MATEIALS SCIENCE

PHASE DIAGRAMS

1) Introduction

A phase diagram is a plot showing the phases of a substance at various temperatures and pressures. Usually pressure vs. temperature or temperature vs. composition graph is plotted

We study phase diagrams because it relates the development of microstructure of a substance. In addition, phase diagrams provide valuable information about melting, casting, crystallization and other phenomena.

2) Definitions

Components: components are pure metals and/or compounds of which an alloy is composed. E.g. copper zinc brass has components copper (Cu) and zinc (Zn).

Solvent: the element or compound that is present in the greatest amount

*Solute*: an element or compound present in minor concentration

System: (1) a specific body under consideration or (2) it relates to the series of possible alloys consisting of the same components e.g. iron-carbon system.

3) 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, this is the **solubility limit**.

Adding more solute atoms than the solubility limit results in the formation of another solid solution or compound that has different composition.

Example: Solubility of sugar in water:
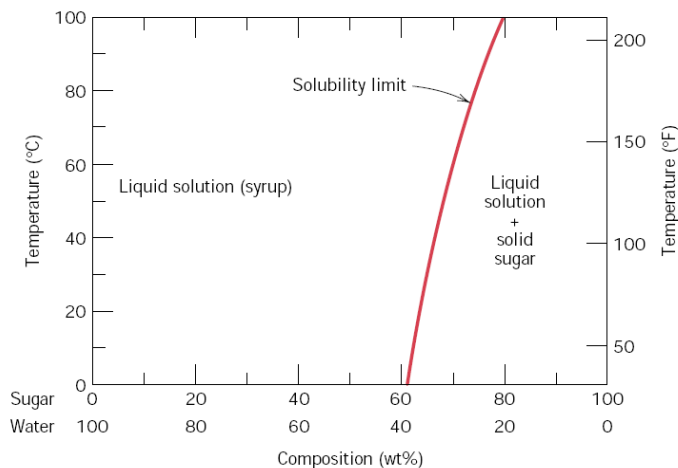
FIGURE **10.1** The solubility of sugar ($C_{12}H_{22}O_{11}$) in a sugar–water syrup.

Solubility limit is temperature dependent as show in Figure 10.1 above.

4) Phase

A **phase** may be defined as a homogenous portion of a system that has uniform physical and chemical characteristics.

A substance usually has a few phases and each phase may have its own physical and chemical properties but not necessarily both.

Two phases can exist together but separated by a boundary.

A single phase system is termed **homogenous**. A system having two or more phases is termed '**mixture**' or **heterogeneous**.

5) Phase Equilibria

A system having more than one phase is said to be in **phase equilibrium** when the phase characteristic is not changing with time.

For **metastability**, the system is not at equilibrium, and there are very slight (and often imperceptible) changes of the phase characteristics with time.

6) One-Component (Or Unary) Phase Diagrams

The simplest and easiest type of phase diagram to understand is that of a one component system, in which the composition is held constant (pure substance). In this case the temperature and pressure are the variables.

A one-component phase diagram (sometimes called unary diagram or pressure-temperature diagram) is a two dimensional plot of pressure (vertical axis) and temperature (horizontal axis)

Example: H_2O phase diagram.

7) Binary Phase Diagrams

A binary phase-diagram is a two dimensional plot of temperature (vertical axis) and composition (horizontal axis), and pressure is held constant – normally at 1 atm.

We will consider binary alloys – alloys that contain two components.

8) Binary Isomorphous Systems

The easiest type of binary phase diagram to understand and interpret is the copper-nickel system (Figure 10.2). Temperature is plotted along the vertical axis and the horizontal axis represents the composition of the alloy, in weight percent (bottom) and atom percent (top) of nickel. The composition ranges form 0 wt% Ni (100 wt% Cu) on the extreme left to 100 wt% Ni (0 wt% Cu) on the right.

Three different phase regions appear on the diagram:

    (i)   alpha (α) region

    (ii)   liquid (L) region

    (iii)   two-phase ($\alpha + L$) region

FIGURE **10.2** (*a*) The copper–nickel phase diagram. (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.) (*b*) A portion of the copper–nickel phase diagram for which compositions and phase amounts are determined at point *B*.

