



Material Science

ME 221

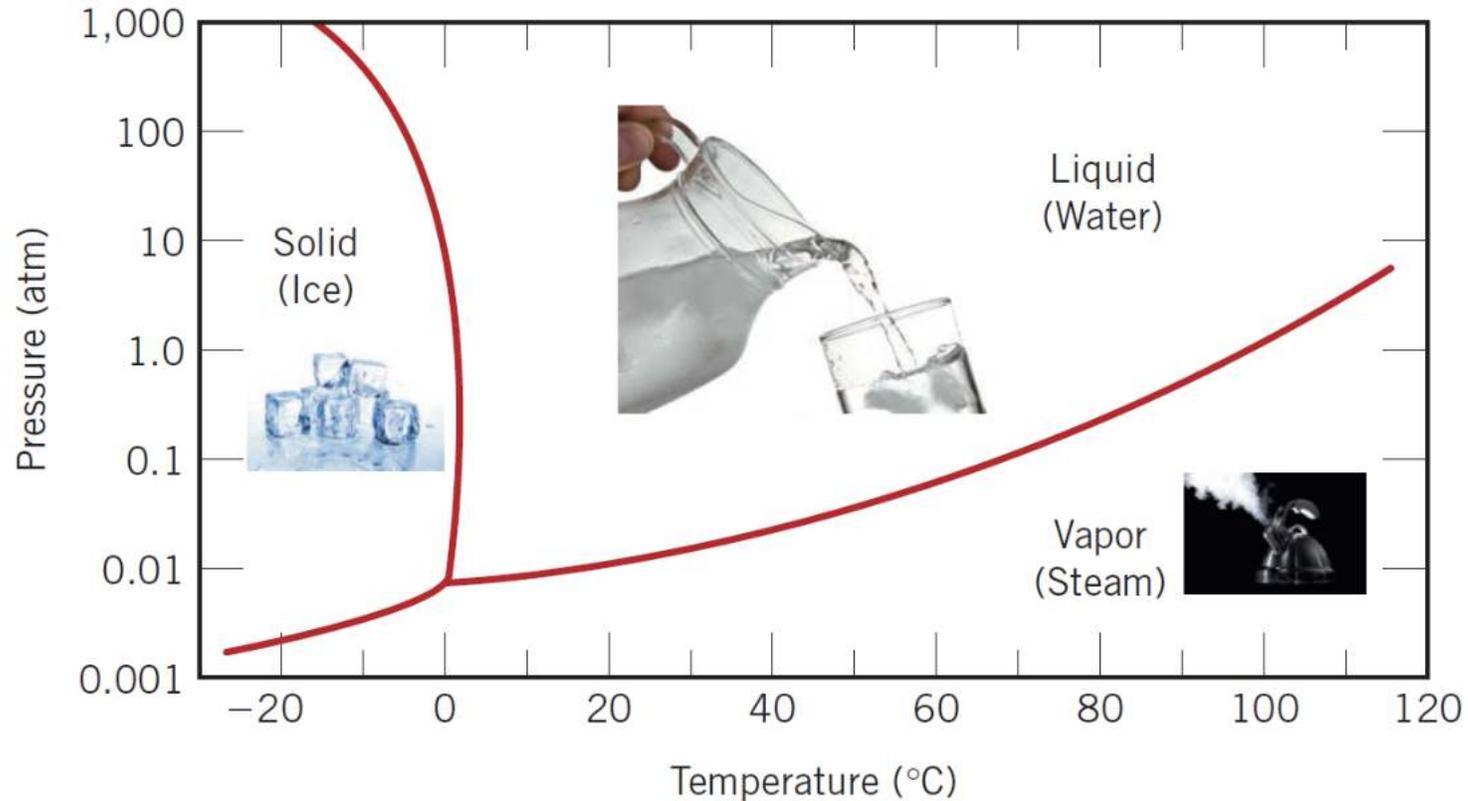
Fall 2020

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Chapter 9: Phase Diagrams

Phase diagrams is important to the **Material Engineer**



processing/structure/properties/performance



Introduction

“There is a strong correlation between microstructure and mechanical properties”

“Development of microstructure of an alloy is related to the characteristics of its phase diagram”

“Phase diagrams provide valuable information about melting, casting, crystallization, and other phenomena”



Introduction

Components: pure metals and/or compounds of which an alloy is composed.

For example, in a copper–zinc brass, the components are Cu and Zn. “*Solute and solvent*”

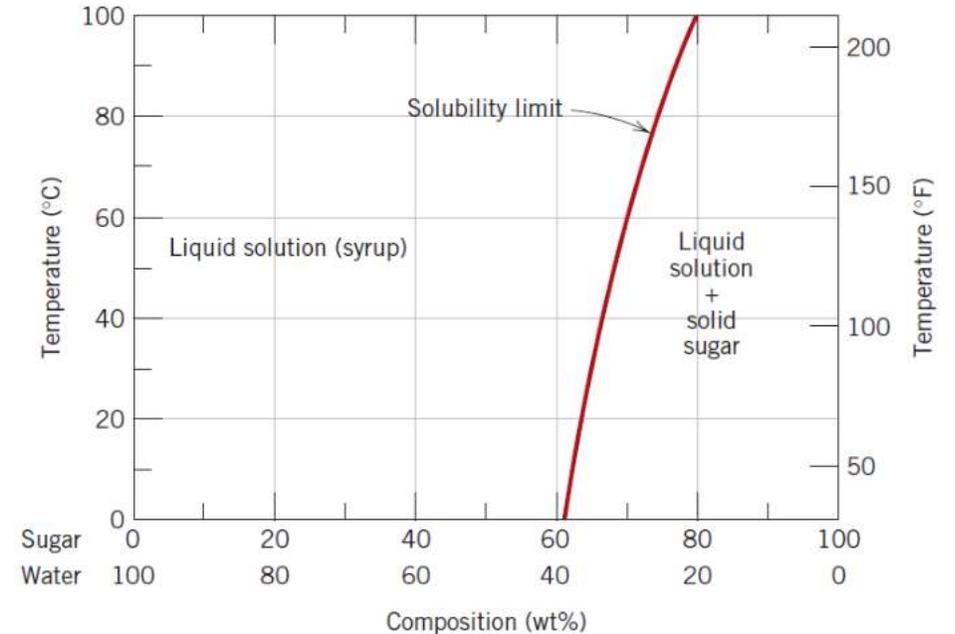
System

“Series of possible alloys consisting of the same components, but without regard to alloy composition (e.g., the iron–carbon system)”

Solubility limit:

in “Maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution”

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



This solubility limit of sugar in water depends on the temperature of the water



PHASES

Phase:

“homogeneous portion of a system that has uniform physical and chemical characteristics”

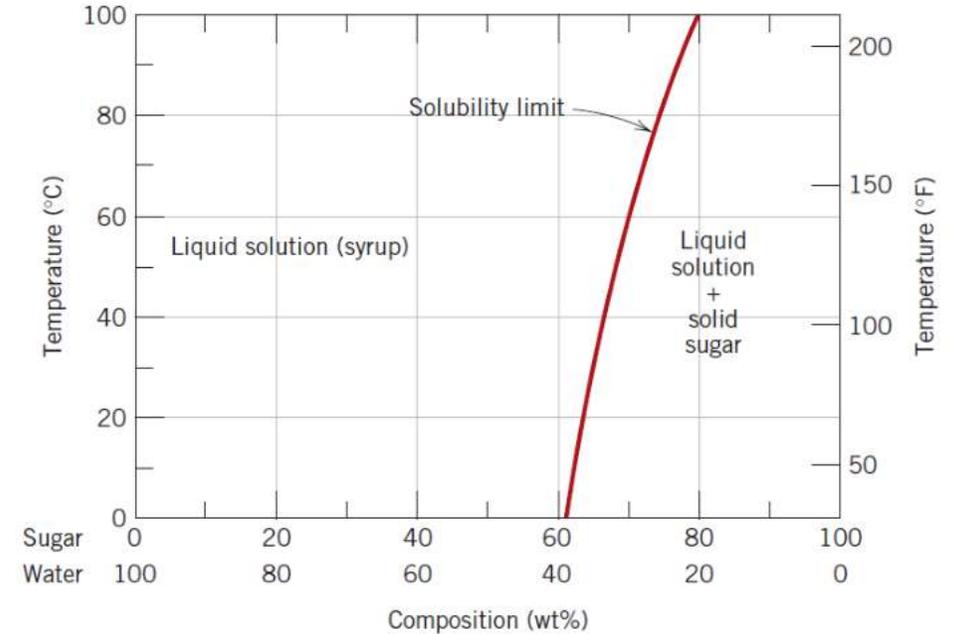
Different physical properties

- One is a liquid, the other is a solid

Different chemically

- One is virtually pure sugar, the other is a solution of water and sugar.

“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”





PHASES

“When water and ice are present in a container, two separate phases exist; they are physically dissimilar (one is a solid, the other is a liquid) but identical in chemical makeup”

“When a substance can exist in two or more polymorphic forms (e.g., having both FCC and BCC structures), each of these structures is a separate phase because their respective physical characteristics differ”

“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, ceramic, polymeric, and composite systems are heterogeneous”



PHASE EQUILIBRIA

Equilibrium “In a macroscopic sense, it means that the characteristics of the system do not change with time, the system is stable”

Phase Equilibrium:

“Equilibrium as it applies to systems in which more than one phase may exist”

“Phase equilibrium is reflected by a constancy with time in the phase characteristics of a system”

Nonequilibrium or metastable

Changes as time progresses



ONE-COMPONENT (OR UNARY) PHASE DIAGRAMS

Also called: equilibrium diagram

Parameters affect phase structure:

- Temperature
- Pressure
- Composition

For a one-component system, in which composition is held constant, it is called *pressure–temperature (or P–T) diagram*.

Triple point:

“Any deviation from this point by a change of temperature and/or pressure will cause at least one of the phases to disappear”

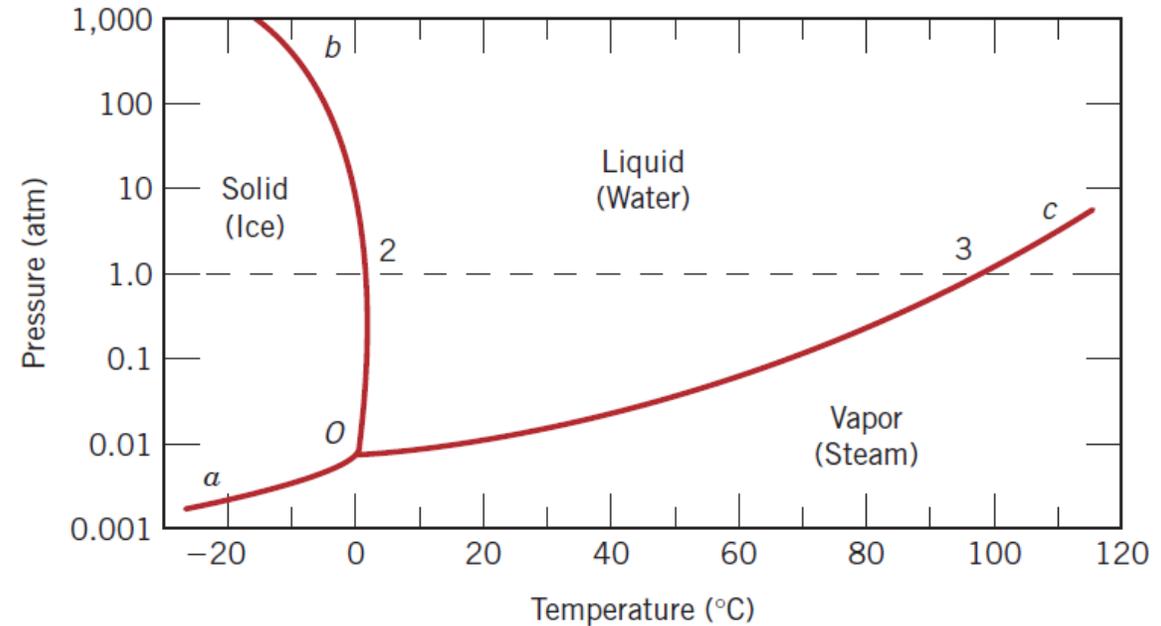


Figure 9.2 Pressure–temperature phase diagram for H_2O . Intersection of the dashed horizontal line at 1 atm pressure with the solid–liquid phase boundary (point 2) corresponds to the melting point at this pressure ($T = 0^\circ\text{C}$). Similarly, point 3, the intersection with the liquid–vapor boundary, represents the boiling point ($T = 100^\circ\text{C}$).

