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Phase Diagrams

6-1- *Introduction*

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

6-2- *Solubility Limit*

For many alloy systems and at some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution; this is called a ***solubility limit.*** The addition of solute in excess of this solubility limit results in the formation of another solid solution or compound that has a distinctly different composition. To illustrate this concept, consider the sugar–water ($C_{12}H_{22}O_{11}$-H_2O) system. Initially, as sugar is added to water, a sugar–water solution or syrup forms. As more sugar is introduced, the solution becomes more concentrated, until the solubility limit is reached, or the solution becomes saturated with sugar. At this time the solution is not capable of dissolving any more sugar, and further additions simply settle to the bottom of the container. Thus, the system now consists of two separate substances: a sugar–water syrup liquid solution and solid crystals of undissolved sugar.

This solubility limit of sugar in water depends on the temperature of the water and may be represented in graphical form on a plot of temperature along the ordinate and composition (in weight percent sugar)

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along the abscissa, as shown in Figure 6.1. Along the composition axis, increasing sugar concentration is from left to right, and percentage of water is read from right to left. Since only two components are involved (sugar and water), the sum of the concentrations at any composition will equal 100 wt%. The solubility limit is represented as the nearly vertical line in the figure. For compositions and temperatures to the left of the solubility line, only the syrup liquid solution exists; to the right of the line, syrup and solid sugar coexist. The solubility limit at some temperature is the composition that corresponds to the intersection of the given temperature coordinate and the solubility limit line. For example, at 20 °C the maximum solubility of sugar in water is 65 wt%. As Figure 6.1 indicates, the solubility limit increases slightly with rising temperature.
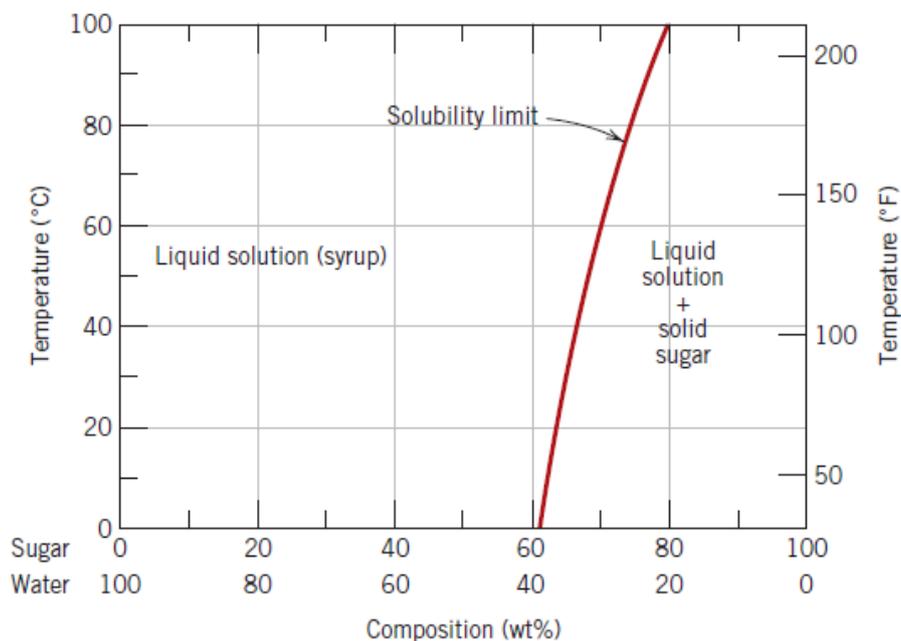

Figure 6.1 The solubility of sugar ($C_{12}H_{22}O_{11}$-H_2O) in a sugar–water syrup.

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6-3- *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.

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.

If more than one phase is present in a given system, each will have its own distinct properties, and a boundary separating the phases will exist across which there will be a discontinuous and abrupt change in physical and/or chemical characteristics. When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties; a disparity in one or the other set of properties is sufficient.

Sometimes, a single-phase system is termed "homogeneous." Systems composed of two or more phases are termed "mixtures" or "heterogeneous systems." Most metallic alloys and, for that matter,

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ceramic, polymeric, and composite systems are heterogeneous. Ordinarily, the phases interact in such a way that the property combination of the multiphase system is different from, and more attractive than, either of the individual phases.

6-4- *Microstructure*

Many times, the physical properties and, in particular, the mechanical behavior of a material depends on the microstructure. In metal alloys, microstructure is characterized by the number of phases present, their proportions, and the manner in which they are distributed or arranged. The microstructure of an alloy depends on such variables as the alloying elements present, their concentrations, and the heat treatment of the alloy (i.e., the temperature, the heating time at temperature, and the rate of cooling to room temperature).

6-5- *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)

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

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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 this equation 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.

As an example of the use of the phase rule, let's consider the case of pure magnesium (Mg). Figure 6-1 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 6-1). 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 phase rule:

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

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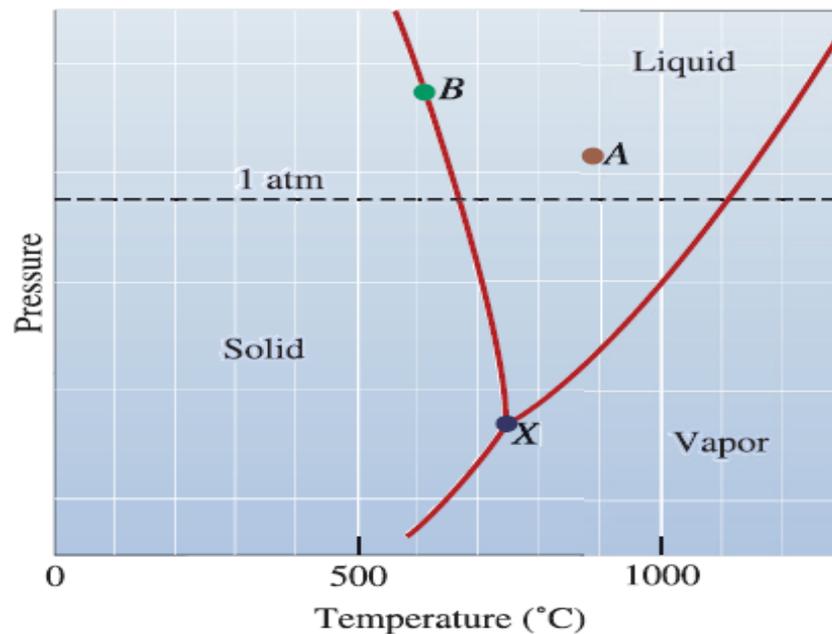*Dept. Of physic*　　　　　　*MATERIALS SCIENCE*　　　　　*Chapter (6)*

Figure 6-1 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.

What does this mean? Within limits, as seen in Figure 6-1, 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.

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,

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

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

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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:

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

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 6-1).

6-6- *Phase Equilibrium*

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

The term **phase equilibrium,** often used in the context of this discussion, refers to equilibrium as it applies to systems in which more than one phase may exist. Phase equilibrium is reflected by a constancy

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with time in the phase characteristics of a system. Perhaps an example best illustrates this concept. Suppose that a sugar–water syrup is contained in a closed vessel and the solution is in contact with solid sugar at 20 ^{o}C. If the system is at equilibrium, the composition of the syrup is 65 wt% $C_{12}H_{22}O_{11}$-35 wt% H_2O (Figure 6.1), and the amounts and compositions of the syrup and solid sugar will remain constant with time. If the temperature of the system is suddenly raised - say, to 100 ^{o}C - this equilibrium or balance is temporarily upset in that the solubility limit has been increased to 80 wt% $C_{12}H_{22}O_{11}$ (Figure 6.1). Thus, some of the solid sugar will go into solution in the syrup. This will continue until the new equilibrium syrup concentration is established at the higher temperature.