(b)
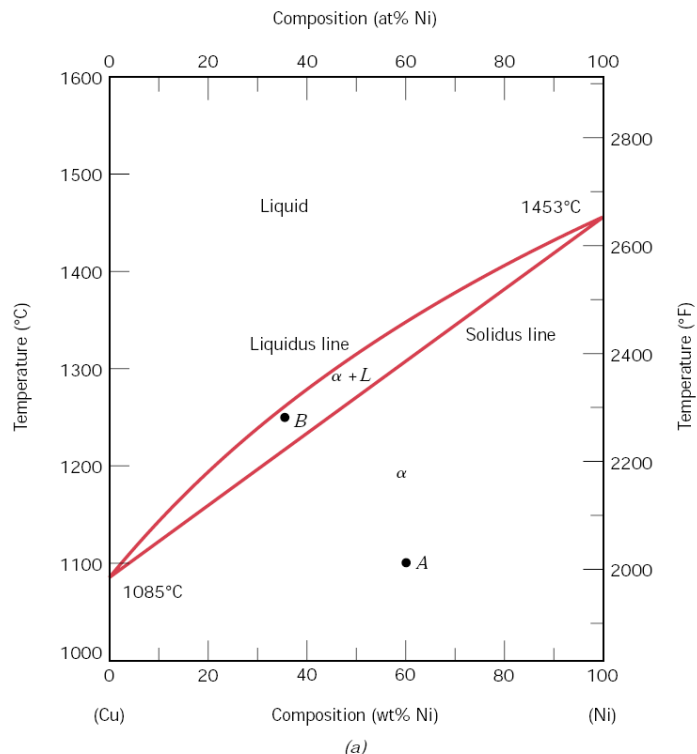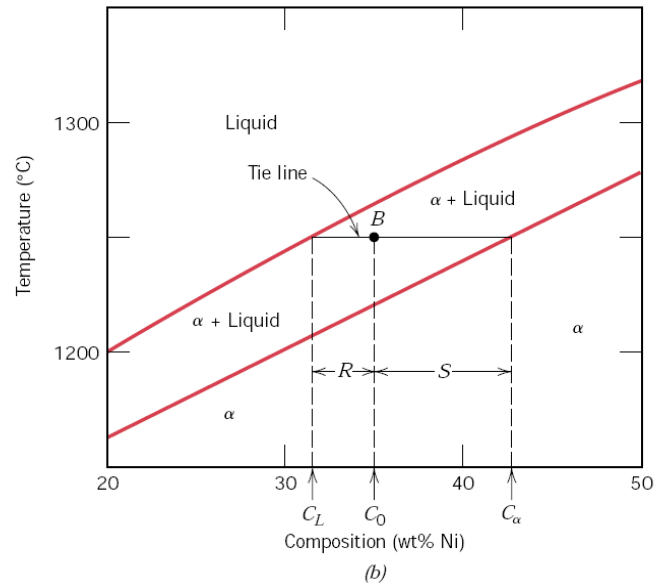
9)   Interpretation of Phase Diagrams

For a binary system, if the composition and temperature is known, we can deduce three information from the phase diagram:

(i)	Phases that are present
(ii)	The composition of these phases and,
(iii)	The percentages or fractions of the phases.

Phases Present

For example, an alloy of composition 60 wt% Ni – 40 wt% Cu at 1100 ºC is at point A in Figure 9.3a. Only one phase is present at point A, that is the α phase.

What about a 35 wt% Ni – 65 wt% Cu alloy at 1250 ºC?

Determination of Phase Compositions

If only one phase is present, the procedure is trivial.

To compute the equilibrium concentrations of the two phases, the following procedure is used:

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

Determination of Phase Amounts

The solution is obvious in the single-phase region, the phase fraction is 1.0 or, alternatively, the percentage is 100%.

If the solution is in the two phase region, things are more complex and the lever rule must be applied as follows:

(i)	The tie line is constructed across the two-phase region at the temperature of the alloy.
(ii)	The overall alloy composition is located on the tie line.