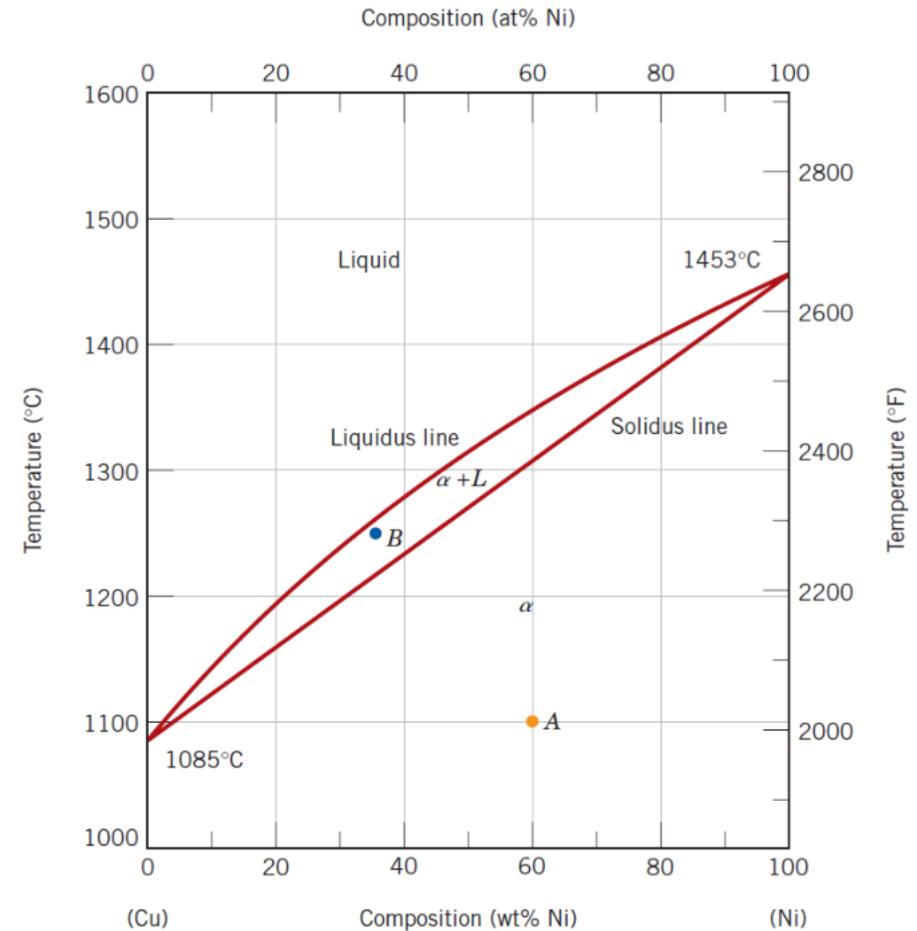


BINARY ISOMORPHOUS SYSTEMS

Temperature and composition are variable parameters, and pressure is held constant—normally 1 atm

For example: copper–nickel system
it is called **isomorphous** because of this complete liquid and solid solubility of the two components.

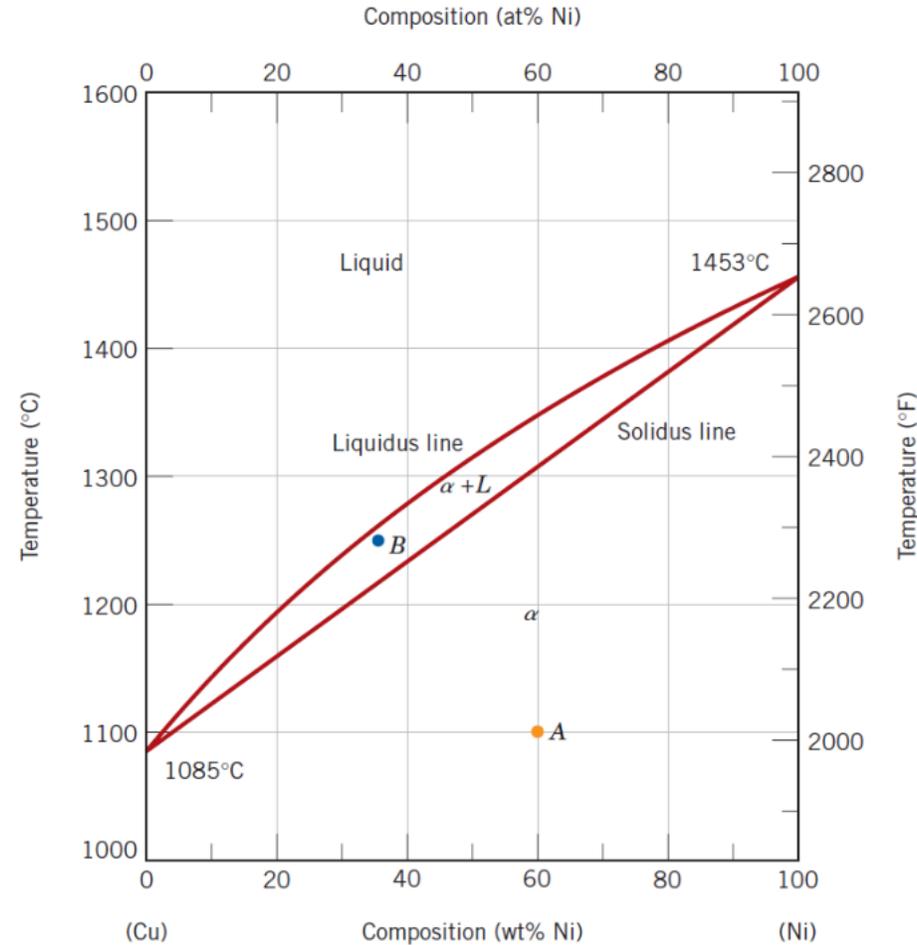
“At temperatures below about 1080C, copper and nickel are mutually soluble in each other in the solid state for all compositions. This complete solubility is explained by the fact that both Cu and Ni have the same crystal structure (FCC), nearly identical atomic radii and electronegativities, and similar valences”





BINARY ISOMORPHOUS SYSTEMS

Melting temperature change depending on the constituents





Phases Present and Compositions

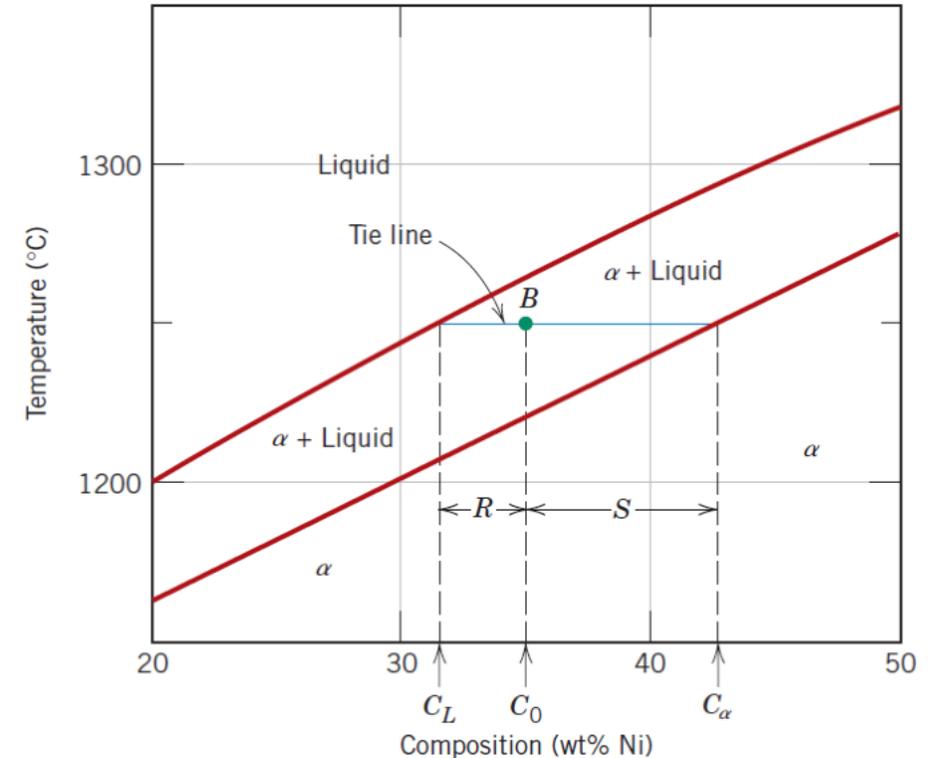
Phases Present

Locates the temperature–composition point on the diagram and notes the phase(s)

Determination of Phase Compositions

“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 **solid-solution phase**, of 42.5 wt% Ni–57.5 wt% Cu.”





Determination of Phase Amounts

$$W_L = \frac{S}{R + S}$$

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

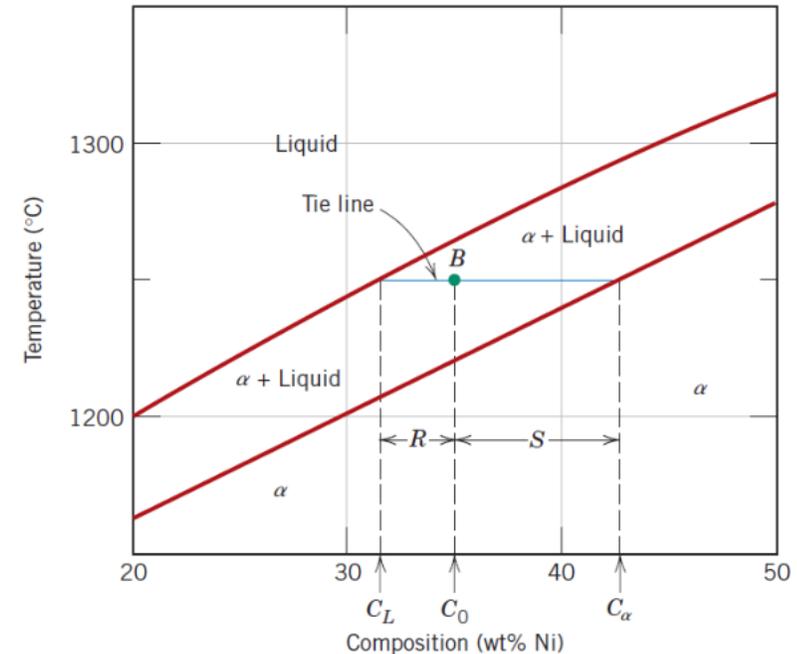
$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

For point B:

$C_0 = 35$ wt, % Ni, $C_\alpha = 42.5$ wt% Ni, and $C_L = 31.5$ wt% Ni

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

$$W_\alpha = \frac{35 - 31.5}{42.5 - 31.5} = 0.32$$





Determination of Phase Amounts

For multiphase alloys, volume fraction is used rather than mass fraction

$$V_{\alpha} = \frac{V_{\alpha}}{V_{\alpha} + V_{\beta}}$$

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

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

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

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

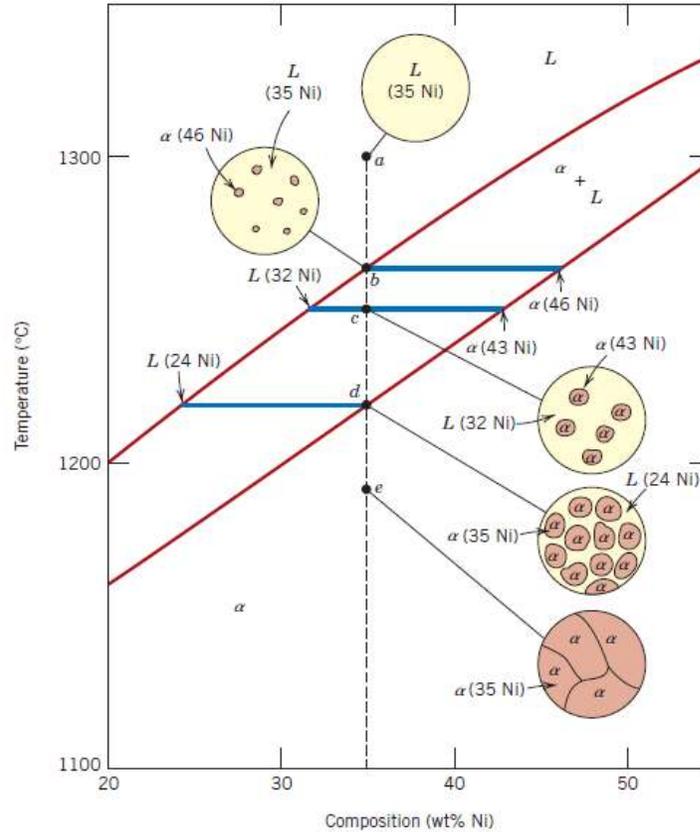
Conversion equations



DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

Isomorphous: complete liquid and solid solubility of the two components.