This sugar–syrup example illustrates the principle of phase equilibrium using a liquid–solid system. In many metallurgical and materials systems of interest, phase equilibrium involves just solid phases. In this regard the state of the system is reflected in the characteristics of the microstructure, which necessarily include not only the phases present and their compositions but, in addition, the relative phase amounts and their spatial arrangement or distribution. It is often the case, especially in solid systems, that a state of equilibrium is never completely achieved because the rate of approach to equilibrium is extremely slow; such a system is said to be in a nonequilibrium or **metastable** state. For example, some steel and aluminum alloys rely for their strength on the development of metastable microstructures during carefully designed heat treatments.

Thus not only is an understanding of equilibrium states and structures important, but also the speed or rate at which they are established and the factors that affect the rate must be considered.

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6-7- *Equilibrium phase diagrams*

Phase diagrams are helpful in predicting phase transformations and the resulting microstructures, which may have equilibrium or nonequilibrium character. Equilibrium phase diagrams represent the relationships between temperature and the compositions and the quantities of phases at equilibrium. There are several different varieties; but in the present discussion, temperature and composition are the variable parameters, for binary alloys. A binary alloy is one that contains two components. If more than two components are present, phase diagrams become extremely complicated and difficult to represent.

External pressure is also a parameter that influences the phase structure. However, in practicality, pressure remains virtually constant in most applications; thus, the phase diagrams presented here are for a constant pressure of one atmosphere (1 atm).

6-7-1- *Binary Isomorphous Systems*

Possibly the easiest type of binary phase diagram to understand and interpret is the type that is characterized by the copper–nickel system (Figure 6.2*a*). Temperature is plotted along the ordinate, and the abscissa represents the composition of the alloy, in weight percent (bottom) and atom percent (top) of nickel. The composition ranges from 0 wt% Ni (100 wt% Cu) on the left horizontal extremity to 100 wt% Ni (0 wt% Cu) on the right. Three different phase regions, or fields, appear on the diagram, an alpha (α) field, a liquid (*L*) field, and a two-phase *α+L* field. Each region is defined by the phase or phases that exist over the range of temperatures and compositions delimited by the phase boundary lines.

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The liquid *L* is a homogeneous liquid solution composed of both copper and nickel. The *α* phase is a substitutional solid solution consisting of both Cu and Ni atoms, and having an FCC crystal structure. At temperatures below about 1080 ^{o}C copper and nickel are mutually soluble in each other in the solid state for all compositions. This complete solubility is explained by the fact that both Cu and Ni have the same crystal structure (FCC).The copper–nickel system is termed **isomorphous** because of this complete liquid and solid solubility of the two components.

For Figure 6.2*a*, the solidus and liquidus lines intersect at the two composition extremities; these correspond to the melting temperatures of the pure components. For example, the melting temperatures of pure copper and nickel are 1085 ^{o}C and 1453 ^{o}C respectively. Heating pure copper corresponds to moving vertically up the left-hand temperature axis. Copper remains solid until its melting temperature is reached.The solid-to-liquid transformation takes place at the melting temperature, and no further heating is possible until this transformation has been completed.

For any composition other than pure components, this melting phenomenon will occur over the range of temperatures between the solidus and liquidus lines; both solid and liquid phases will be in equilibrium within this temperature range. For example, upon heating an alloy of composition 50 wt% Ni–50 wt% Cu (Figure 6.2*a*), melting begins at approximately 1280 ^{o}C (2340 ^{o}F); the amount of liquid phase continuously increases with temperature until about 1320 ^{o}C (2410 ^{o}F), at which the alloy is completely liquid.

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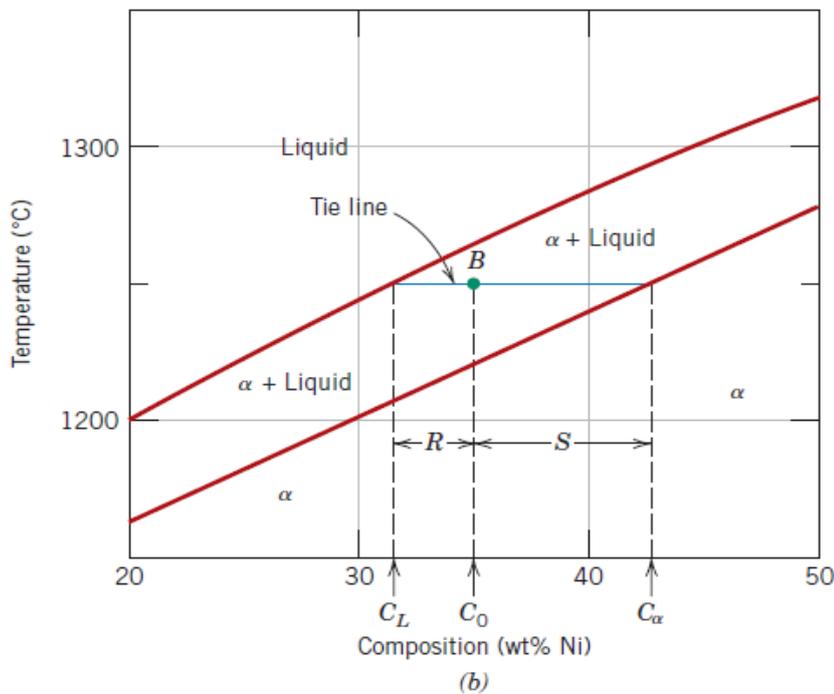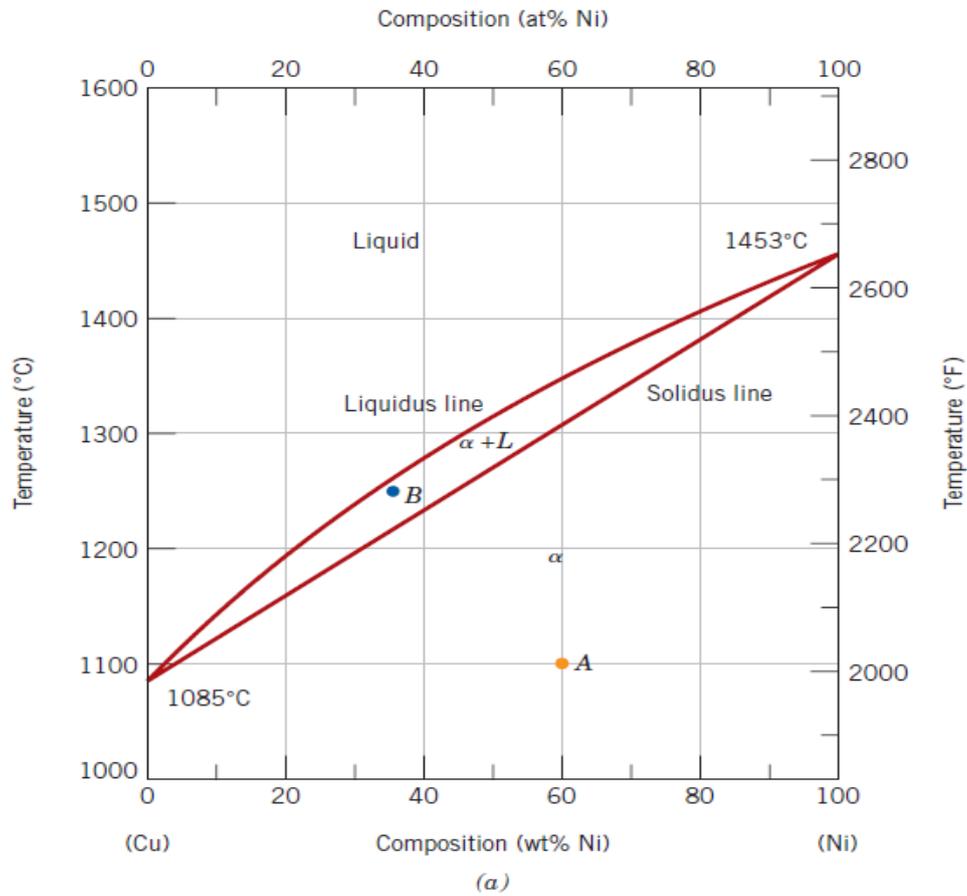*Dr. Mohammed Ghazi*
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Figure 6.2 (*a*) The copper–nickel phase diagram. (*b*) A portion of the copper–nickel phase diagram for which compositions and phase amounts are determined at point *B*. (Adapted from *Phase Diagrams of Binary Nickel Alloys,*

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6-8- *Interpretation of Phase Diagrams*

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

6-8-1- *Phases Present*

The establishment of what phases are present is relatively simple. One just locates the temperature–composition point on the diagram and notes the phase(s) with which the corresponding phase field is labeled. For example, an alloy of composition 60 wt% Ni–40 wt% Cu at 1100 ^{o}C would be located at point *A* in Figure 6.2*a*; since this is within the *α* region, only the single *α* phase will be present. On the other hand, a 35 wt% Ni–65 wt% Cu alloy at 1250 ^{o}C (point *B*) will consist of both *α* and liquid phases at equilibrium.

