KMU 496
MATERIALS SCIENCE AND TECHNOLOGY III

CHAPTER 10
SOLID SOLUTIONS AND PHASE DIAGRAMS

Dr. Damla ÇETİN ALTINDAL

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Outline

❑ Phases and the Phase Diagram
❑ Solubility and Solid Solutions
❑ Conditions for Unlimited Solid Solubility
❑ Solid-Solution Strengthening
❑ Isomorphous Phase Diagrams
❑ Relationship Between Properties and the Phase Diagram
❑ Solidification of a Solid-Solution Alloy
❑ Nonequilibrium Solidification and Segregation

Main objectives of this chapter are to explore

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

Section 10.1- Phases and The Phase Diagram

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 circuits.

➢ 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.

There are two types of alloys:

➢ **single-phase alloys** and **multiple-phase alloys**.

➢ In this chapter, we will examine the behaviors of single-phase alloys.

➢ A plain carbon steel is an alloy of iron and carbon.
➢ Corrosion-resistant stainless steels are alloys that usually contain iron, carbon, chromium, nickel and some other elements.
➢ There are alloys based on aluminum, copper, cobalt, nickel, titanium, zinc and zirconium.

Phases and The Phase Diagram

Phase - Any portion of a system which is physically homogeneous within it and bounded by a surface so that it is mechanically separable from any other portions.

Phases and The Phase Diagram

➤ *A phase has the following characteristics:*

- the same structure or atomic arrangement
- the same composition and properties
- a definite interface between the phase and surrounding

➤ Water has three phases:
- Liquid water
- Solid ice
- Steam

Phases and The Phase Diagram

➤ Phases do not always have to be solid, liquid, and gaseous forms of a material.

– 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.

– Carbon can exist in many forms (e.g., graphite or diamond).

Phases and The Phase Diagram

➤ **Gibbs phase rule:**

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.).

$$2 + C = F + P$$

- C: the number of chemically independent components, usually elements or compounds, in the system
- F: the number of degrees of freedom, or the number of variables
- P: the number of phases

Phases and The Phase Diagram

- P-T diagram: A diagram describing thermodynamic stability of phases under different temperature and pressure conditions.
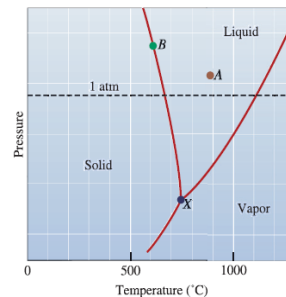
Figure 10-2
Schematic unary phase diagram for magnesium, showing the melting and boiling temperatures at one atmosphere pressure. On this diagram, point X is the triple point.

Point A

$2 + C = F + P$

$2 + 1 = F + 1$

$F = 2$

2 degrees of freedom

3

Example 10.1
Design of an Aerospace Component

Because magnesium (Mg) is a low-density material (ρ_{Mg} = 1.738 g/cm³), it has been suggested for use in an aerospace vehicle intended to enter the outer space environment. Is this a good design?
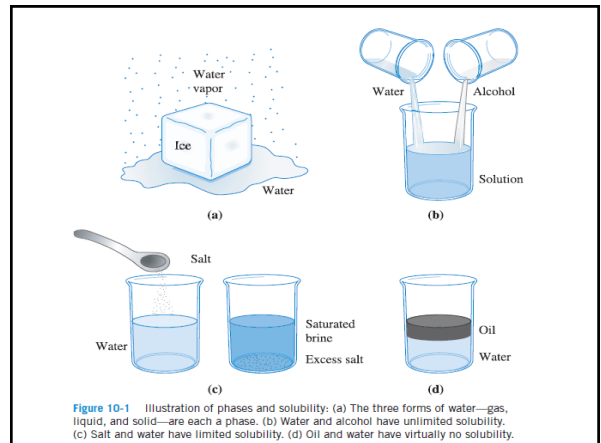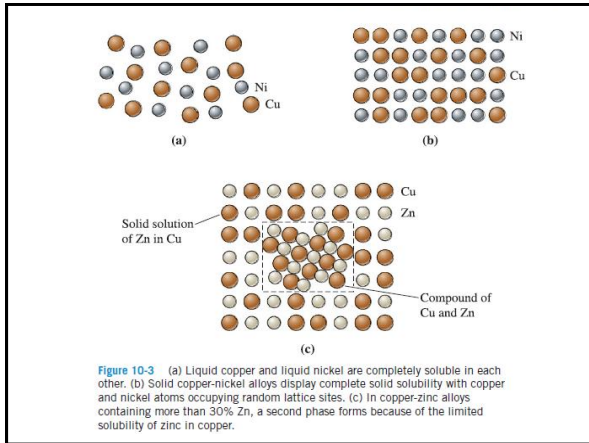
Example 10.1 SOLUTION