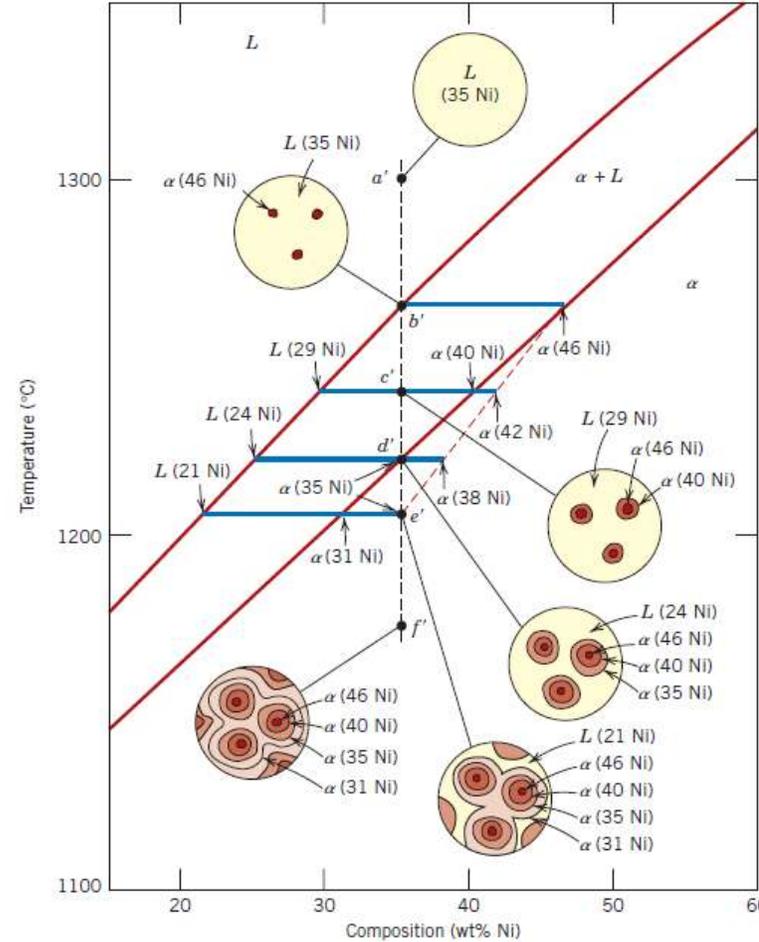
Equilibrium Cooling: cooling at very low rate.





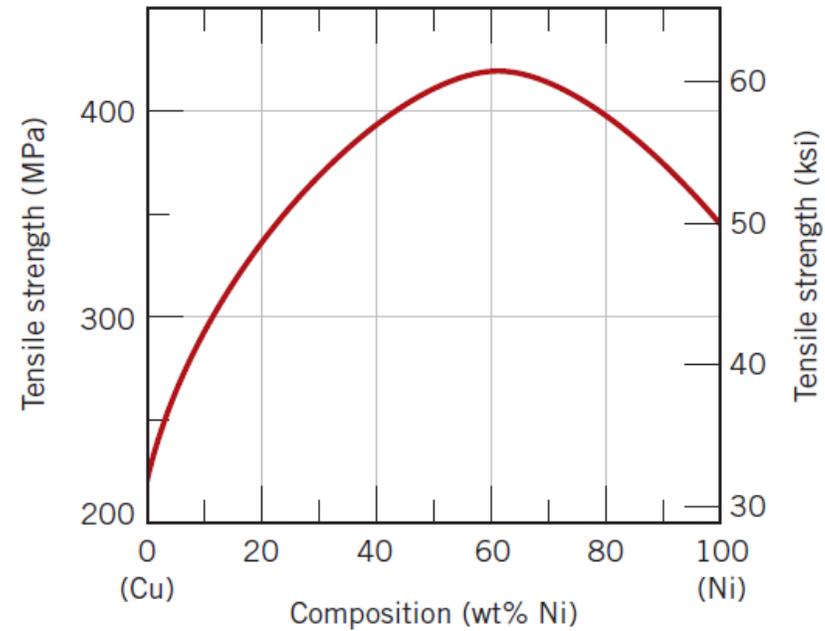
DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

Nonequilibrium Cooling: rapid cooling





MECHANICAL PROPERTIES OF ISOMORPHOUS ALLOYS





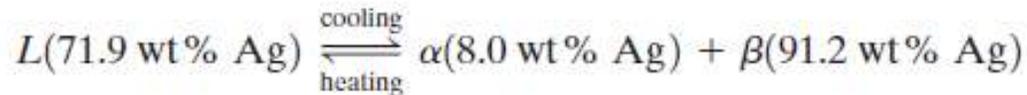
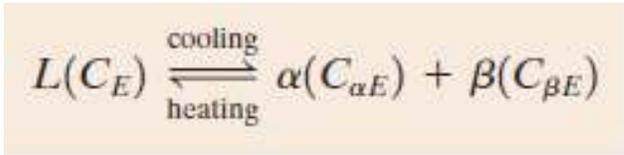
BINARY EUTECTIC SYSTEMS

The α phase is a solid solution rich in copper

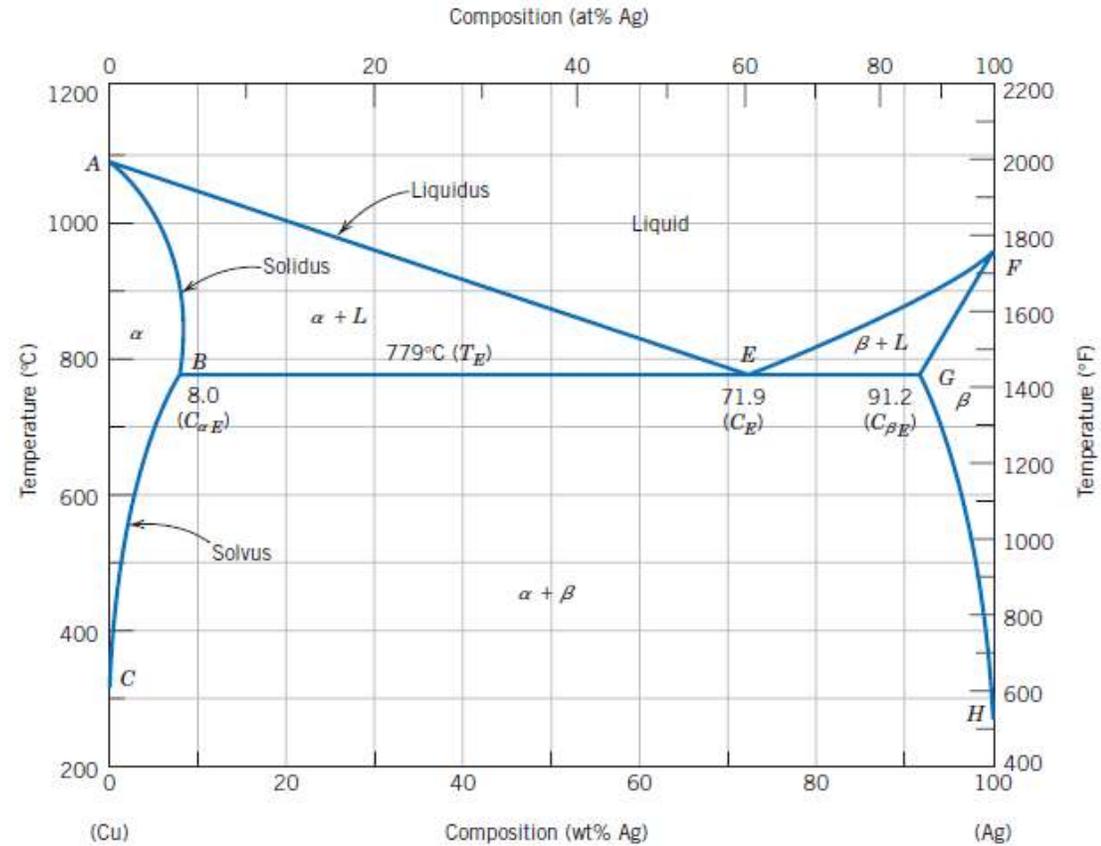
The β -phase solid solution rich in silver

Pure copper and pure silver are also considered to be α and β phases, respectively.

invariant point (point E): from liquid to solid phase.



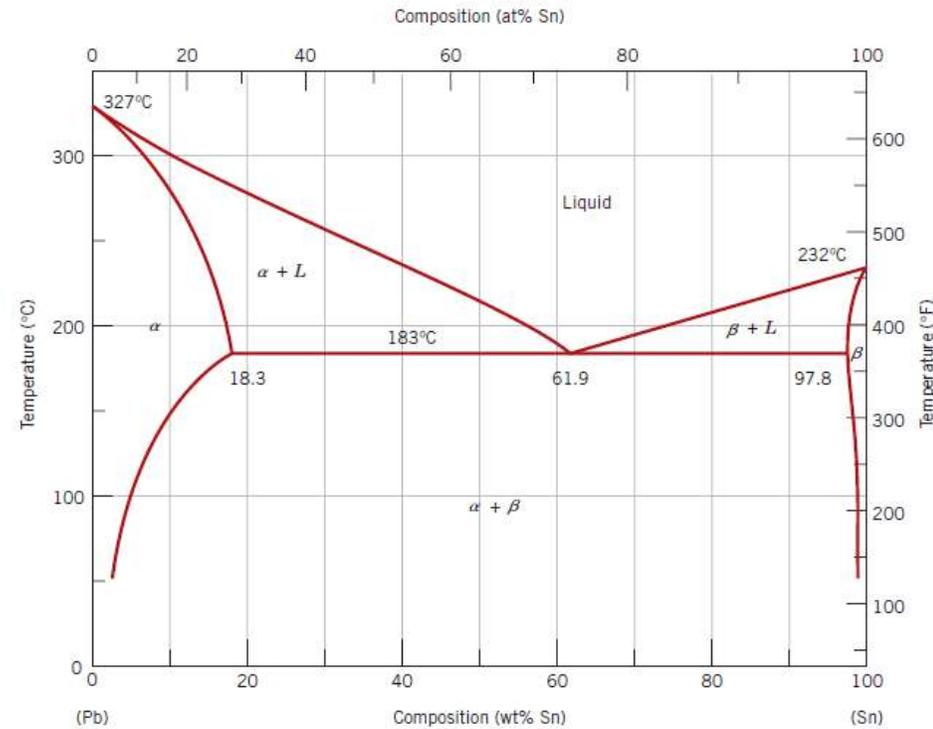
The eutectic reaction



Example 1



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



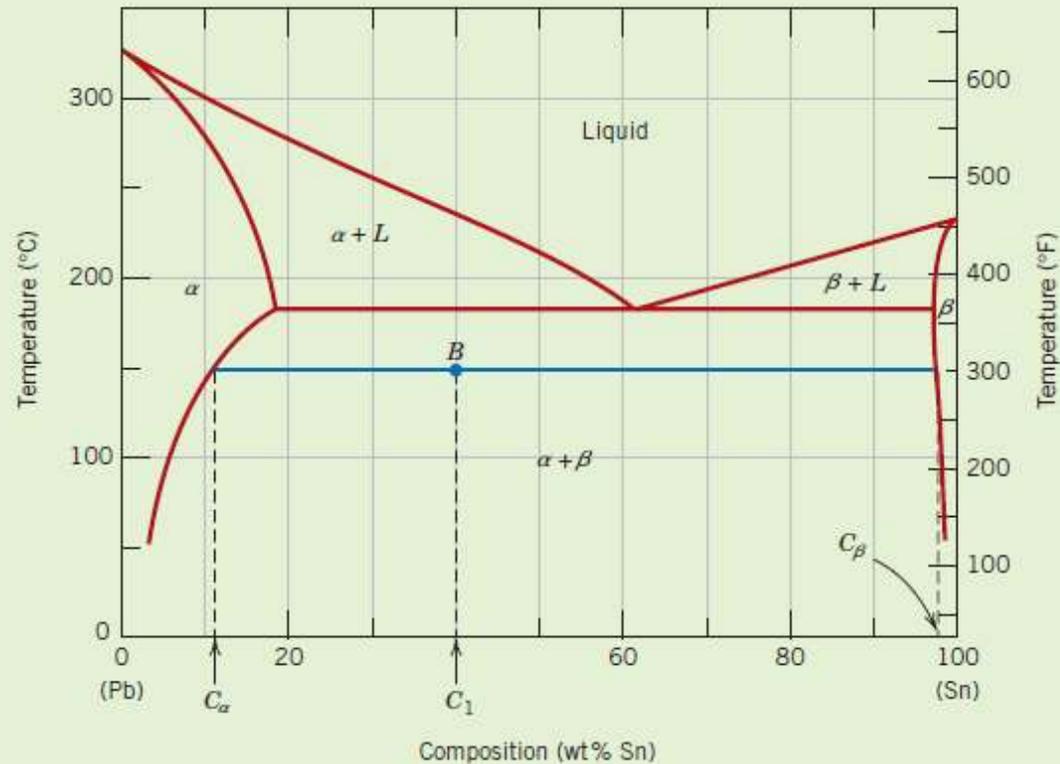


Figure 9.9 The lead–tin phase diagram. For a 40 wt% Sn–60 wt% Pb alloy at 150°C (point *B*), phase compositions and relative amounts are computed in Example Problems 9.2 and 9.3.