6-8-2- *Determination of Phase Compositions*

The first step in the determination of phase compositions (in terms of the concentrations of the components) is to locate the temperature–composition point on the phase diagram. Different methods are used for single- and two-phase regions. If only one phase is present, the procedure is trivial: the composition of this phase is simply the same as the overall composition of the alloy.

For an alloy having composition and temperature located in a two-phase region, the situation is more complicated. In all two-phase regions

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

1. A tie line is constructed across the two-phase region at the temperature of the alloy.

2. The intersections of the tie line and the phase boundaries on either side are noted.

3. Perpendiculars are dropped from these intersections to the horizontal composition axis, from which the composition of each of the respective phases is read.

For example, consider again the 35 wt% Ni–65 wt% Cu alloy at located at point B in Figure 6.2*b* and lying within the $\alpha+L$ region. Thus, the problem is to determine the composition (in wt% Ni and Cu) for both the α and liquid phases. The tie line has been constructed across the $\alpha+L$ phase region, as shown in Figure 6.2*b*. The perpendicular from the intersection of the tie line with the liquidus boundary meets the composition axis at 31.5 wt% Ni–68.5 wt% Cu, which is the composition of the liquid phase, C_L. Likewise, for the solidus–tie line intersection, we find a composition for the α solid-solution phase, C_α, of 42.5 wt% Ni– 57.5 wt% Cu.

6-8-3- *Determination of Phase Amounts*

The relative amounts (as fraction or as percentage) of the phases present at equilibrium may also be computed with the aid of phase

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diagrams. Again, the single- and two-phase situations must be treated separately. The solution is obvious in the single-phase region: Since only one phase is present, the alloy is composed entirely of that phase; that is, the phase fraction is 1.0 or, alternatively, the percentage is 100%. From the previous example for the 60 wt% Ni–40 wt% Cu alloy at 1100 ^{o}C (point *A* in Figure 6.2*a*), only the α phase is present; hence, the alloy is completely or 100% α.

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

1. The tie line is constructed across the two-phase region at the temperature of the alloy.

2. The overall alloy composition is located on the tie line.

3. The fraction of one phase is computed by taking the length of tie line from the overall alloy composition to the phase boundary for the *other* phase, and dividing by the total tie line length.

4. The fraction of the other phase is determined in the same manner.

5. If phase percentages are desired, each phase fraction is multiplied by 100. When the composition axis is scaled in weight percent, the phase fractions computed using the lever rule are mass fractions-the mass (or weight) of a specific phase divided by the total alloy mass (or weight). The mass of each phase is computed from the product of each phase fraction and the total alloy mass.

Consider again the example shown in Figure 6.2*b*, in which at 1250 ^{o}C both α and liquid phases are present for a 35 wt% Ni–65 wt% Cu alloy. The problem is to compute the fraction of each of the α and liquid

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phases. The tie line has been constructed that was used for the determination of α and L phase compositions. Let the overall alloy composition be located along the tie line and denoted as C_o, and mass fractions be represented by W_L and W_α for the respective phases. From the lever rule, W_L may be computed according to:

$$W_L = \frac{S}{R + S} \qquad .... (1)$$

Or, by subtracting compositions,

$$W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} \qquad .... (2)$$

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

$$W_L = \frac{42.5 - 35}{42.5 - 31.5} = 0.68$$

Similarly, for the α phase,

$$W_\alpha = \frac{R}{R + S} \qquad .... (3)$$

$$W_L = \frac{C_o - C_L}{C_\alpha - C_L} \qquad .... (4)$$

$$W_L = \frac{35 - 31.5}{42.5 - 31.5} = 0.32$$

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

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

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For any alloy consisting of a single phase, the composition of that phase is the same as the total alloy composition. If two phases are present, the tie line must be employed, the extremities of which determine the compositions of the respective phases.

Example (1):

Lever Rule Derivation

Derive the lever rule.

Solution

Consider the phase diagram for copper and nickel (Figure 6-2b) and alloy of composition C_0 at 1250°C, and let C_α, C_L, W_α, and W_L represent the same parameters as above. This derivation is accomplished through two conservation-of-mass expressions. With the first, since only two phases are present, the sum of their mass fractions must be equal to unity; that is,

$$W_\alpha + W_L = 1$$

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

$$W_\alpha C_\alpha + W_L C_L = C_0$$

Simultaneous solution of these two equations leads to the lever rule expressions for this particular situation, Equations 9.1b and 9.2b:

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

$$W_\alpha = \frac{C_0 - C_L}{C_\alpha - C_L}$$

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

For an alloy consisting of α and β phases, the volume fraction of the α phase, V_a is defined as:

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$$V_a = \frac{v_\alpha}{v_\alpha + v_\beta} \qquad \ldots \ldots \ldots (5)$$

Where v_a and v_B denote the volumes of the respective phases in the alloy. Of course, an analogous expression exists for and, for an alloy consisting of just two phases, it is the case that $V_a + V_B = 1$

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

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}} \qquad \ldots \ldots \ldots (6)$$

$$V_\beta = \frac{\dfrac{W_\beta}{\rho_\beta}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}} \qquad \ldots \ldots \ldots (7)$$

$$W_\alpha = \frac{V_\alpha \rho_\alpha}{V_\alpha \rho_\alpha + V_\beta \rho_\beta} \qquad \ldots \ldots \ldots (8)$$

$$W_\beta = \frac{V_\beta \rho_\beta}{V_\alpha \rho_\alpha + V_\beta \rho_\beta} \qquad \ldots \ldots \ldots (9)$$

In these expressions, ρ_α and ρ_β are the densities of the respective phases.