- In space the pressure is very low. Even at relatively low temperatures, solid magnesium can begin to change to a vapor, causing metal loss that could damage a space vehicle.

- A low-density material with a higher boiling point (and, therefore, lower vapor pressure at any given temperature) might be a better choice.

- Other factors to consider: In load-bearing applications, we should not only look for density but also for relative strength. Therefore, the ratio of Young's modulus to density or yield strength to density could be a better parameter to compare different materials.

Solubility and Solid Solutions

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

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

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

Section 10.2- Solubility and Solid Solutions

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.

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.

Polymeric Systems

➢ We can process polymeric materials to enhance their usefulness, which is similar to the formation of solid solutions in *metallic* and *ceramic systems*.

➢ We can form materials that are known as **copolymers** that consist of different monomers.

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

Polymeric Systems
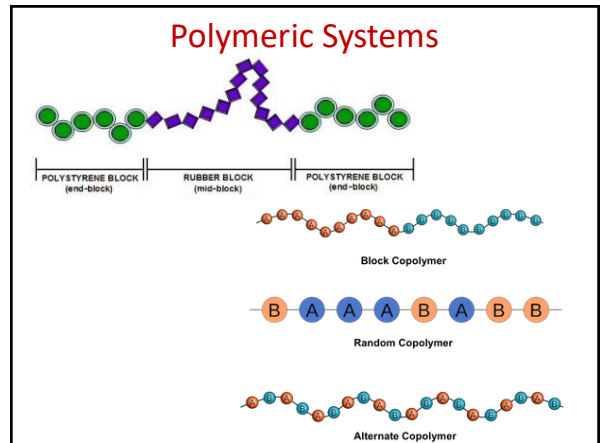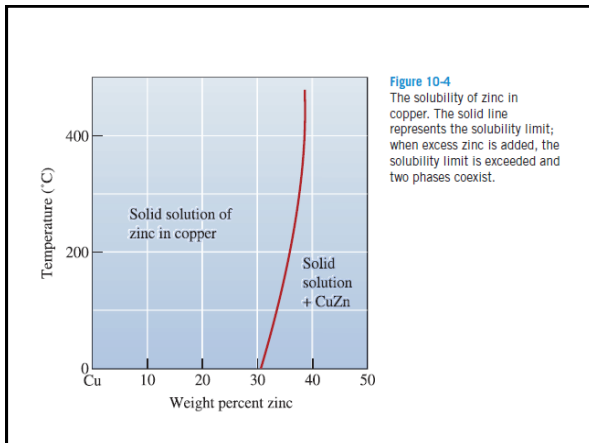
> For example, acrylonitrile (A), butadiene (B), and styrene (S) monomers can form a copolymer known as ABS.