(b) Because 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 11 wt% Sn–89 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).



Example 2

For the lead–tin alloy in previous Example, 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.



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

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

where $C_{\text{Sn}(\alpha)}$ and $C_{\text{Pb}(\alpha)}$ denote the concentrations in weight percent of tin and lead, respectively, in the α phase. From Example Problem 9.2, these values are 11 wt% and 89 wt%. Incorporation of these values along with the densities of the two components leads to

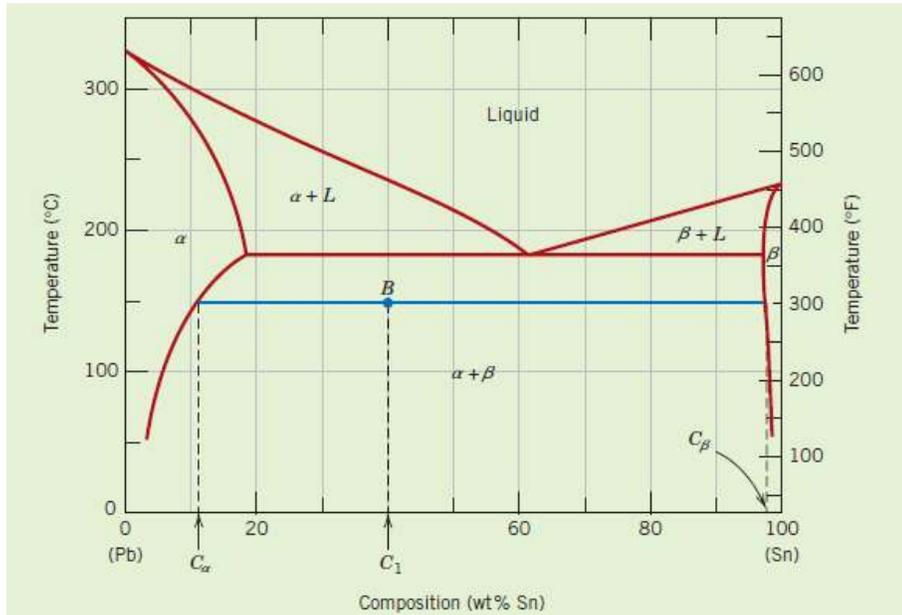
$$\rho_{\alpha} = \frac{100}{\frac{11}{7.24 \text{ g/cm}^3} + \frac{89}{11.23 \text{ g/cm}^3}} = 10.59 \text{ g/cm}^3$$

Similarly for the β phase:

$$\begin{aligned} \rho_{\beta} &= \frac{100}{\frac{C_{\text{Sn}(\beta)}}{\rho_{\text{Sn}}} + \frac{C_{\text{Pb}(\beta)}}{\rho_{\text{Pb}}}} \\ &= \frac{100}{\frac{98}{7.24 \text{ g/cm}^3} + \frac{2}{11.23 \text{ g/cm}^3}} = 7.29 \text{ g/cm}^3 \end{aligned}$$

Now it becomes necessary to employ Equations 9.6a and 9.6b to determine V_{α} and V_{β} as

$$\begin{aligned} V_{\alpha} &= \frac{\frac{W_{\alpha}}{\rho_{\alpha}}}{\frac{W_{\alpha}}{\rho_{\alpha}} + \frac{W_{\beta}}{\rho_{\beta}}} \\ &= \frac{\frac{0.67}{10.59 \text{ g/cm}^3}}{\frac{0.67}{10.59 \text{ g/cm}^3} + \frac{0.33}{7.29 \text{ g/cm}^3}} = 0.58 \\ V_{\beta} &= \frac{\frac{W_{\beta}}{\rho_{\beta}}}{\frac{W_{\alpha}}{\rho_{\alpha}} + \frac{W_{\beta}}{\rho_{\beta}}} \\ &= \frac{\frac{0.33}{7.29 \text{ g/cm}^3}}{\frac{0.67}{10.59 \text{ g/cm}^3} + \frac{0.33}{7.29 \text{ g/cm}^3}} = 0.42 \end{aligned}$$



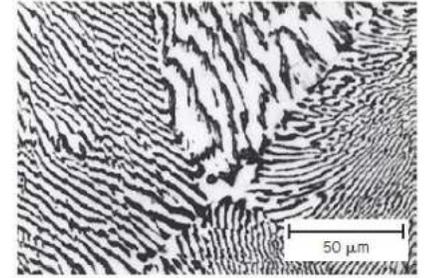
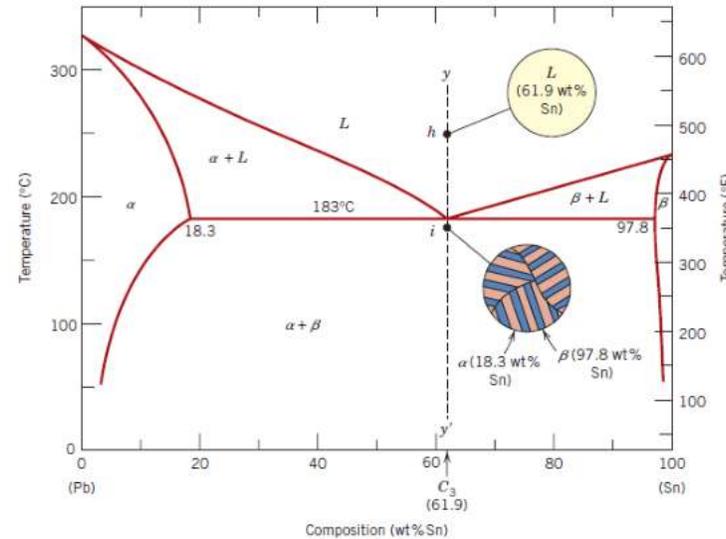
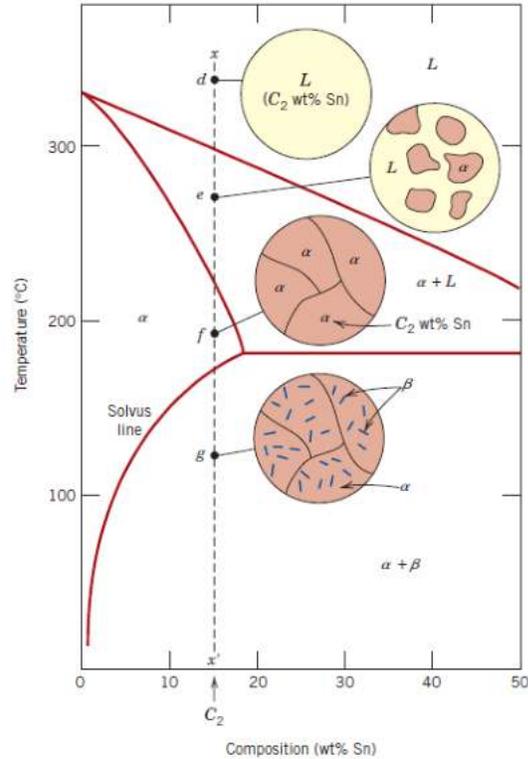
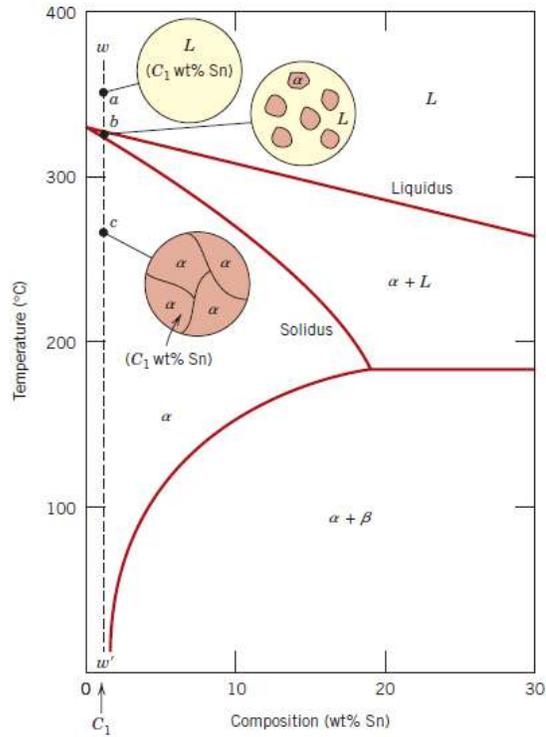
(a) Because the alloy consists of two phases, it is necessary to employ the lever rule. If C_1 denotes the overall alloy composition, mass fractions may be computed by subtracting compositions, in terms of weight percent tin, as follows:

$$W_{\alpha} = \frac{C_{\beta} - C_1}{C_{\beta} - C_{\alpha}} = \frac{98 - 40}{98 - 11} = 0.67$$

$$W_{\beta} = \frac{C_1 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{40 - 11}{98 - 11} = 0.33$$

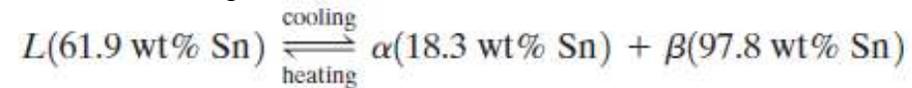


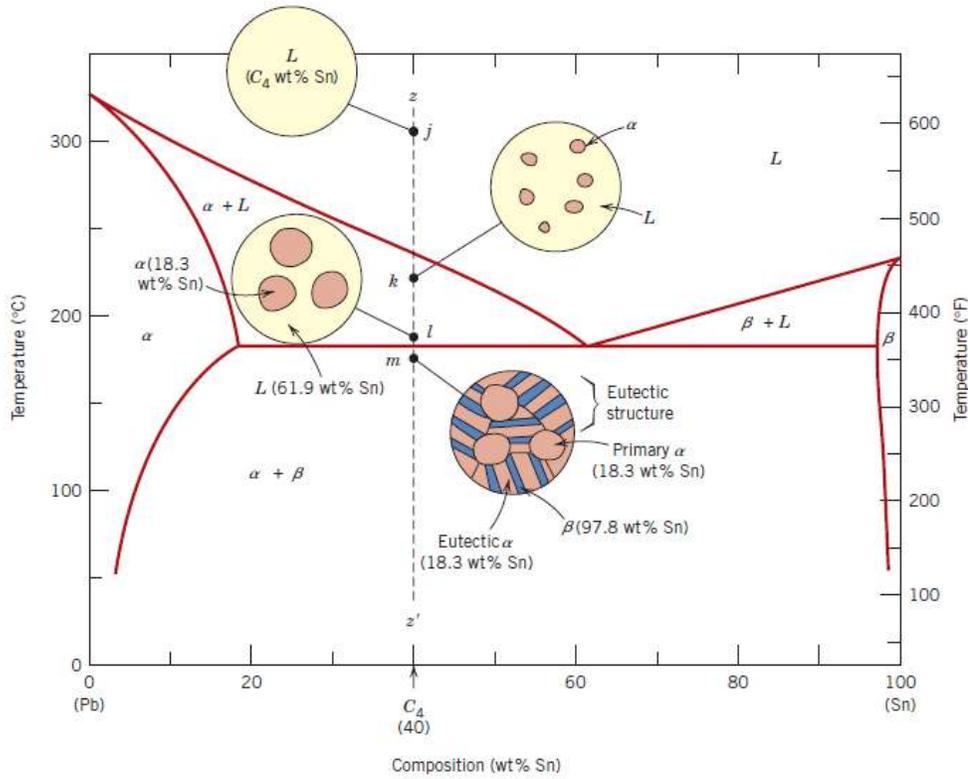
DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS



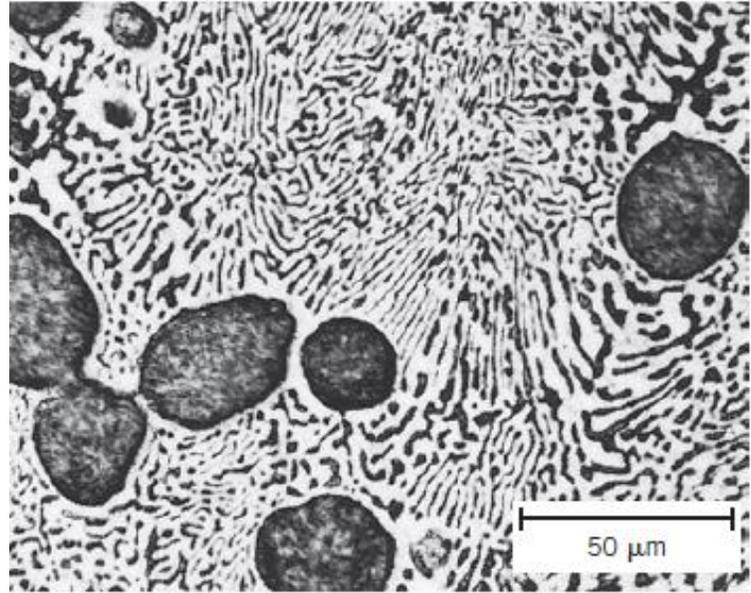
Photomicrograph showing the microstructure of a lead-tin alloy of eutectic composition. This microstructure consists of alternating layers of a lead rich -phase solid solution (dark layers), and a tin-rich -phase solid solution (light layers)

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

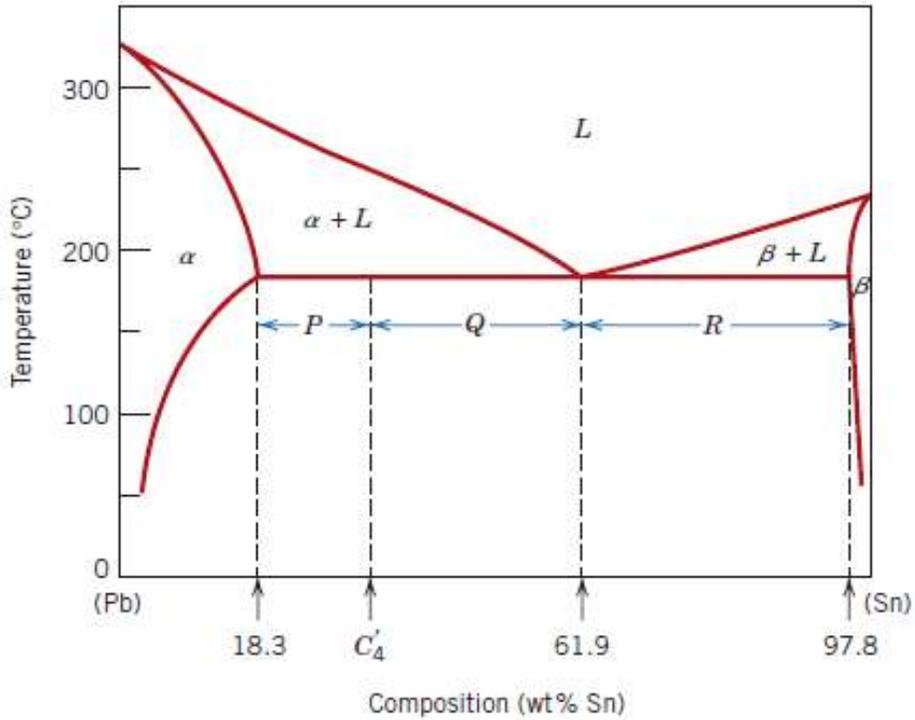




Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_4 as it is cooled from the liquid-phase region



Photomicrograph showing the microstructure of a lead–tin alloy of composition 50 wt% Sn–50 wt% Pb. This microstructure is composed of a primary lead-rich phase (large dark regions) within a lamellar eutectic structure consisting of a tin-rich phase (light layers) and a lead-rich phase (dark layers).



The lead–tin phase diagram used in computations for relative amounts of primary and eutectic microconstituents for an alloy of composition C_4 .

$$W_e = W_L = \frac{P}{P + Q} = \frac{C_4' - 18.3}{61.9 - 18.3} = \frac{C_4' - 18.3}{43.6}$$

$$W_\alpha = \frac{Q}{P + Q} \quad \text{primary}$$

$$= \frac{61.9 - C_4'}{61.9 - 18.3} = \frac{61.9 - C_4'}{43.6}$$

$$W_\alpha = \frac{Q + R}{P + Q + R} \quad \text{eutectic and primary}$$

$$= \frac{97.8 - C_4'}{97.8 - 18.3} = \frac{97.8 - C_4'}{79.5}$$

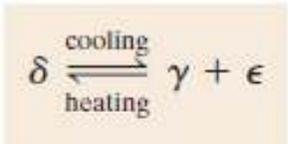
$$W_\beta = \frac{P}{P + Q + R} = \frac{C_4' - 18.3}{97.8 - 18.3} = \frac{C_4' - 18.3}{79.5}$$



EUTECTOID AND PERITECTIC REACTIONS

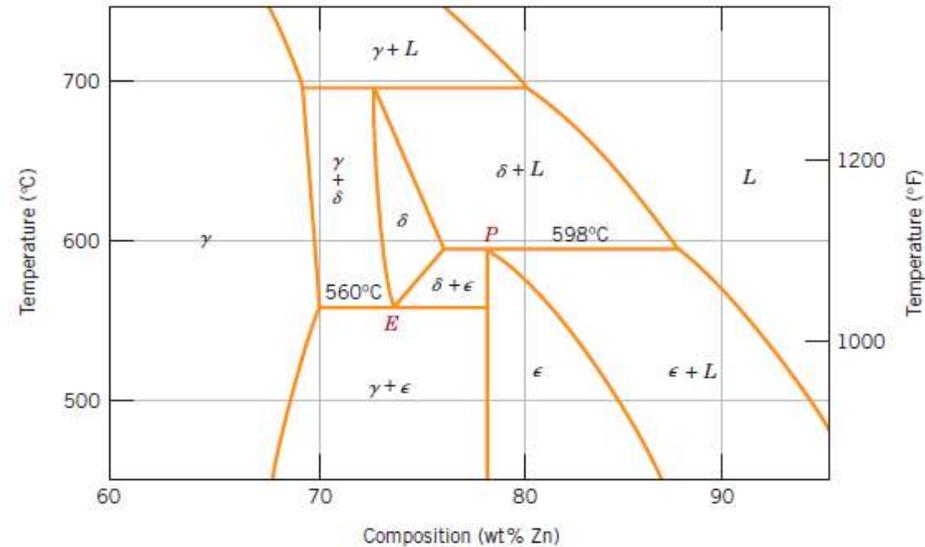
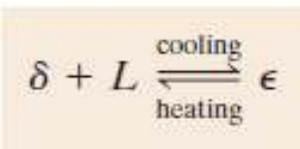
Eutectoid reaction

solid phase transforms into two other solid phases



Peritectic reaction

one solid phase transforms into a liquid phase and another solid phase



A region of the copper–zinc phase diagram that has been enlarged to show eutectoid and peritectic invariant points, labeled *E* (560C, 74 wt% Zn) and *P* (598C, 78.6 wt% Zn), respectively.



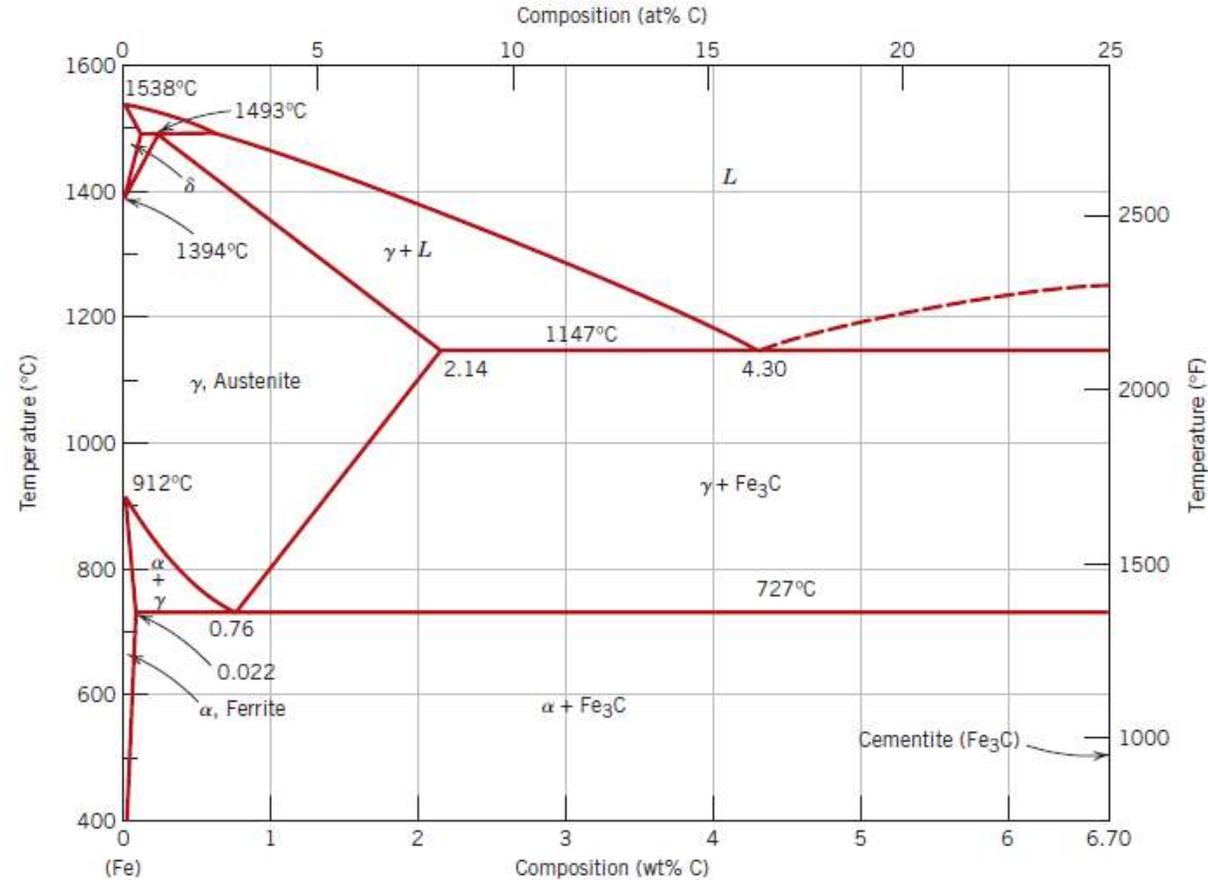
The Iron–Carbon System

THE IRON–IRON CARBIDE (Fe–Fe₃C) PHASE DIAGRAM

Ferrite

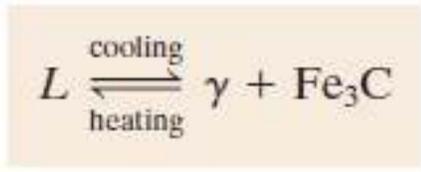
Austenite

Cementite

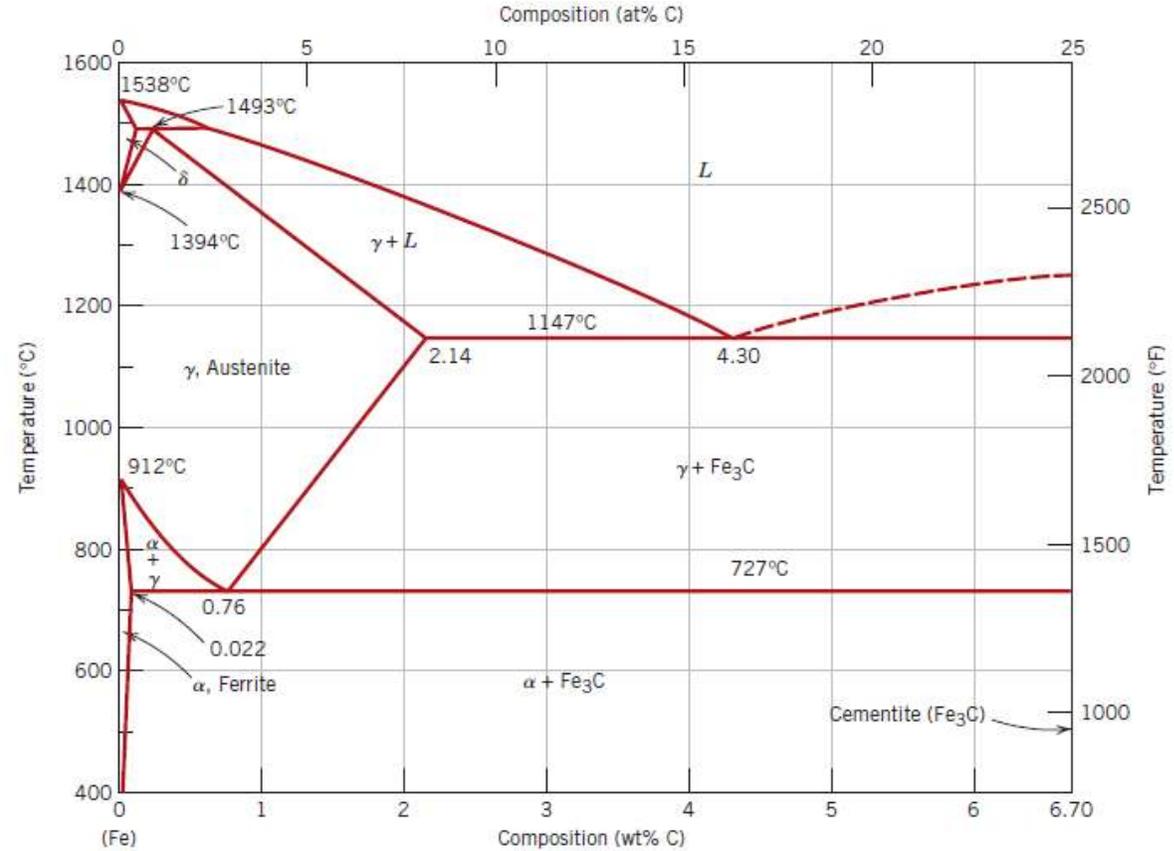
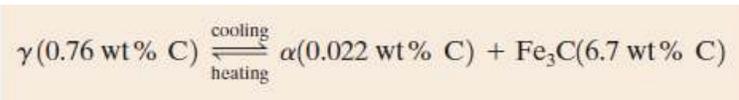