(iii) 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.

(iv) The fraction of the other phase is determined in the same manner.

(v) 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.

## 10) Development of Microstructure in Isomorphous Alloys

Equilibrium Cooling

FIGURE 10.3   Schematic representation of the development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy.
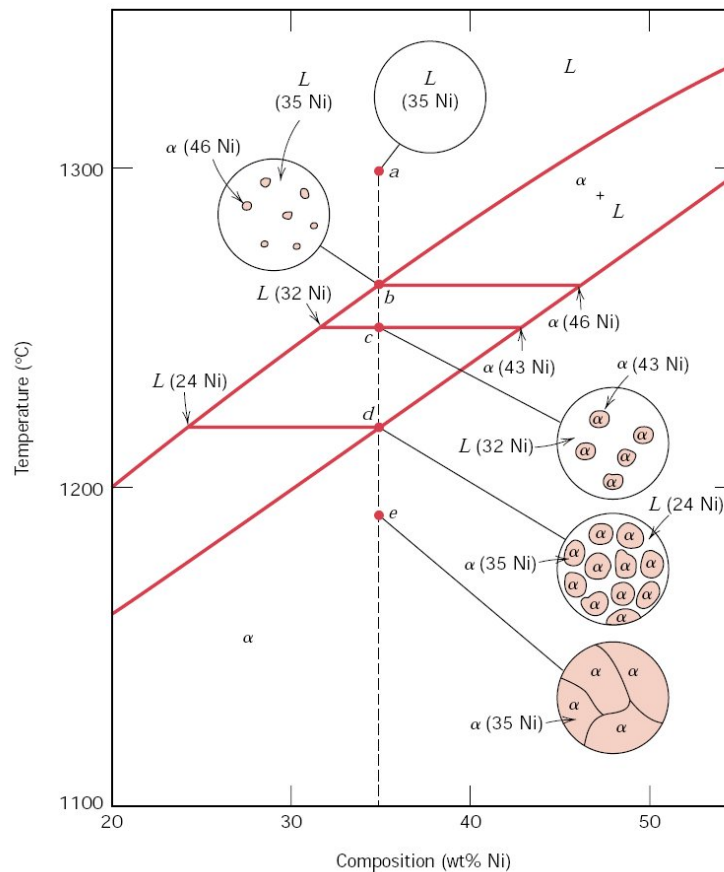
(a) Binary Eutectic Systems

Another type of common and relatively simple phase diagram found for binary alloys is shown in Figure 10.6 for the copper-silver system.
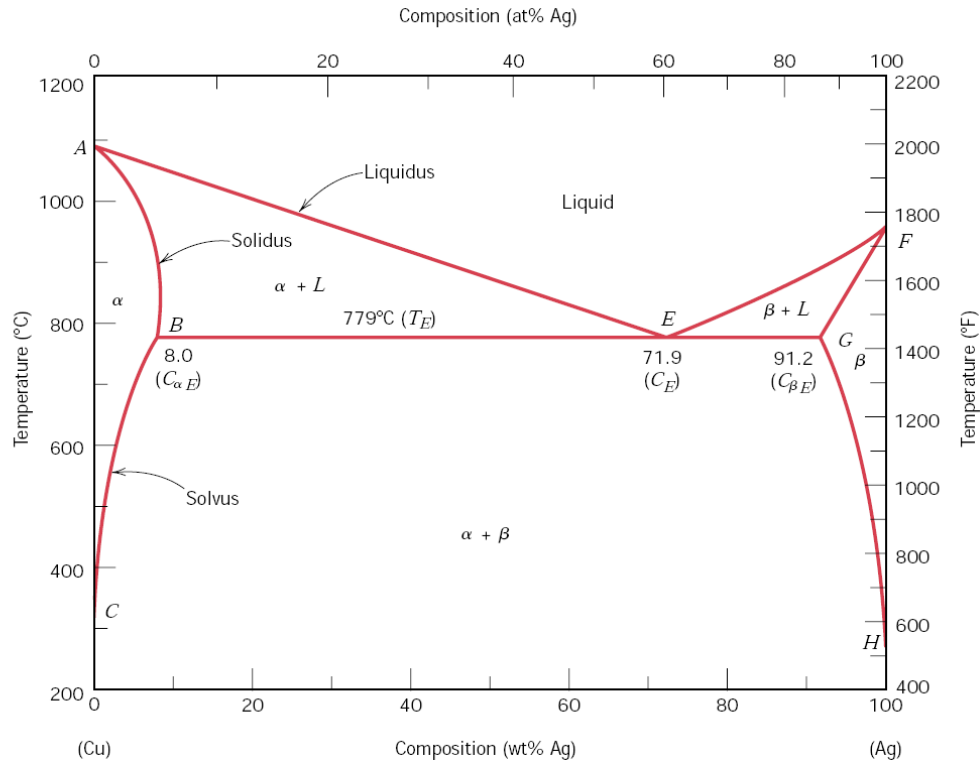