> This copolymer is similar to a solid solution in that it has the functionalities of the three monomers from which it is derived, blending their properties.
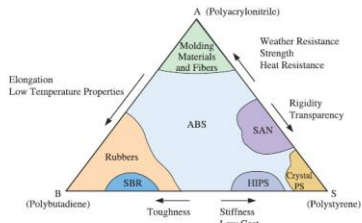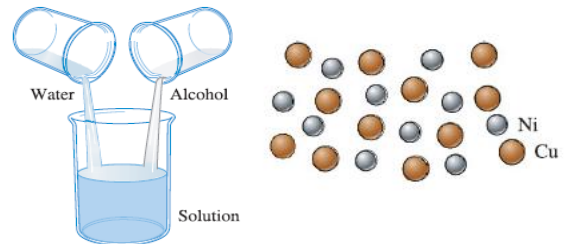

Figure 10-5   Diagram showing how the properties of copolymers formed in the ABS system vary. This is not a phase diagram. (From STRONG, A. BRENT, PLASTICS: MATERIALS AND PROCESSING, 2nd, ©2000. Electronically reproduced by permission of Pearson Education, Inc., Upper Saddle River, New Jersey.)

Conditions for Unlimited Solid Solubility

Section 10.3- Conditions for Unlimited Solid Solubility
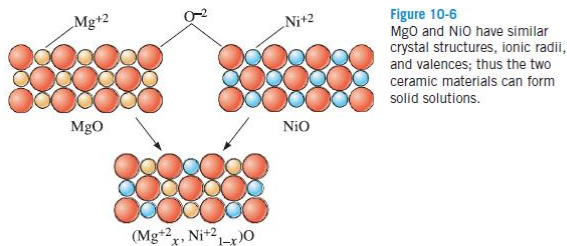

Conditions for Unlimited Solid Solubility

> 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:
> - *Size factor*
> - *Crystal structure*
> - *Valence*
> - *Electronegativity*

Conditions for Unlimited Solid Solubility

o *Size Factor*: The atoms or ions must be of similar size, with no more than a 15% difference in atomic radius.
o *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.
o *Valence*: The ions must have the same valence; otherwise, the valence electron difference encourages the formation of compounds rather than solutions.
o *Electronegativity*: The atoms must have approximately the same electronegativity.

Section 10.4- Solid Solution Strengthening

Conditions for Unlimited Solid Solubility

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

Solid-Solution Strengthening

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

❖Jewelry could be made out from pure gold or silver; however, pure gold and pure silver are extremely soft.

❖Jewelers add copper to gold and silver so that the jewelry will retain its shape.

Solid-Solution Strengthening

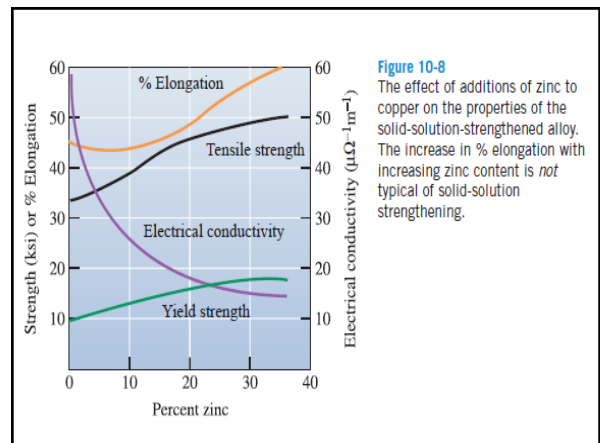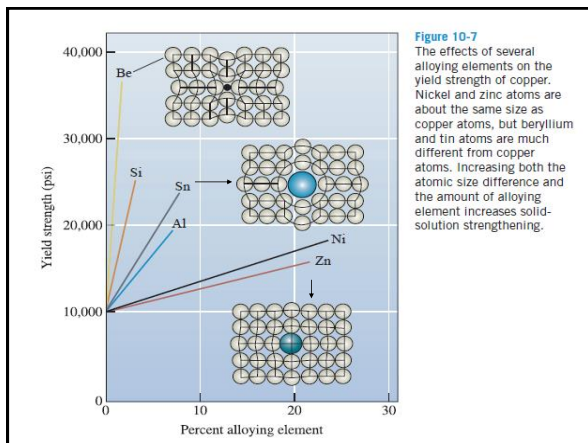- *Degree of solid-solution strengthening*

  Depends on two factors:

  – 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.

