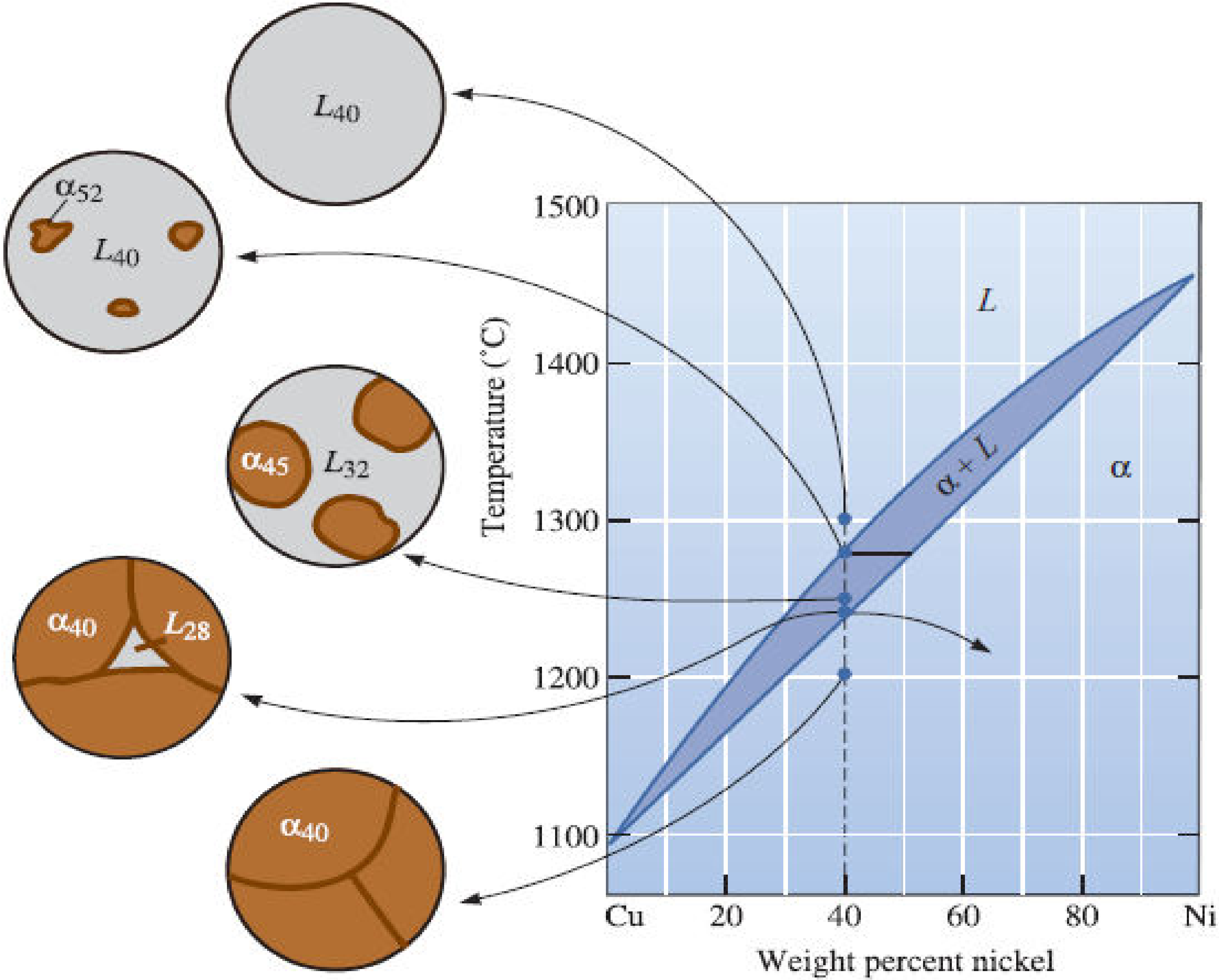


Figure 10-15 The change in structure of a Cu-40% Ni alloy during equilibrium solidification. The nickel and copper atoms must diffuse during cooling in order to satisfy the phase diagram and produce a uniform equilibrium structure.