FIGURE 10.6 The copper–silver phase diagram. (Adapted from *Binary Alloy Phase Diagrams,* 2nd edition, Vol. 1, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)

- Three single phase regions (α - solid solution of Ag in Cu matrix, β = solid solution of Cu in Ag marix, L - liquid).

- Three two-phase regions ($\alpha + L$, β +L, α +β)

- **Solvus** line separates one solid solution from a mixture of solid solutions. The **Solvus line shows limit of solubility**

- **Eutectic or invariant point - Liquid and two solid phases co-exist in equilibrium at the eutectic composition CE and the eutectic temperature TE.**

- **Eutectic isotherm - the horizontal solidus line at TE.**

- **Eutectic reaction** – transition between liquid and mixture of two solid phases, α + β at eutectic concentration CE.

- The melting point of the eutectic alloy is lower than that of the components (*eutectic = easy to melt in Greek*).

At most two phases can be in equilibrium within a phase field.
Single-phase regions are separated by 2-phase regions.

## Binary Eutectic Systems (IV)

Compositions and relative amounts of phases are determined from the same tie lines and lever rule, as for isomorphous alloys
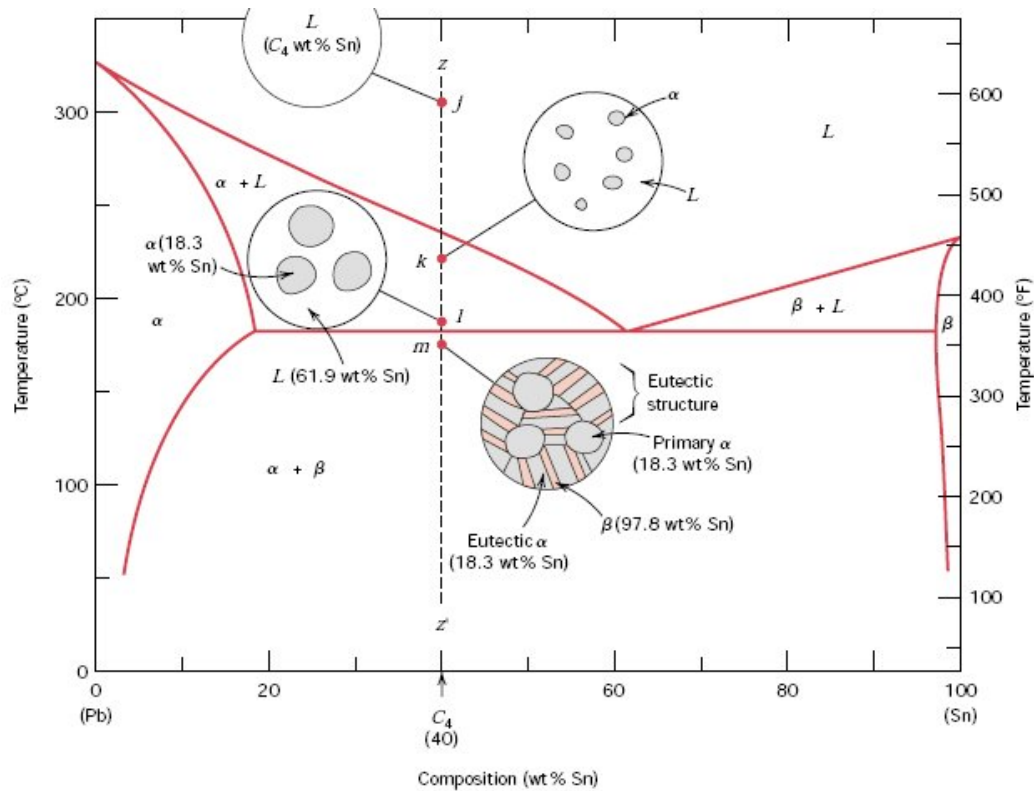
FIGURE 10.14 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_4 as it is cooled from the liquid-phase region.
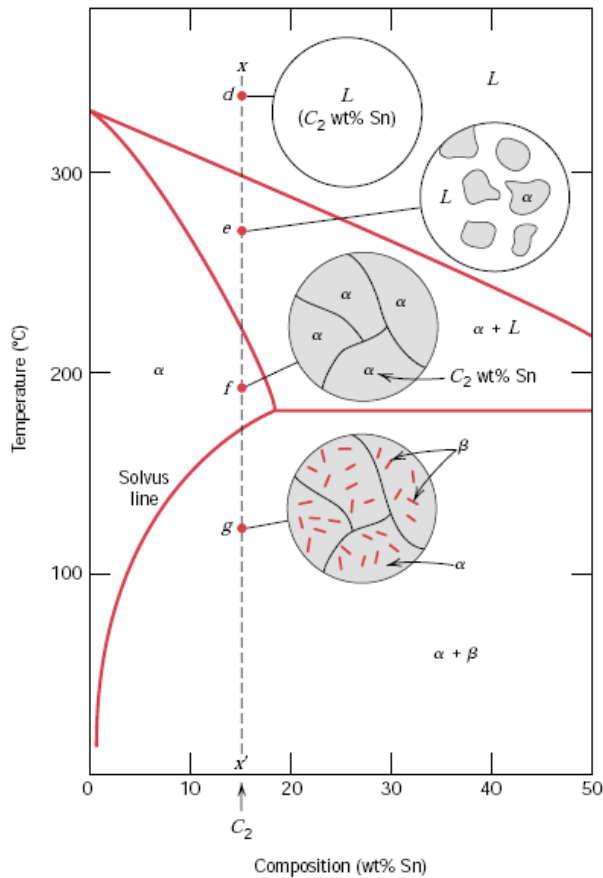
Development of Microstructure In Eutectic Alloys