  – the greater the amount of alloying element added, the greater the strengthening effect.

Effect of Solid-Solution Strengthening on Properties

1. The yield strength, tensile strength, and hardness of the alloy are greater than those of the pure metals.

**2.** Almost always, the ductility of the alloy is less than that of the pure metal.

  NOTE: 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. Therefore, solid-solution strengthening of copper or aluminum wires for transmission of electrical power is not recommended.

4. The resistance to creep and strength at elevated temperatures is improved by solid solution strengthening.

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.

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.

Section 10.5 - Isomorphous Phase Diagrams

Isomorphous Phase Diagrams
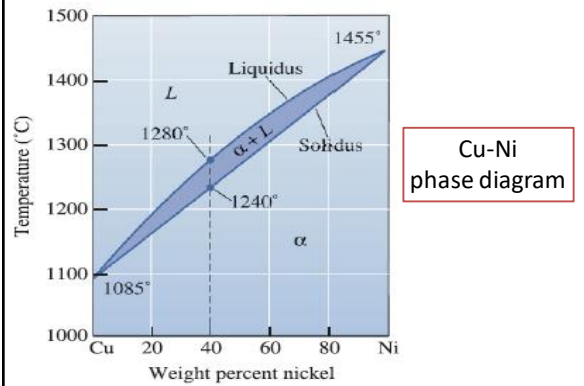
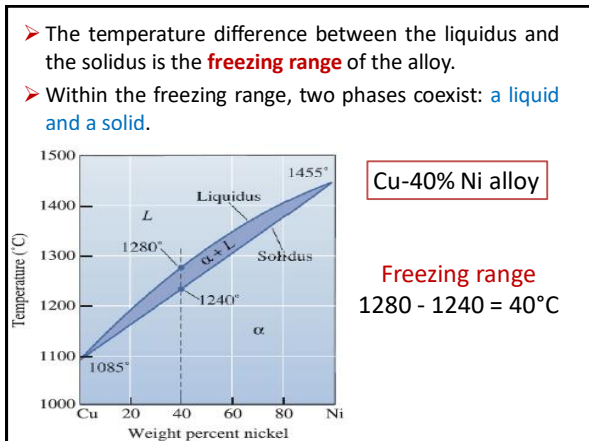Cu-Ni phase diagram

Isomorphous Phase Diagrams

❑ Phase diagram: A phase diagram shows the phases and their compositions at any combination of temperature and alloy composition.

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

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

❑ Ternary phase diagram: A phase diagram for a system with three components.

Isomorphous Phase Diagrams

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

☐ The liquidus temperature is defined as the temperature above which a material is *completely liquid*.

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

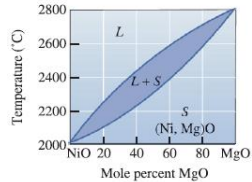☐ The solidus temperature is the temperature below which the alloy is *completely solid*.

Cu-40% Ni alloy

Liquidus temperature
1280°C

Solidus temperature
1240°C
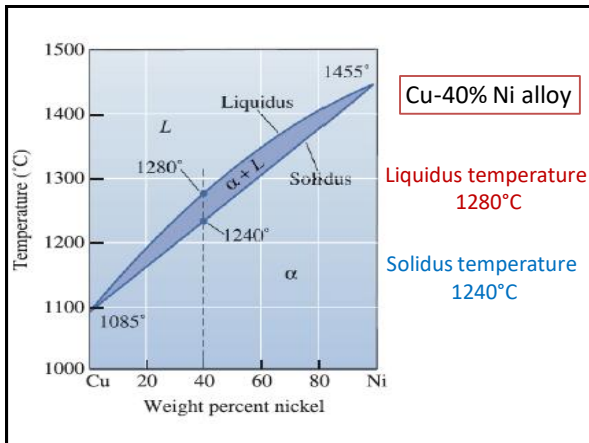
Pure metals solidify at a **fixed temperature**
(i.e., the freezing range is zero degrees).