Eutectic reaction for the iron–iron carbide system

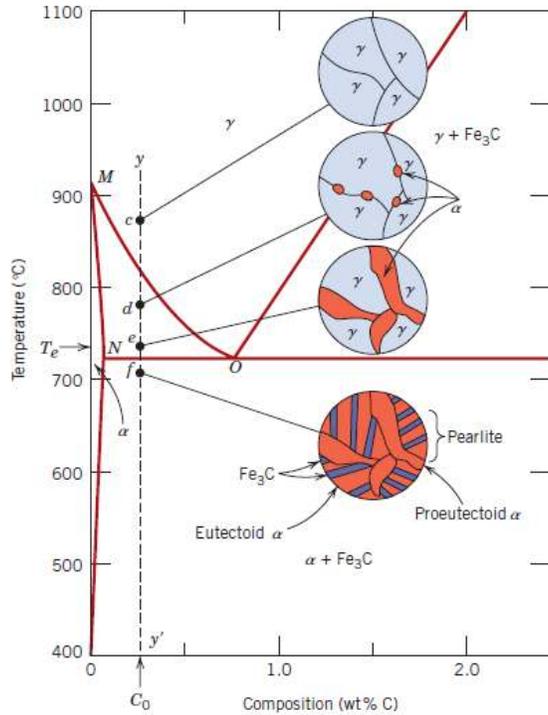


Eutectoid reaction for the iron–iron carbide system

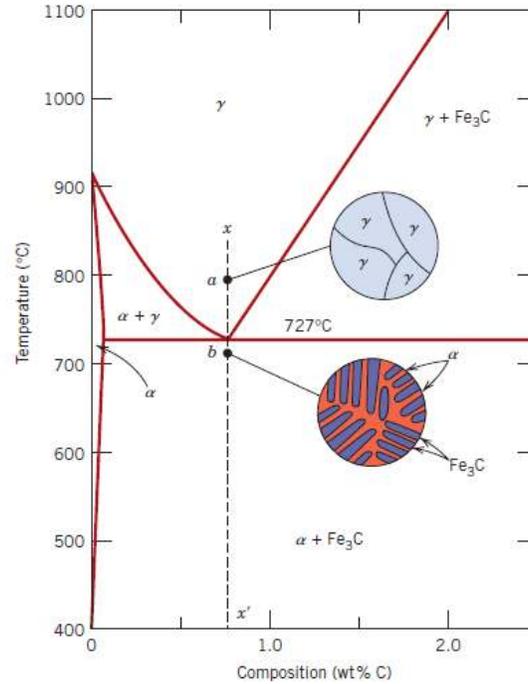




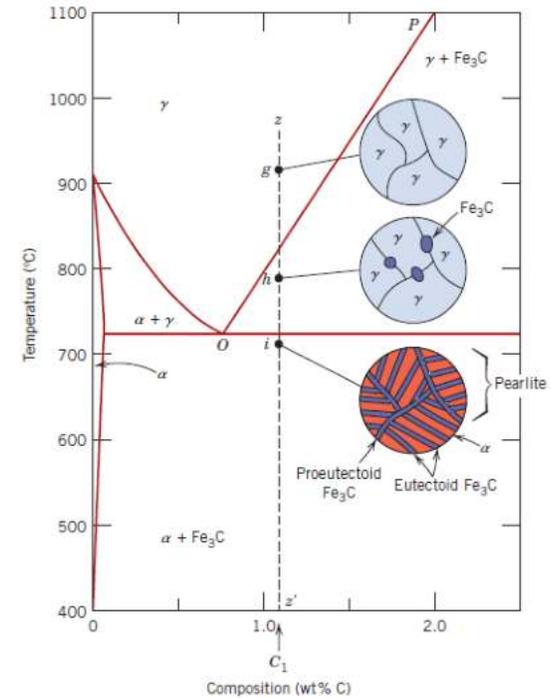
DEVELOPMENT OF MICROSTRUCTURE IN IRON-CARBON ALLOYS



Hypoeutectoid Alloys



Eutectoid Alloys



Hypereutectoid Alloys



Lever rule expression for computation of pearlite mass fraction C_0 ,

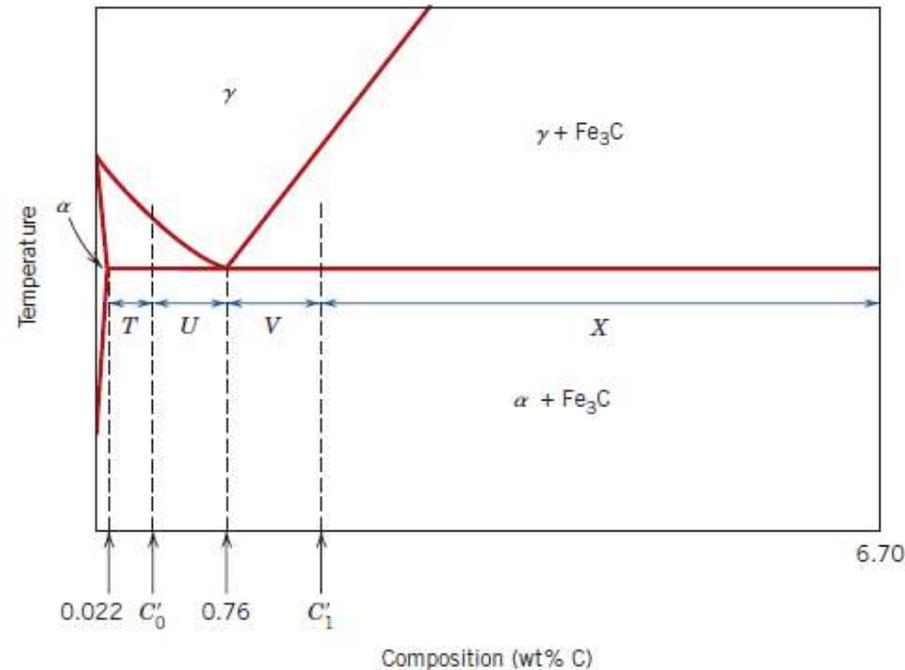
$$W_p = \frac{T}{T + U}$$

$$= \frac{C'_0 - 0.022}{0.76 - 0.022} = \frac{C'_0 - 0.022}{0.74}$$

Lever rule expression for computation of proeutectoid ferrite mass fraction

$$W_{\alpha'} = \frac{U}{T + U}$$

$$= \frac{0.76 - C'_0}{0.76 - 0.022} = \frac{0.76 - C'_0}{0.74}$$



Thus, for an alloy having composition, fractions of pearlite W_p and proeutectoid cementite W_{Fe_3C} are determined from the following lever rule expressions:

$$W_p = \frac{X}{V + X} = \frac{6.70 - C'_1}{6.70 - 0.76} = \frac{6.70 - C'_1}{5.94}$$

$$W_{Fe_3C'} = \frac{V}{V + X} = \frac{C'_1 - 0.76}{6.70 - 0.76} = \frac{C'_1 - 0.76}{5.94}$$



Chapter 10: Phase Transformation

“A variety of **phase transformations** are important in the processing of materials, and usually they involve some alteration of the microstructure”

Types of phase transformation:

1- Diffusion-dependent transformations

a. “No change in either the number or composition of the phases present”

b. “There is some alteration in phase compositions and often in the number of phases present”

2- Diffusionless transformation, wherein a metastable phase is produced



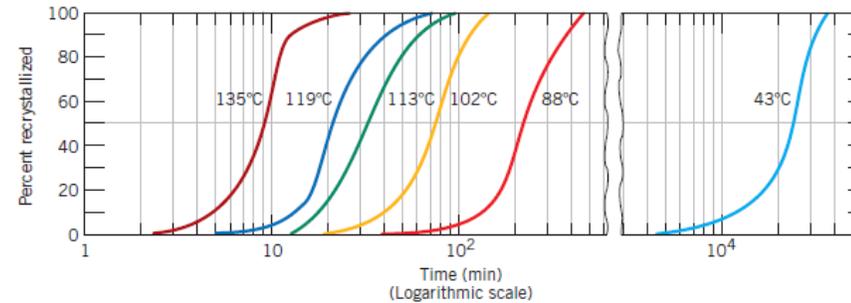
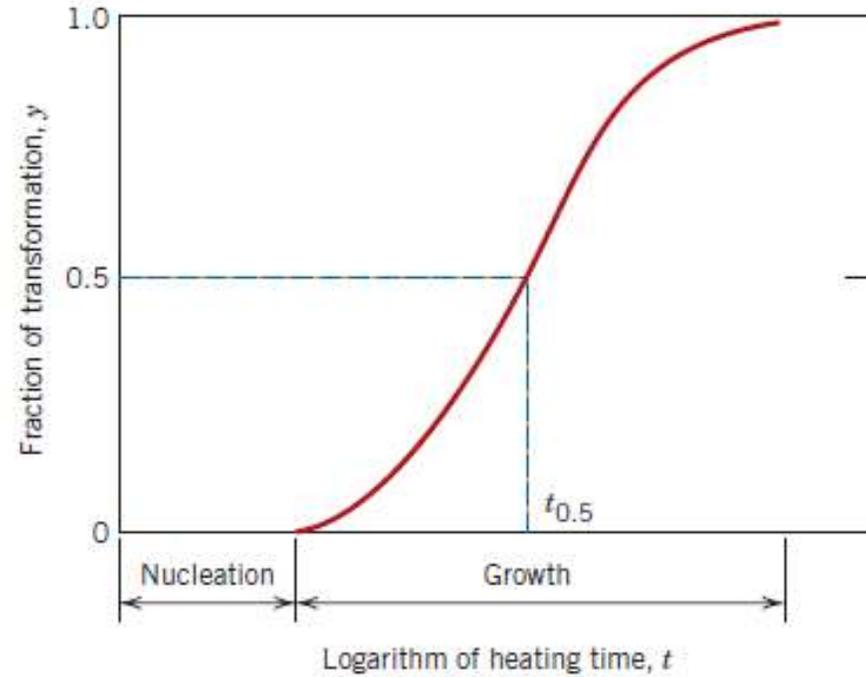
Phase transformation stages:

Nucleation:

“Involves the appearance of very small particles, or nuclei of the new phase (often consisting of only a few hundred atoms), which are capable of growing”

Growth:

“During the growth stage these nuclei increase in size, which results in the disappearance of some (or all) of the parent phase



Percent recrystallization as a function of time and at constant temperature for pure copper.