Case 1:
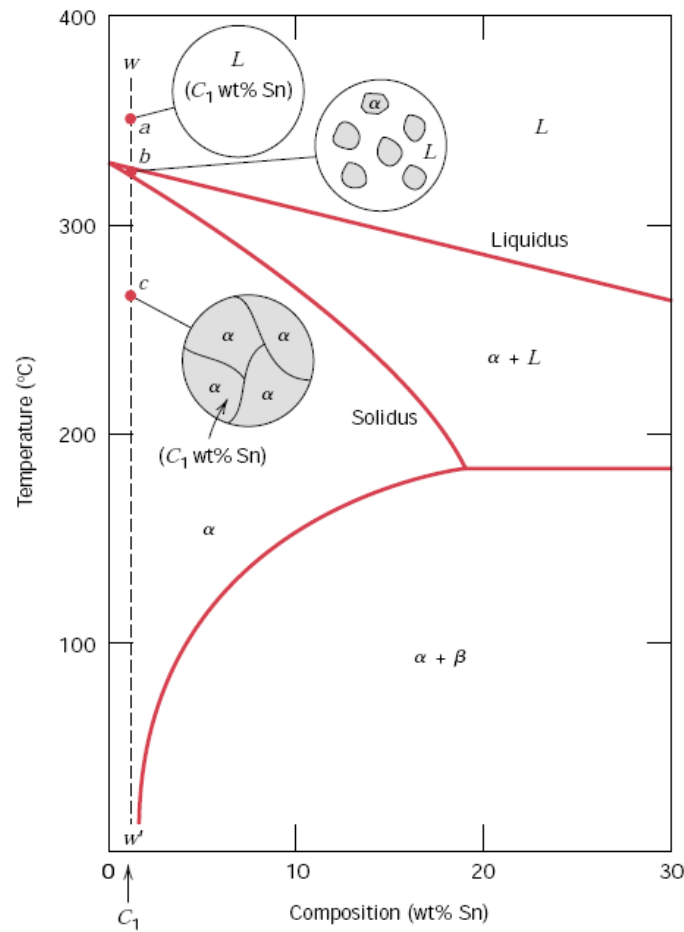
FIGURE 10.9 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_1 as it is cooled from the liquid-phase region.
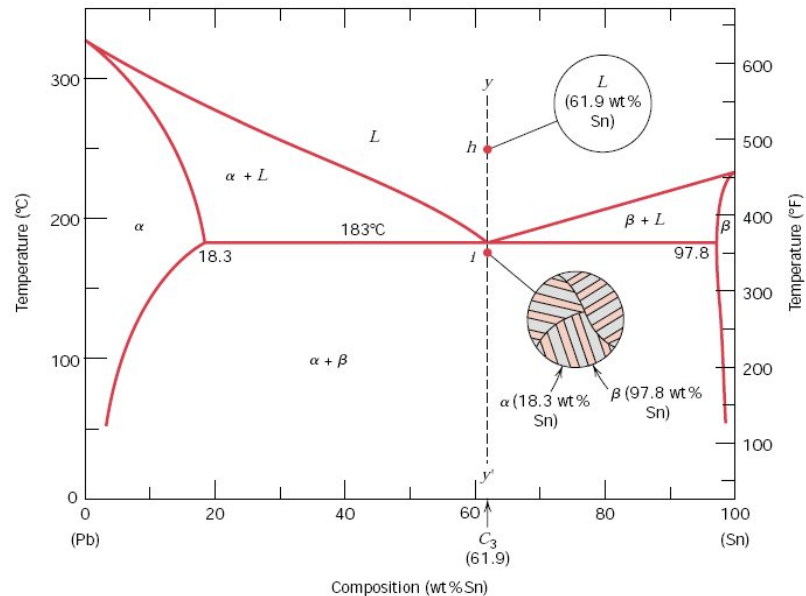