➤ 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.

Cu-40% Ni alloy

Freezing range
1280 - 1240 = 40°C

✓ 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 an alloy component, we must be sure that no liquid forms during the process.

Example 10-4 NiO-MgO Isomorphous System

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

Mole percent MgO

SOLUTION

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

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

➤ We keep the pressure fixed at one atmosphere, which is normal for binary phase diagrams. The phase rule can be rewritten as:

$$1 + C = F + P \quad \textit{(for constant pressure)}$$

C is the number of independent chemical components,
P is the number of phases (*not pressure*),
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.

Compositions 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, the composition of the phase equals the overall composition of the material.

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).

Weight percent nickel

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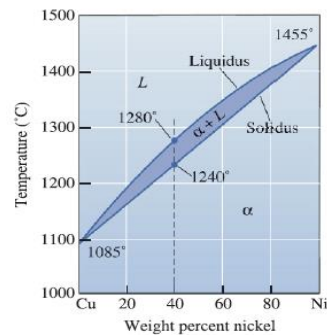
SOLUTION

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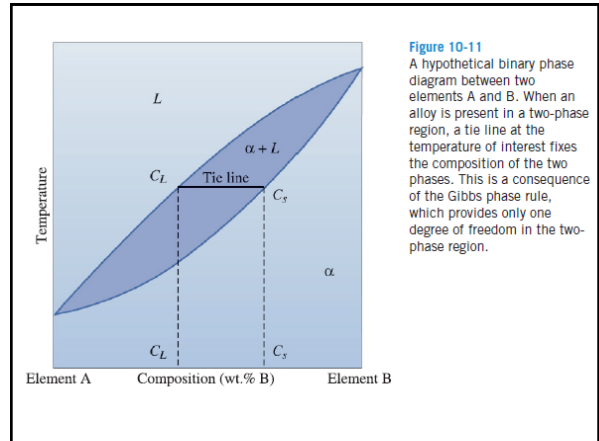
$$1 + C = F + P \quad \therefore 1 + 2 = F + 2 \text{ or } F = 1$$

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.

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.

➢ 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.

➢ 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.

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).
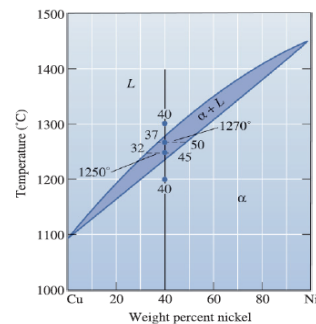
SOLUTION

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.

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.
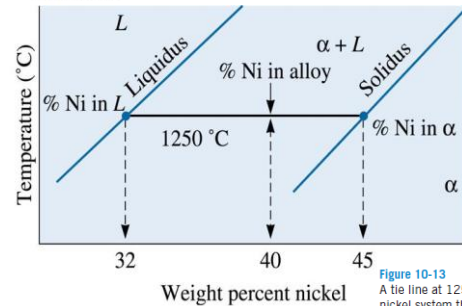

Figure 10-13
A tie line at 1250°C in the copper-nickel system that is used in Example 10-8 to find the amount of each phase.

Amount of Each Phase (the Lever Rule)

- We are interested in the *relative amounts of each phase* present in the alloy.

- These amounts are generally expressed as weight percent (wt %).

- We express absolute amounts of different phases in units of mass or weight (grams, kilograms, pounds, etc.).

Example 10.8 SOLUTION

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

Total mass of nickel in 100 grams of the alloy = mass of nickel in liquid + mass of nickel in α.

So,

$100 \times$ (% Ni in alloy) = [(100)(1 – x)](% Ni in L) + (100)[x](% Ni in α)

x = (40-32)/(45-32) = 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 Ni in α phase (at 1250°C) is 45% and concentration of nickel in liquid phase (at 1250°C) is 32%.

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> The lever rule in general can be written as;

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

> 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:

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

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

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.