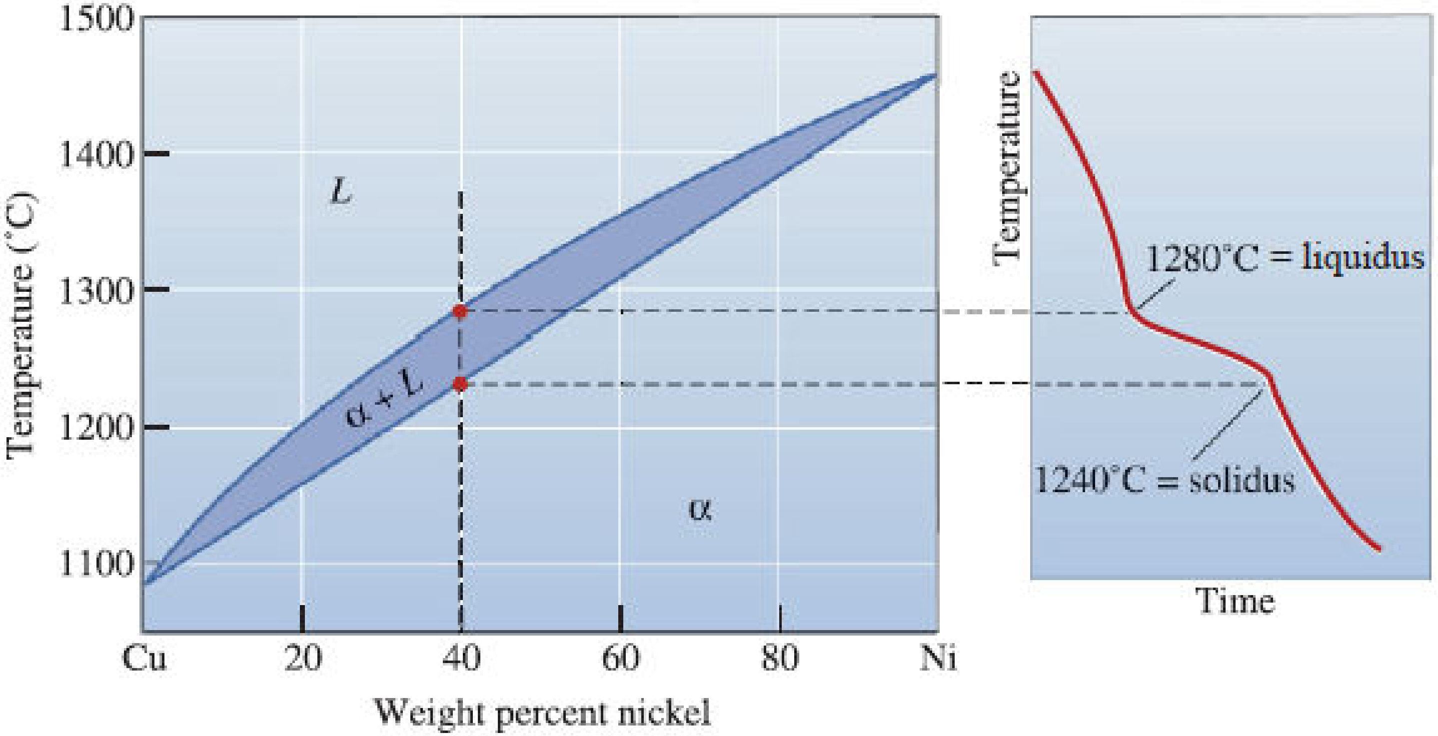


Figure 10-16 The cooling curve for an isomorphous alloy during solidification. We assume that cooling rates are low so that thermal equilibrium is maintained at each temperature. The changes in slope of the cooling curve indicate the liquidus and solidus temperatures, in this case, for a Cu-40% Ni alloy.

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.