Case 2:

FIGURE 10.10 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_2 as it is cooled from the liquid-phase region.
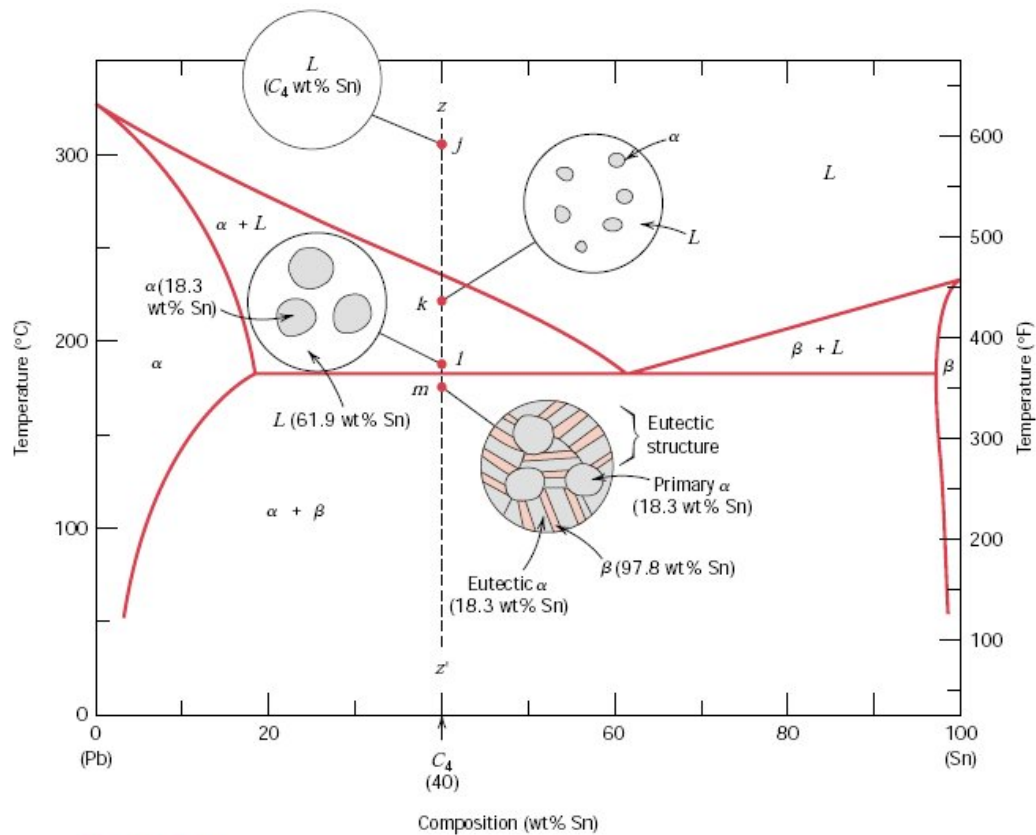
Case 3:

FIGURE 10.11 Schematic representations of the equilibrium microstructures for a lead–tin alloy of eutectic composition C_3 above and below the eutectic temperature.

Point i is called the **eutectic structure**. This microstructure consists of alternating layers (sometimes called lamellae) of the α and β phases.

Case 4:

FIGURE 10.14 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_4 as it is cooled from the liquid-phase region.

The α phase in the eutectic structure is called eutectic α, while the other that formed prior to crossing the eutectic isotherm is called primary α.

Questions

1) Cite the phases that are present and the phase compositions for the following alloys:

   (b) 15 wt% Sn – 85 wt % Pb at 100 ºC

   (c) 85 wt% Ag – 15 wt % Cu at 800 ºC

   (d) 50 wt% Cu – 50 wt % Ni at 1300 ºC

2) Is it possible to have a copper-silver alloy that, at equilibrium, consists of a β phase of composition 92 wt% Ag – 8 wt% Cu, and also a liquid phase of composition 76 wt% Ag – 24 wt% Cu? If so, what will the approximate temperature of the alloy?

3) A lead-tin alloy of composition 30 wt% Sn – 70 wt% Pb is slowly heated from a temperature of 150 ºC.

   (a) At what temperature does the first liquid phase form?

   (b) What is the composition of this liquid phase?

   (c) At what temperature does complete melting of the alloy occur?

   (d) What is the composition of the last solid remaining prior to complete melting?

4) A 20 wt% Ni – 50 wt% Cu alloy is slowly cooled from 1400 ºC to 1200 ºC.

   (a) At thaw temperature does the first solid phase form?

   (b) What is the composition of this solid phase?

   (c) At what temperature does the liquid solidify?

   (d) What is the composition of this last remaining liquid phase?

5) Consider an alloy containing 70 wt% Ni and 30 wt % Cu.

   (a) At 1350 ºC make a phase analysis assuming equilibrium conditions. In the phase analysis include the following:

      i.   What phases are present?

      ii. What is the chemical composition of each phase?

      iii. What amount of each phase is present?

   (b) Make a similar phase analysis at 1500 ºC

   (c) Sketch the microstructure of the alloy at each of the above temperature using circular microscopic fields.

   (d) Consider the binary eutectic copper-silver phase diagram. Make phase analysis of a 75 wt % Cu – 25 wt % Ag at the temperature (a) 1000 ºC, (b) 800 ºC. In the phase analysis include the following:

      iv. What phases are present?

      v.   What is the chemical composition of each phase?

      vi. What amount of each phase is present?

      vii. Sketch the microstructure of the alloy at each of the above temperature using 2-cm diameter circular microscopic fields.