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

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6-9- *Development of Microstructure in Isomorphous Alloys*

6-9-1- *Equilibrium Cooling*

At this point it is instructive to examine the development of microstructure that occurs for isomorphous alloys during solidification. We first treat the situation in which the cooling occurs very slowly, in that phase equilibrium is continuously maintained.
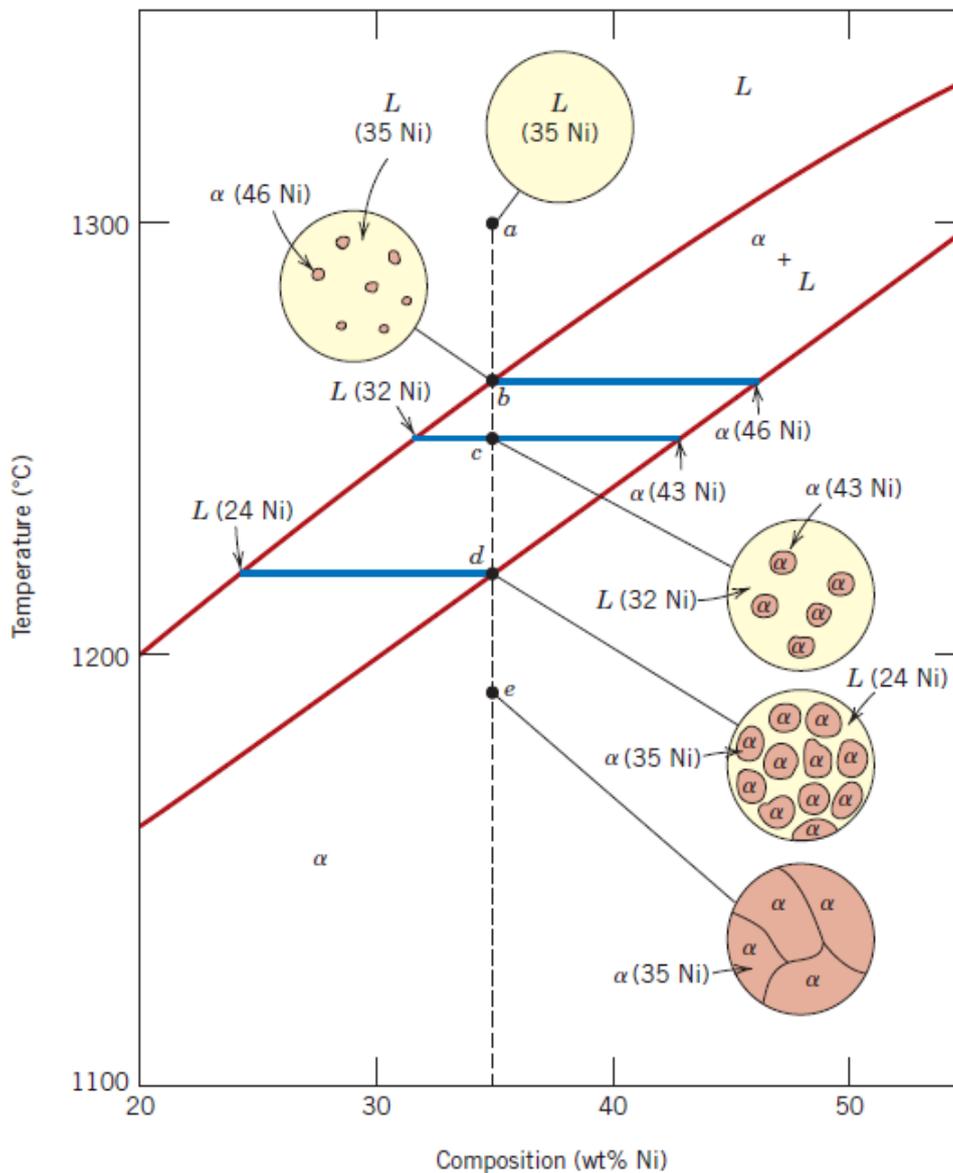
Figure 6.3 Schematic representation of the development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy.

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Let us consider the copper–nickel system (Figure 6.2*a*), specifically an alloy of composition 35 wt% Ni–65 wt% Cu as it is cooled from 1300 ^{o}C. The region of the Cu–Ni phase diagram in the vicinity of this composition is shown in Figure 6.3.

Cooling of an alloy of the above composition corresponds to moving down the vertical dashed line. At 1300 ^{o}C, point **a**, the alloy is completely liquid (of composition 35 wt% Ni–65 wt% Cu) and has the microstructure represented by the circle inset in the figure. As cooling begins, no microstructural or compositional changes will be realized until we reach the liquidus line (point **b**, ~1260 ^{o}C).At this point, the first solid α begins to form, which has a composition dictated by the tie line drawn at this temperature [i.e., 46 wt% Ni–54 wt% Cu, noted as α(46 Ni)]; the composition of liquid is still approximately 35 wt% Ni–65 wt% Cu [L(35 Ni)], which is different from that of the solid α.With continued cooling, both compositions and relative amounts of each of the phases will change. The compositions of the liquid and α phases will follow the liquidus and solidus lines, respectively. Furthermore, the fraction of the α phase will increase with continued cooling. Note that the overall alloy composition (35 wt% Ni–65 wt% Cu) remains unchanged during cooling even though there is a redistribution of copper and nickel between the phases.

At 1250 ^{o}C, point **c** in Figure 6.3, the compositions of the liquid and α phases are 32 wt% Ni–68 wt% Cu [L(32 Ni)] and 43 wt% Ni–57 wt% Cu [α(43 Ni)], respectively.

The solidification process is virtually complete at about 1220 ^{o}C, point **d**; the composition of the solid α is approximately 35 wt% Ni–65 wt% Cu (the overall alloy composition) while that of the last remaining liquid is 24 wt% Ni–76 wt% Cu. Upon crossing the solidus

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line, this remaining liquid solidifies; the final product then is a polycrystalline α-phase solid solution that has a uniform 35 wt% Ni–65 wt% Cu composition (point **e**, Figure 6.3). Subsequent cooling will produce no microstructural or compositional alterations.

6-9-2- *Nonequilibrium Cooling*

Some of the consequences of nonequilibrium solidification for isomorphous alloys will now be discussed by considering a 35 wt% Ni– 65 wt% Cu alloy, the same composition that was used for equilibrium cooling in the previous section. The portion of the phase diagram near this composition is shown in Figure 6.4; in addition, microstructures and associated phase compositions at various temperatures upon cooling are noted in the circular insets. To simplify this discussion it will be assumed that diffusion rates in the liquid phase are sufficiently rapid such that equilibrium is maintained in the liquid.

Let us begin cooling from a temperature of about 1300 ^{o}C; this is indicated by point α' in the liquid region. This liquid has a composition of 35 wt% Ni–65 wt% Cu [noted as *L*(35 Ni) in the figure], and no changes occur while cooling through the liquid phase region (moving down vertically from point α'). At point b' (approximately 1260 ^{o}C), α-phase particles begin to form, which, from the tie line constructed, have a composition of 46 wt% Ni–54 wt% Cu [α(46 Ni)].

Upon further cooling to point c' (about 1240 ^{o}C), the liquid composition has shifted to 29 wt% Ni–71 wt% Cu; furthermore, at this temperature the composition of the α phase that solidified is 40 wt% Ni– 60 wt% Cu [α(40 Ni)]. However, since diffusion in the solid α phase is relatively slow, the α phase that formed at point b' has not changed