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

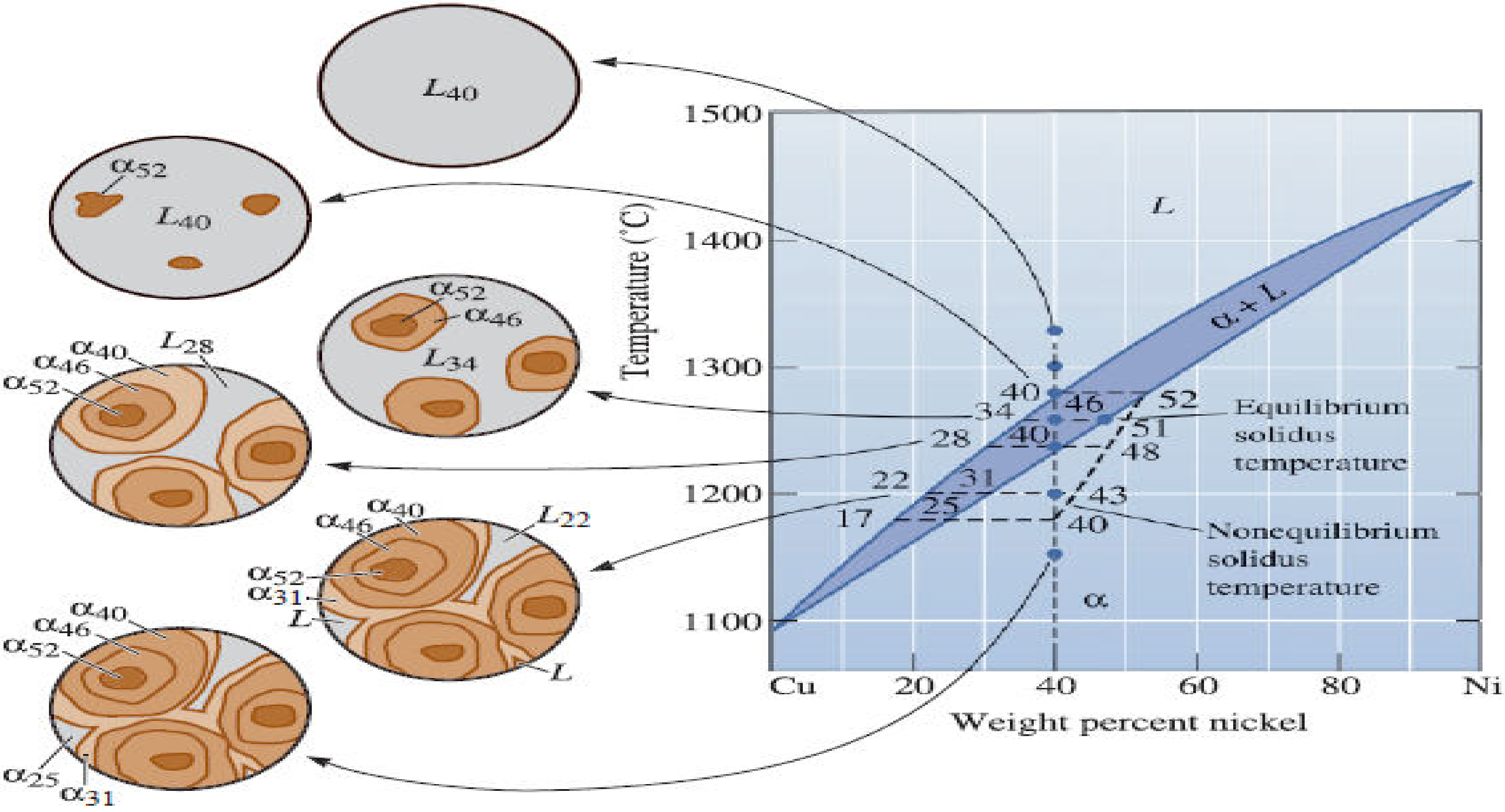


Figure 10-17 The change in structure of a Cu-40% Ni alloy during nonequilibrium solidification. Insufficient time for diffusion in the solid produces a segregated structure. Notice the nonequilibrium solidus curve.

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

Thank you for your attentions