11) The Iron-Carbon System

The Iron – Iron Carbide (Fe – Fe$_3$C) Phase Diagram
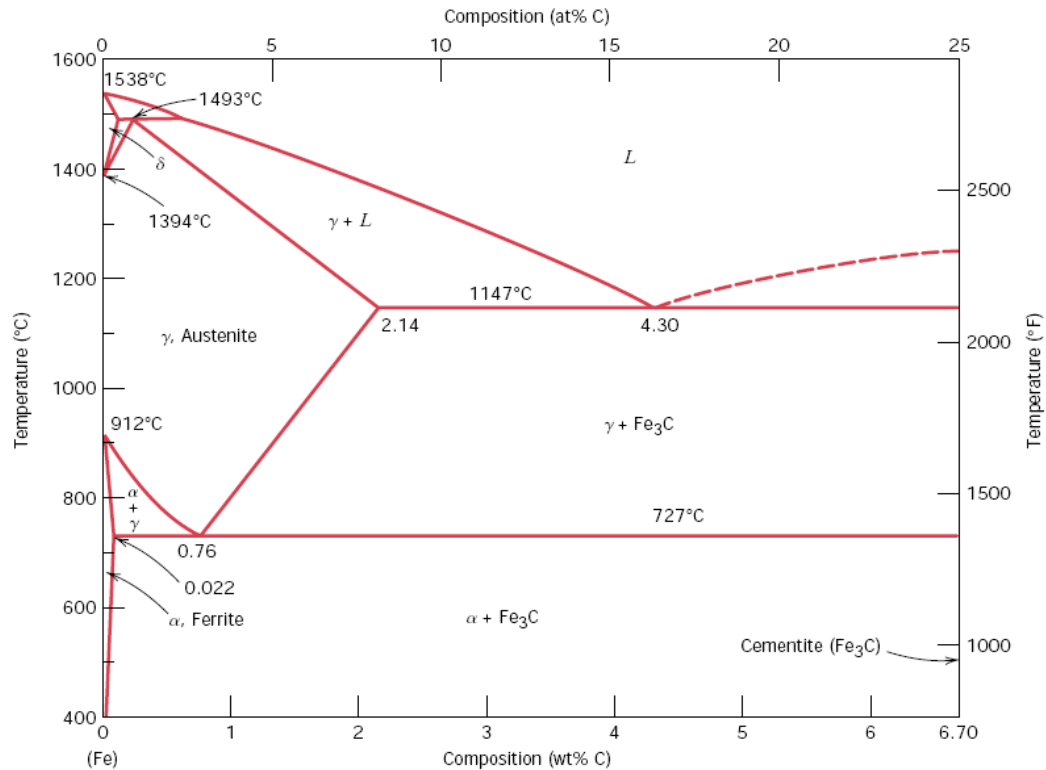
FIGURE 10.26   The iron–iron carbide phase diagram. (Adapted from *Binary Alloy Phase Diagrams,* 2nd edition, Vol. 1, T. B. Massalski, Editor-in-Chief,

At room temperature, α iron is called **α ferrite** has a BCC crystal structure. Ferrite changes to **austenite** or γ iron at 912 ºC. This austenite persists to 1394 ºC, at which temperature the FCC austenite reverts back to a BCC phase known as **δ ferrite**, which finally melts at 1538 ºC.

The figure only extends to 6.7 wt% ºC where the compound is called **cementite** (Fe$_3$C). The reason why only 6.7 wt% ºC is considered is because all steels and case irons have carbon contents less than 6.7 wt% ºC.

Carbon is and interstitial impurity in iron that forms a solid solution with α and δ ferrite and austenite γ.

α ferrite – this particular iron phase is soft, may be magnetic at temperatures below 768 ºC.

Austenite (γ) – it has solubility of carbon 100 greater than carbon. Austenite is non magnetic.

δ ferrite – is the same as α ferrite except for the range of temperature over which it exist. It is of no technological importance because it is only stable at high temperatures. It will not be discussed further.

Cementite (Fe$_3$C) – is hard and brittle.

12) Development of Microstructure In Iron – Carbon Alloys

The microstructure that develops depends on both carbon content and heat treatment.

This discussion is only focuses on slow cooling of steel alloys

If a sample of a 0.76% (eutectoid) carbon steel is heated to about 800 ºC (point a) and held for sufficient time, its structure will become homogenous austenite. This process is called austenizing.

If this eutectoid steel is then cooled very slowly to just above the eutectoid

Figure