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composition appreciably—i.e., it is still about 46 wt% Ni—and the composition of the α grains has continuously changed with radial position, from 46 wt% Ni at grain centers to 40 wt% Ni at the outer grain perimeters. Thus, at point **c'**, the *average composition* of the solid α grains that have formed would be some volume weighted average composition, lying between 46 and 40 wt% Ni; for the sake of argument, let us take this average composition to be 42 wt% Ni–58 wt% Cu [α(42 Ni)].
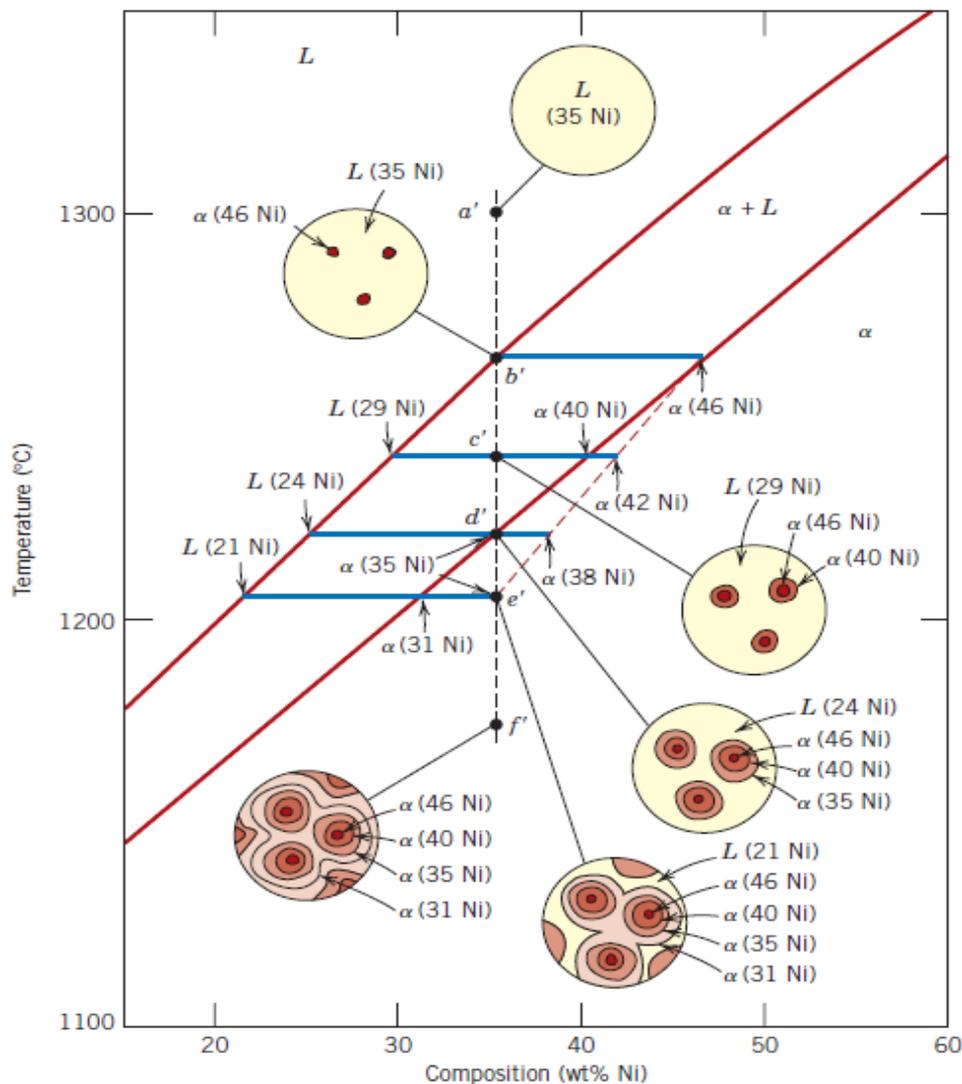
Figure 6.4 Schematic representation of the development of microstructure during the nonequilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy.

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At point ***d′*** (~1220 ^{o}C) and for equilibrium cooling rates, solidification should be completed. However, for this nonequilibrium situation, there is still an appreciable proportion of liquid remaining, and the *α* phase that is forming has a composition of 35 wt% Ni [*α*(35 Ni)]; also the *average α*-phase composition at this point is 38 wt% Ni [*α*(38 Ni)].

Nonequilibrium solidification finally reaches completion at point ***e′*** (~1205 ^{o}C). The composition of the last *α* phase to solidify at this point is about 31 wt% Ni; the *average* composition of the *α* phase at complete solidification is 35 wt% Ni. The inset at point ***f′*** shows the microstructure of the totally solid material.

The degree of displacement of the nonequilibrium solidus curve from the equilibrium one will depend on rate of cooling. The slower the cooling rate, the smaller this displacement; that is, the difference between the equilibrium solidus and average solid composition is lower. Furthermore, if the diffusion rate in the solid phase is increased, this displacement will be diminished.

There are some important consequences for isomorphous alloys that have solidified under nonequilibrium conditions. As discussed above, the distribution of the two elements within the grains is nonuniform, a phenomenon termed *segregation;* that is, concentration gradients are established across the grains that are represented by the insets of Figure 6.4. The center of each grain, which is the first part to freeze, is rich in the high-melting element (e.g., nickel for this Cu–Ni system), whereas the concentration of the low-melting element increases with position from this region to the grain boundary.

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6-10- *Mechanical Properties of Isomorphous Alloys*

We shall now briefly explore how the mechanical properties of solid isomorphous alloys are affected by composition as other structural variables (e.g., grain size) are held constant. For all temperatures and compositions below the melting temperature of the lowest-melting component, only a single solid phase will exist. Therefore, each component will experience solid-solution strengthening, or an increase in strength and hardness by additions of the other component. This effect is demonstrated in Figure 6.5*a* as tensile strength versus composition for the copper–nickel system at room temperature; at some intermediate composition, the curve necessarily passes through a maximum. Plotted in Figure 6.5*b* is the ductility (%EL)–composition behavior, which is just the opposite of tensile strength; that is, ductility decreases with additions of the second component, and the curve exhibits a minimum.
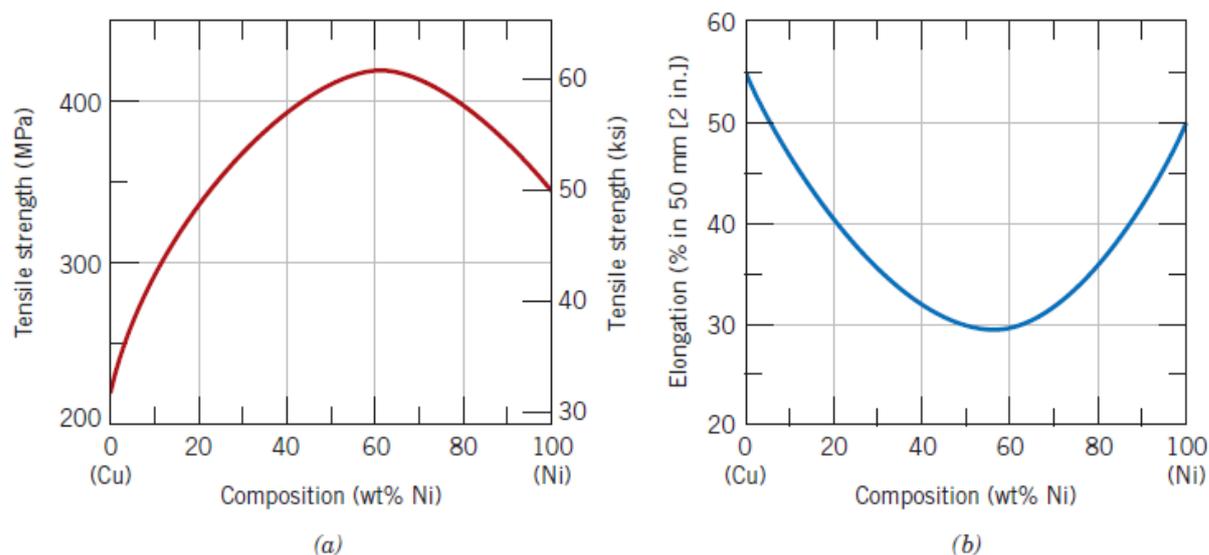

Figure 6.5 For the copper–nickel system, (*a*) tensile strength versus composition, and (*b*) ductility (%EL) versus composition at room temperature. A solid solution exists over all compositions for this system.