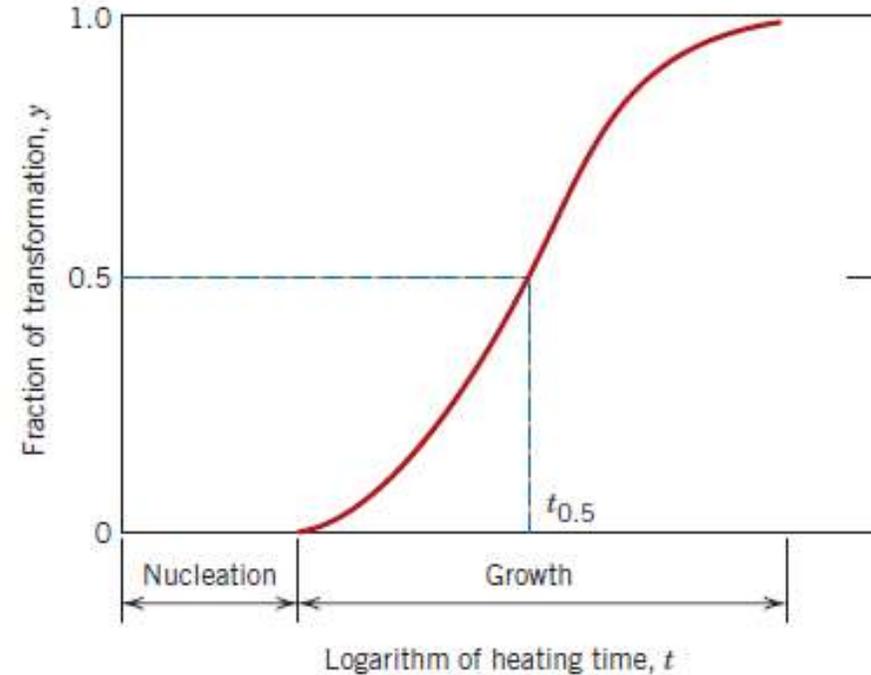


Avrami equation—
dependence of fraction of
transformation on time

$$y = 1 - \exp(-kt^n)$$

Transformation
rate—reciprocal of
the halfway-to-completion
transformation time

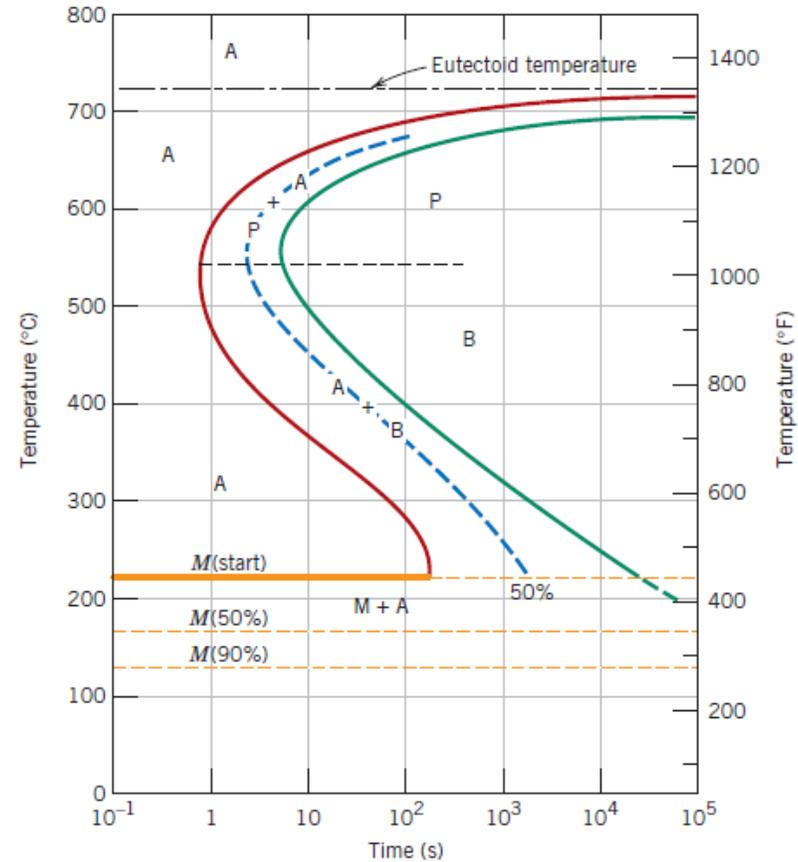
$$\text{rate} = \frac{1}{t_{0.5}}$$





ISOTHERMAL TRANSFORMATION DIAGRAMS

Isothermal transformation diagrams, or sometimes as *time–temperature–transformation* (or *T–T–T*) plots.

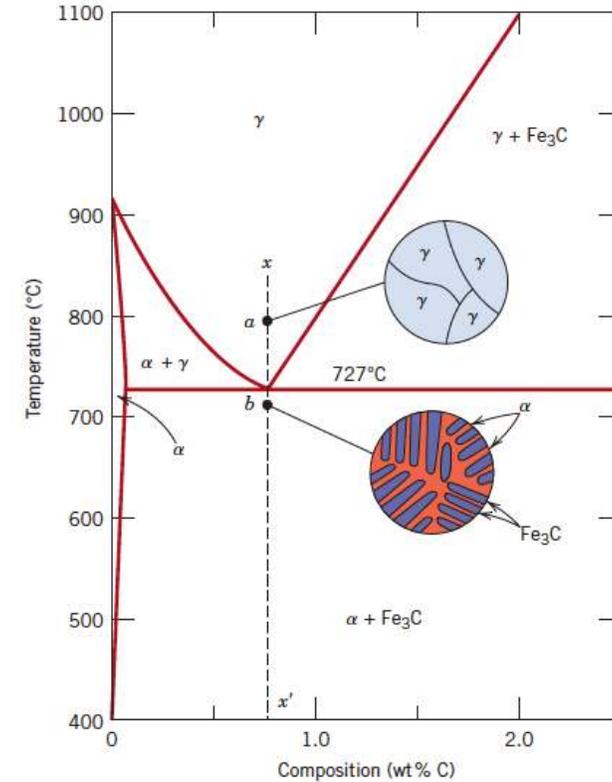
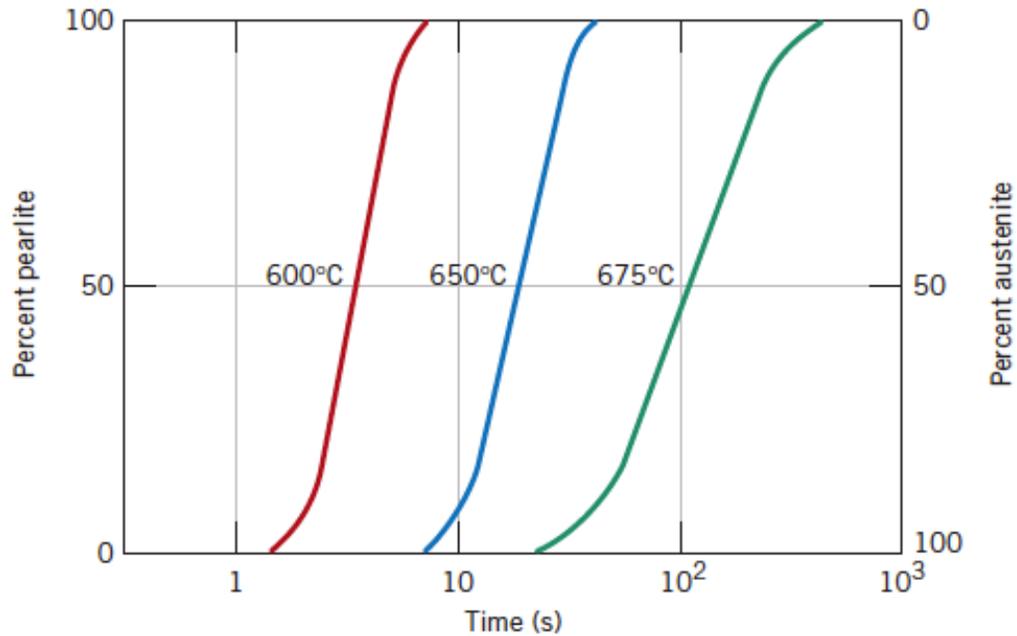
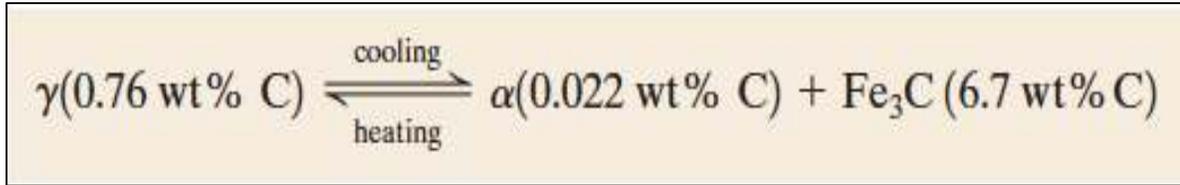


The complete isothermal Transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite

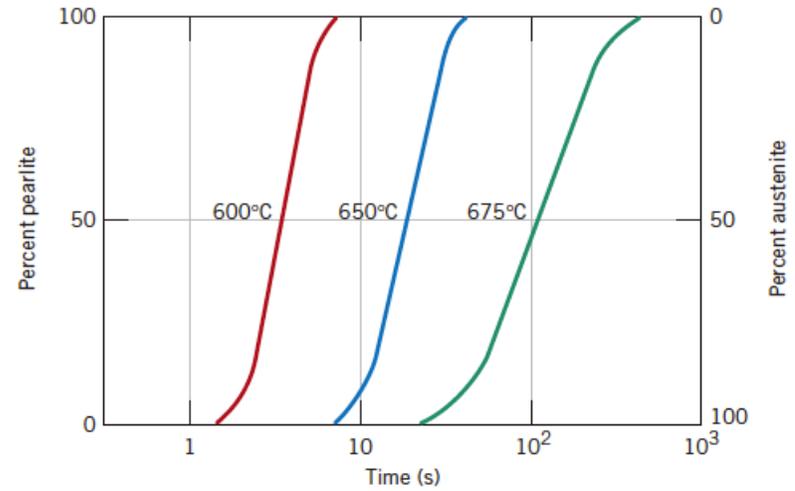
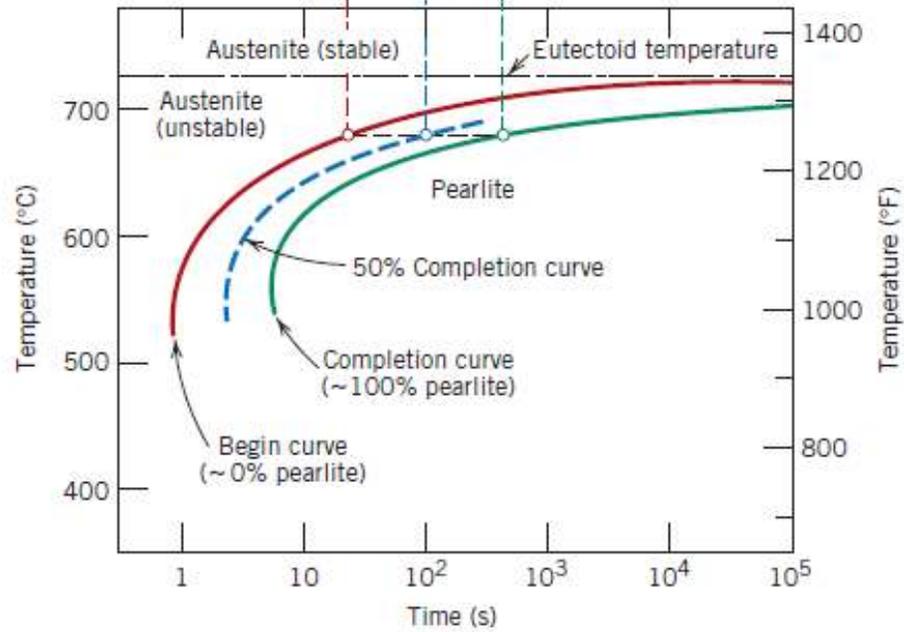
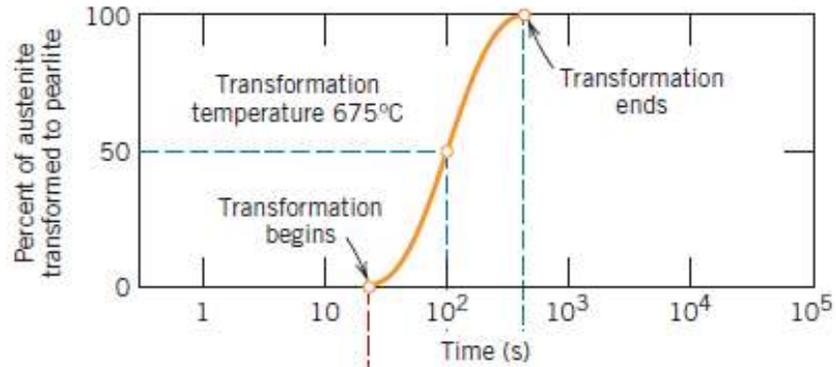