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6-11- *Binary Eutectic system*

Another type of common and relatively simple phase diagram found for binary alloys is shown in Figure 6.6 for the copper–silver system; this is known as a binary eutectic phase diagram. A number of features of this phase diagram are important and worth noting. First, three single-phase regions are found on the diagram: α, β, and liquid. The α phase is a solid solution rich in copper; it has silver as the solute component and an FCC crystal structure. The β phase solid solution also has an FCC structure, but copper is the solute. Pure copper and pure silver are also considered to be α and β phases, respectively.
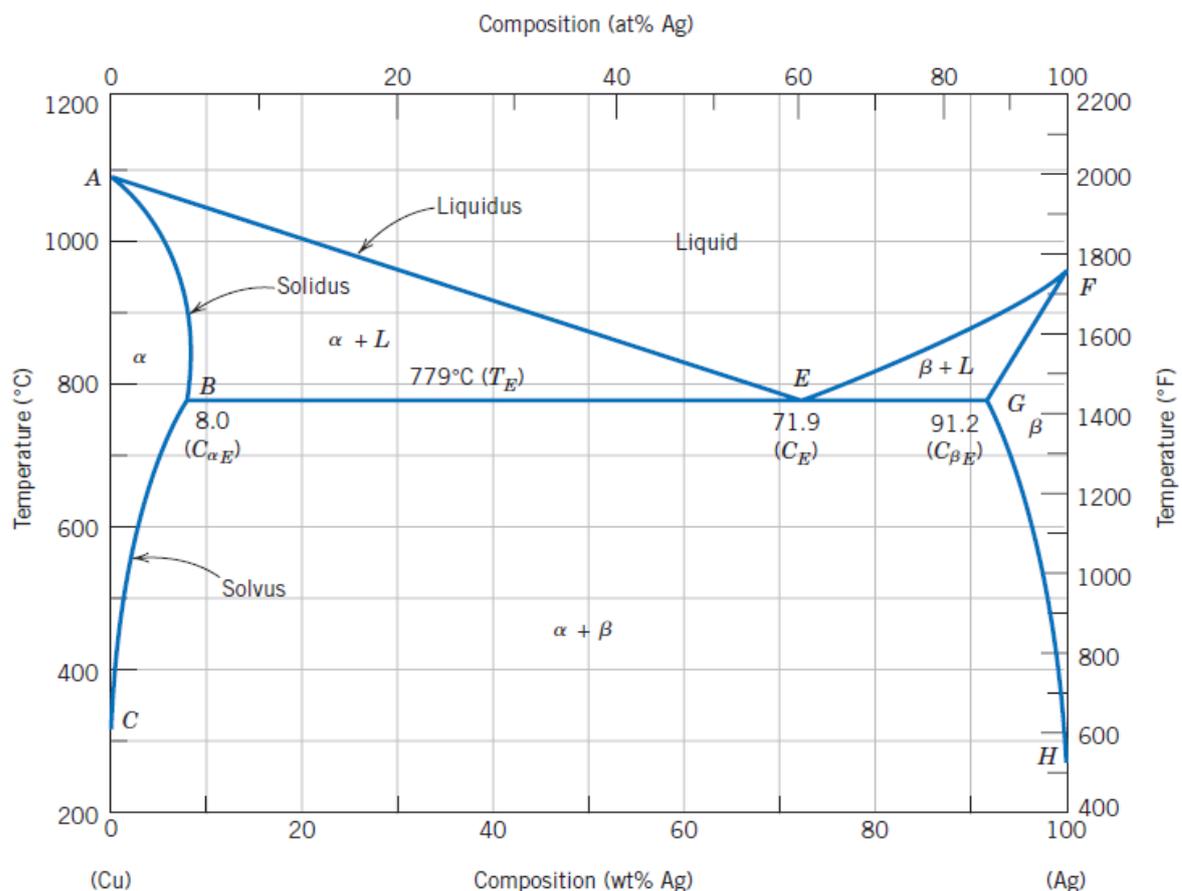

Figure 6.6 The copper–silver phase diagram.

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Thus, the solubility in each of these solid phases is limited, in that at any temperature below line *BEG* only a limited concentration of silver will dissolve in copper (for the α phase), and similarly for copper in silver (for the β phase). The solubility limit for the α phase corresponds to the boundary line, labeled *CBA*, between the $\alpha/(\alpha + \beta)$ and $\alpha/(\alpha + L)$ phase regions; it increases with temperature to a maximum [8.0 wt% Ag at 779 $^{\circ}$C(1434 $^{\circ}$F)] at point *B*, and decreases back to zero at the melting temperature of pure copper, point *A* [1085 $^{\circ}$C(1985 $^{\circ}$F)]. At temperatures below 779 $^{\circ}$C(1434 $^{\circ}$F), the solid solubility limit line separating the α and $\alpha + \beta$ phase regions is termed a **solvus line;** the boundary *AB* between the α and $\alpha + L$ fields is the **solidus line,** as indicated in Figure 6.6. For the β phase, both solvus and solidus lines also exist, *HG* and *GF*, respectively, as shown. The maximum solubility of copper in the β phase, point *G* (8.8 wt% Cu), also occurs at 779 $^{\circ}$C(1434 $^{\circ}$F). This horizontal line *BEG*, which is parallel to the composition axis and extends between these maximum solubility positions, may also be considered a solidus line; it represents the lowest temperature at which a liquid phase may exist for any copper–silver alloy that is at equilibrium.

There are also three two-phase regions found for the copper–silver system (Figure 6.6): $\alpha + L$, $\beta + L$ and $\alpha + \beta$. The α and β phase solid solutions coexist for all compositions and temperatures within the $\alpha + \beta$ phase field; the α + liquid and β + liquid phases also coexist in their respective phase regions. Furthermore, compositions and relative amounts for the phases may be determined using tie lines and the lever rule as outlined previously.
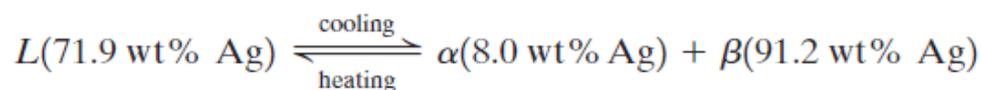
As silver is added to copper, the temperature at which the alloys become totally liquid decreases along the **liquidus line,** line *AE*; thus, the melting temperature of copper is lowered by silver additions. The same

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

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

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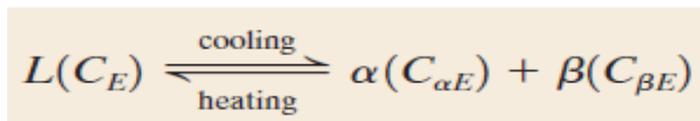
Or, upon cooling, a liquid phase is transformed into the two solid α and β phases at the temperature T_E, the opposite reaction occurs upon heating. This is called a **eutectic reaction** (eutectic means easily melted), and C_E and T_E represent the eutectic composition and temperature, respectively;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

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

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

On occasion, low-melting-temperature alloys are prepared having near-eutectic compositions. A familiar example is the 60–40 solder, containing 60 wt% Sn and 40 wt% Pb. Figure 6.7 indicates that an alloy of this composition is completely molten at about 185 $^{\circ}$C (365 $^{\circ}$F), which

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makes this material especially attractive as a low-temperature solder, since it is easily melted.
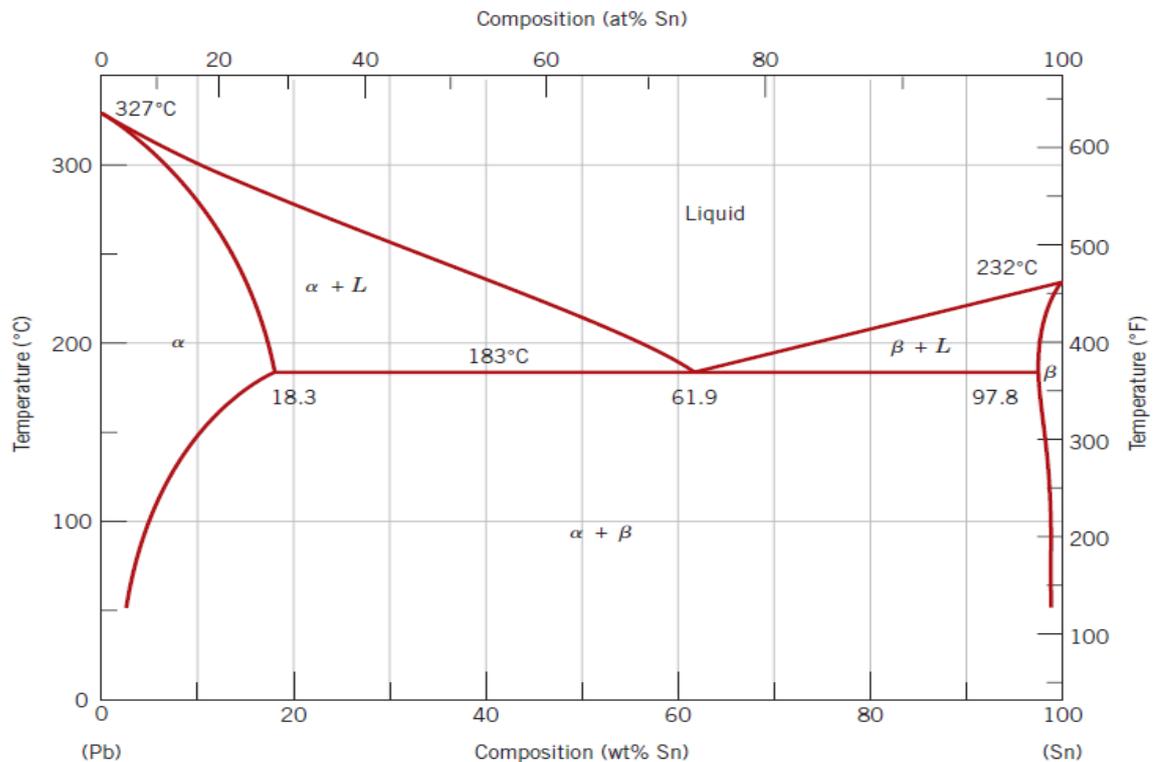

Figure 6.7 The lead–tin phase diagram.

Example2:

Determination of Phases Present and Computation of Phase Compositions

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

Solution

(a) Locate this temperature–composition point on the phase diagram (point B in Figure 6.9). Inasmuch as it is within the $\alpha + \beta$ region, both α and β phases will coexist.

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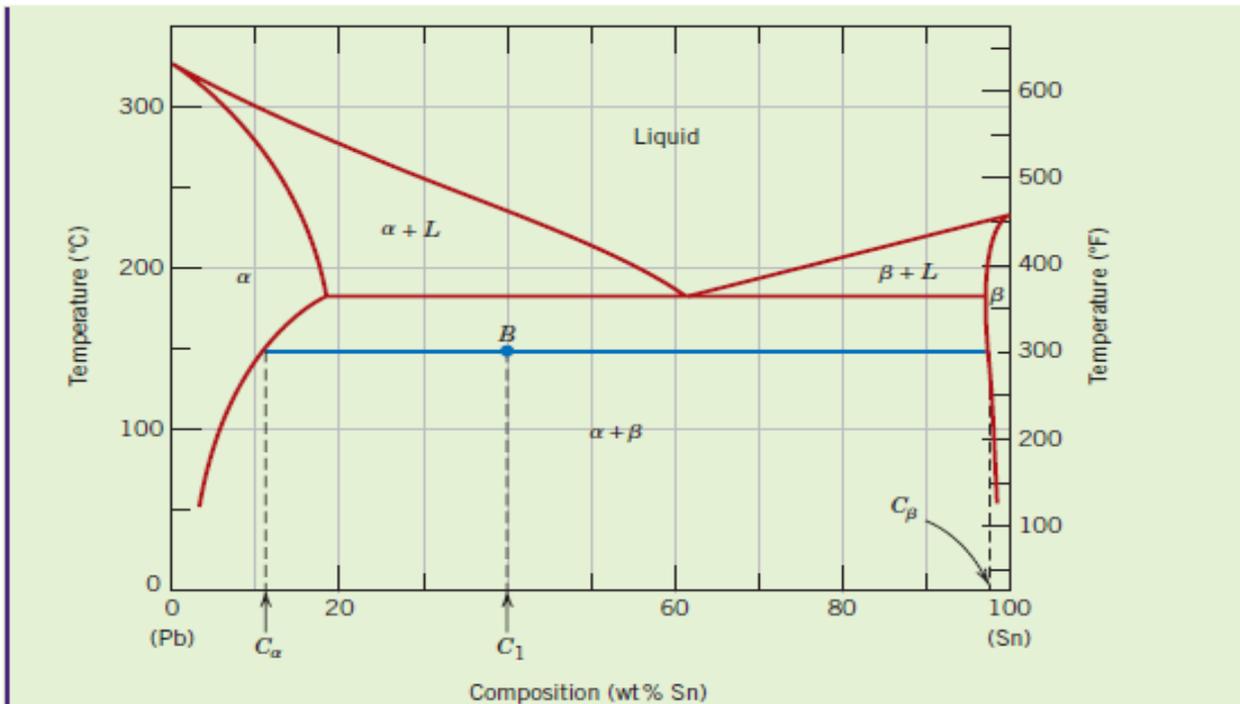*Dept. Of physic*　　　　　*MATERIALS SCIENCE*　　　　*Chapter (6)*

Figure 9.9　The lead–tin phase diagram. For a 40 wt% Sn–60 wt% Pb alloy at 150°C (point *B*), phase compositions and relative amounts are computed in Example Problems 9.2 and 9.3.

(b) Since two phases are present, it becomes necessary to construct a tie line across the $\alpha + \beta$ phase field at 150°C, as indicated in Figure 9.9. The composition of the α phase corresponds to the tie line intersection with the $\alpha/(\alpha + \beta)$ solvus phase boundary—about 10 wt% Sn–90 wt% Pb, denoted as C_α. Similarly for the β phase, which will have a composition of approximately 98 wt% Sn–2 wt% Pb (C_β).

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Example 3:

Relative Phase Amount Determinations—Mass and Volume Fractions

For the lead–tin alloy in Example Problem .2, calculate the relative amount of each phase present in terms of (a) mass fraction and (b) volume fraction. At 150°C take the densities of Pb and Sn to be 11.23 and 7.24 g/cm³, respectively.

Solution

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

$$W_\alpha = \frac{C_\beta - C_1}{C_\beta - C_\alpha} = \frac{98 - 40}{98 - 10} = 0.66$$

$$W_\beta = \frac{C_1 - C_\alpha}{C_\beta - C_\alpha} = \frac{40 - 10}{98 - 10} = 0.34$$

(b) To compute volume fractions it is first necessary to determine the density of each phase using Equation 4.10a. Thus

$$\rho_\alpha = \frac{100}{\dfrac{C_{Sn(\alpha)}}{\rho_{Sn}} + \dfrac{C_{Pb(\alpha)}}{\rho_{Pb}}}$$

where $C_{Sn(\alpha)}$ and $C_{Pb(\alpha)}$ denote the concentrations in weight percent of tin and lead, respectively, in the α phase. From Example Problem 9.2, these values are 10 wt% and 90 wt%. Incorporation of these values along with the densities of the two components lead to

$$\rho_\alpha = \frac{100}{\dfrac{10}{7.24 \text{ g/cm}^3} + \dfrac{90}{11.23 \text{ g/cm}^3}} = 10.64 \text{ g/cm}^3$$

Similarly for the β phase:

$$\rho_\beta = \frac{100}{\dfrac{C_{Sn(\beta)}}{\rho_{Sn}} + \dfrac{C_{Pb(\beta)}}{\rho_{Pb}}}$$

$$= \frac{100}{\dfrac{98}{7.24 \text{ g/cm}^3} + \dfrac{2}{11.23 \text{ g/cm}^3}} = 7.29 \text{ g/cm}^3$$

Now it becomes necessary to employ Equations 9.6a and 9.6b to determine V_α and V_β as

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

$$= \frac{\dfrac{0.66}{10.64 \text{ g/cm}^3}}{\dfrac{0.66}{10.64 \text{ g/cm}^3} + \dfrac{0.34}{7.29 \text{ g/cm}^3}} = 0.57$$

$$V_\beta = \frac{\dfrac{W_\beta}{\rho_\beta}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

$$= \frac{\dfrac{0.34}{7.29 \text{ g/cm}^3}}{\dfrac{0.66}{10.64 \text{ g/cm}^3} + \dfrac{0.34}{7.29 \text{ g/cm}^3}} = 0.43$$

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Example **4:**

From the phase diagram for the NiO-MgO binary system [Figure 6-8], describe a composition that can melt at 2600°C but will not melt when placed into service at 2300°C.
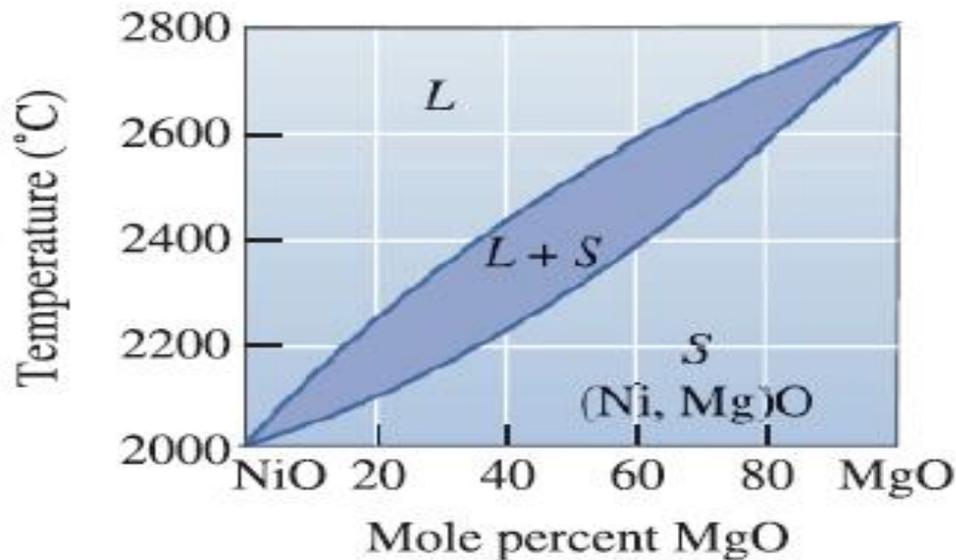

Figure 6-8 The equilibrium phase diagrams for the Cu-Ni and NiO-MgO systems.

Solution:

The material must have a liquidus temperature below 2600°C, but a solidus temperature above 2300°C. The NiO-MgO phase diagram [Figure 6-8] 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 **5:**

Determine the degrees of freedom in a Cu-40% Ni alloy at (a) 1300°C, (b) 1250°C, and (c) 1200°C. Use Figure 6-9.

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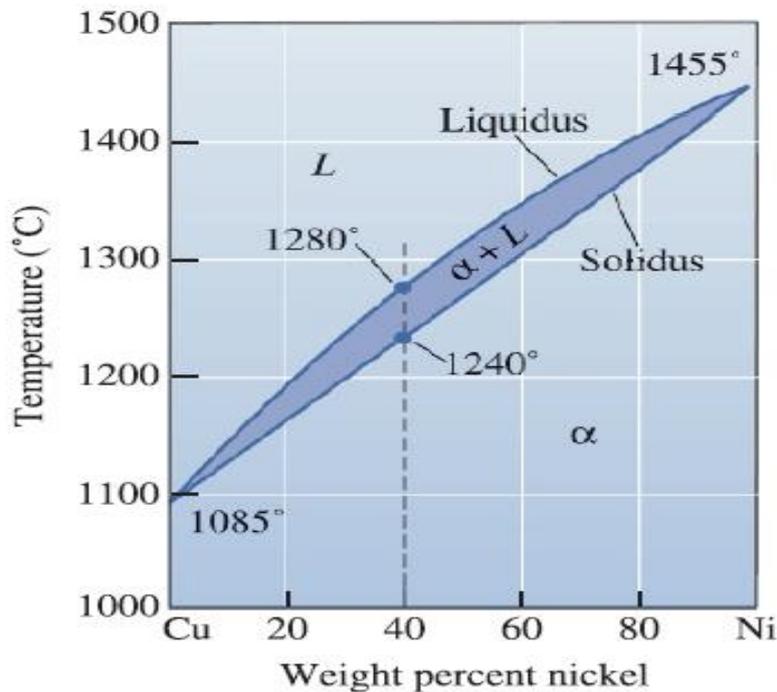*Dept. Of physic*   *MATERIALS SCIENCE*   *Chapter (6)*

Figure 6-9 The equilibrium phase diagrams for the Cu-Ni
and NiO-MgO systems.

Solution:

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

$1+C = F+P$ OR $1+2 = F+1$ 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,

$1+C = F+P$ OR $1+2 = F+2$ 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,

$1+C = F+P$ OR $1+2 = F+1$ OR $F=2$

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

Example 6:

Determine the composition of each phase in a Cu-40% Ni alloy at 1300°C, 1270°C, 1250°C, and 1200°C. (See Figure 6-10)
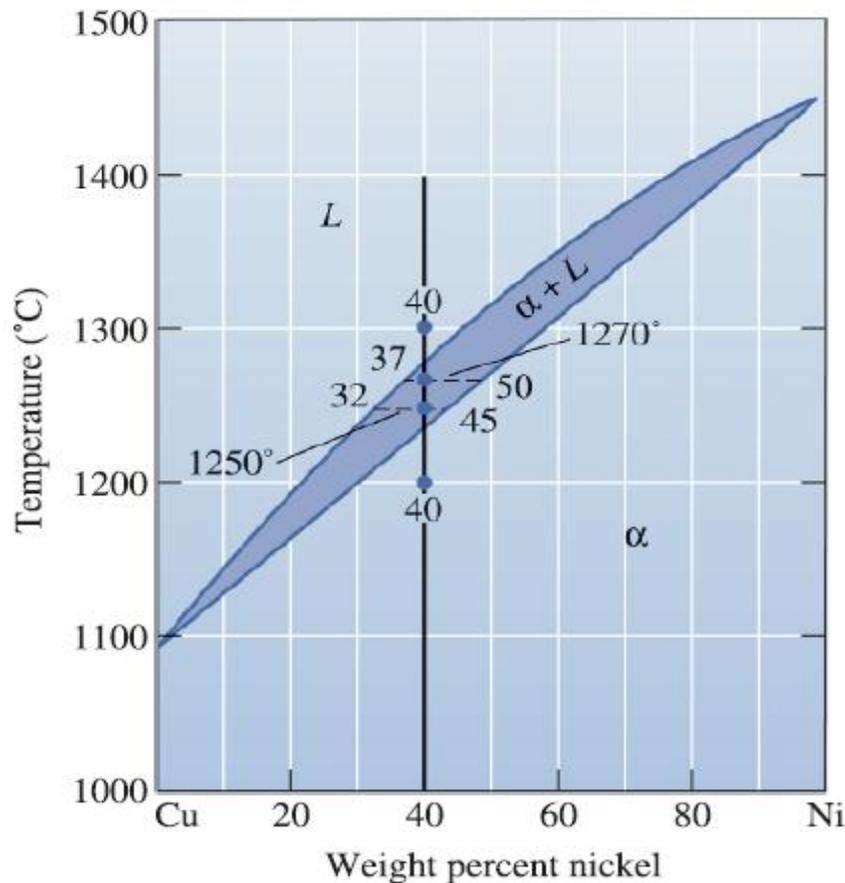

Figure 6-10 Tie lines and phase compositions for
a Cu-40% Ni alloy at several temperatures

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 *a+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 _ region, is at 50% Ni. Therefore, the liquid contains 37% Ni, and the solid contains 50% Ni.

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- **1250°C**: Again two phases are present. The tie line drawn at this temperature show that the liquid contains 32% Ni, and the solid contains 45% Ni.
- **1200°C**: Only solid *a* is present, so the solid must contain 40% Ni.

In Example 6, we find that, in the two-phase region, solid *a* 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.

Example 7:
Determine the amount of each phase in the Cu-40% Ni alloy shown in Figure 6-10 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.