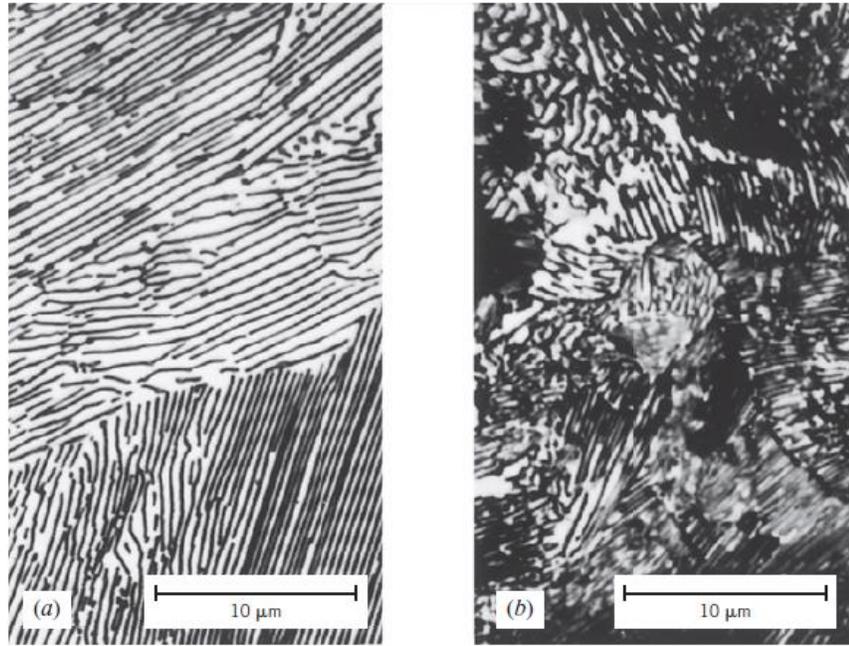
ISOTHERMAL TRANSFORMATION DIAGRAMS

Pearlite

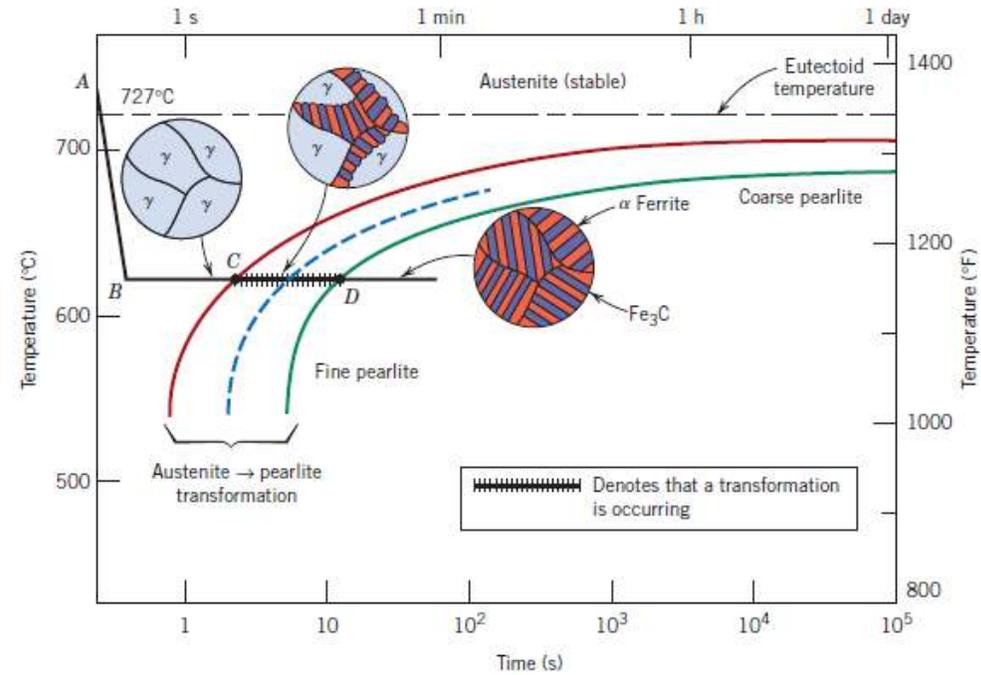


At 0.76 wt% C and 727°C:



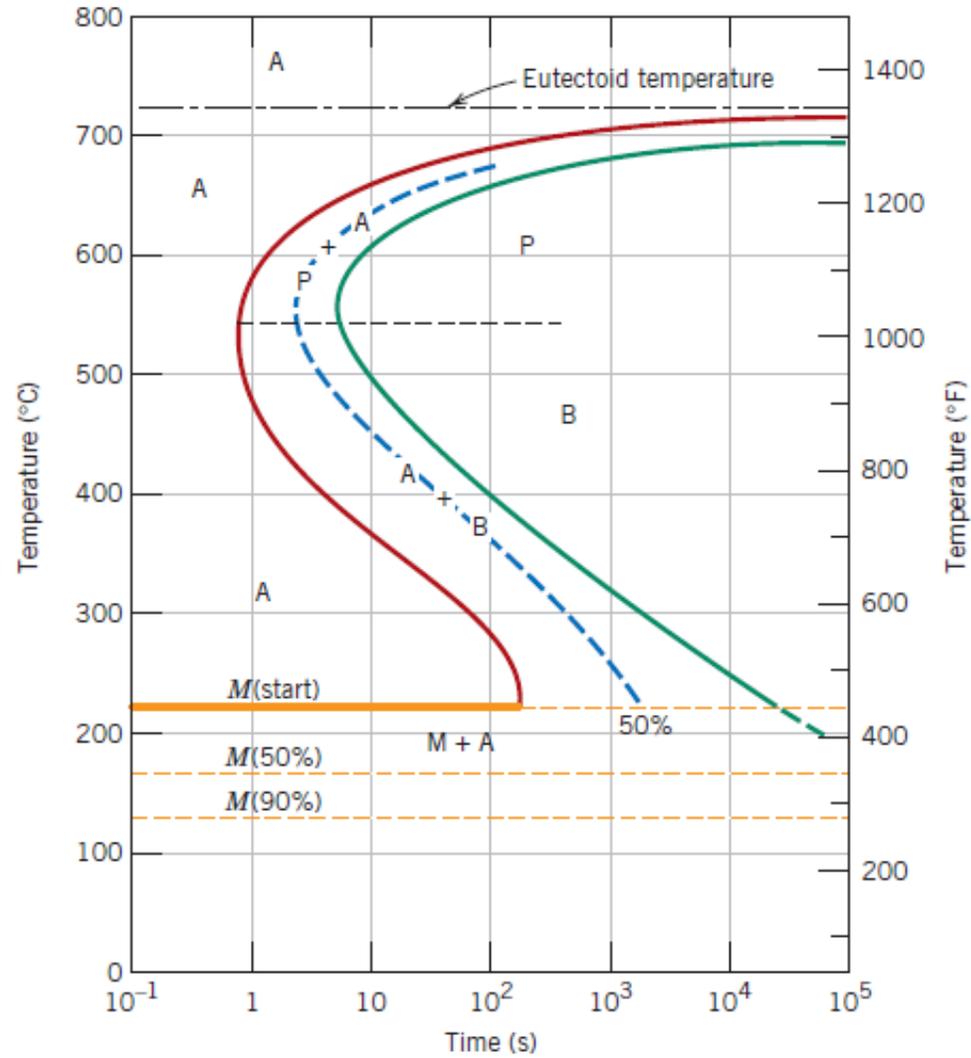


Photomicrographs of
 (a) coarse pearlite
 and (b) fine pearlite.

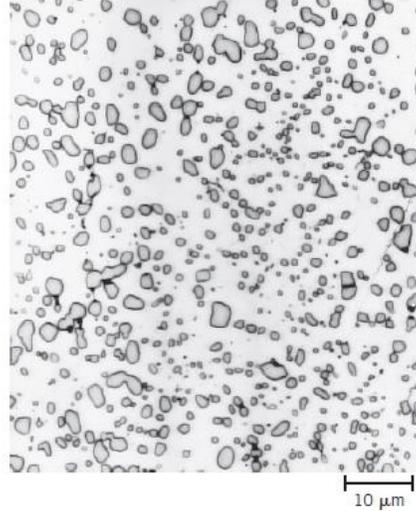




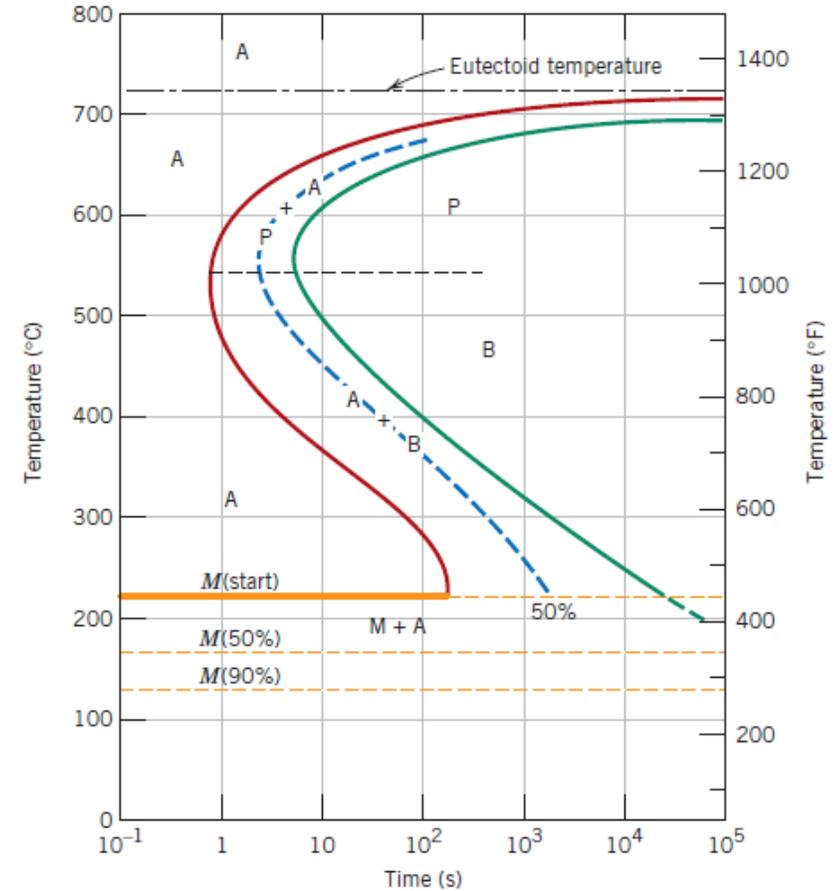
Bainite



Spheroidite



“If a steel alloy having either pearlitic or bainitic microstructures is heated to, and left at, a temperature below the eutectoid for a sufficiently long period of time— for example, at about 700C (1300F) for between 18 and 24 h—yet another microstructure will form. It is called **spheroidite**

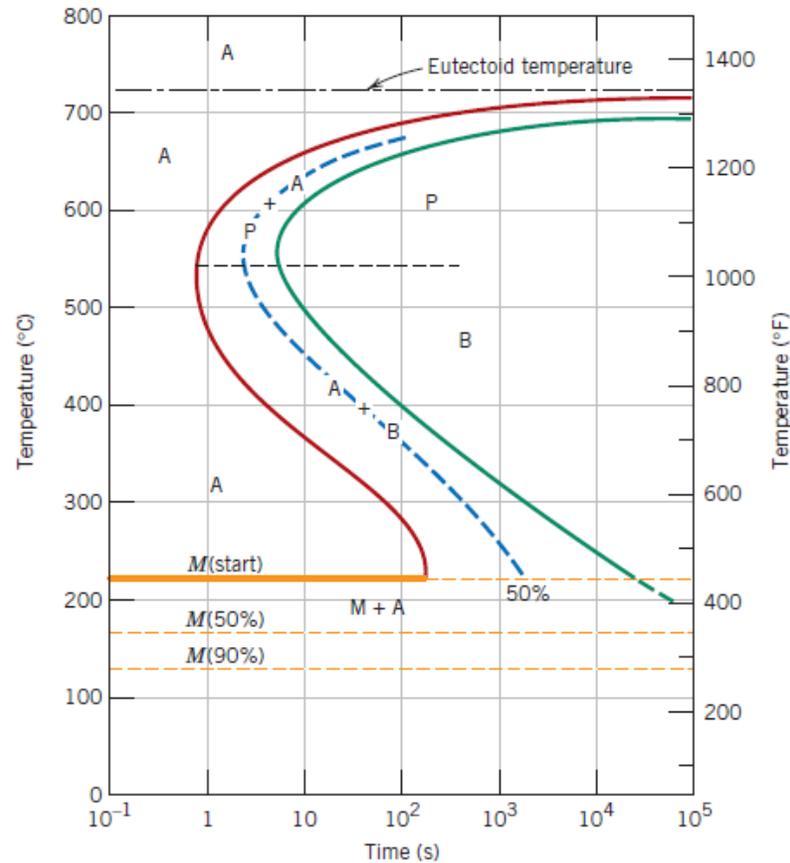




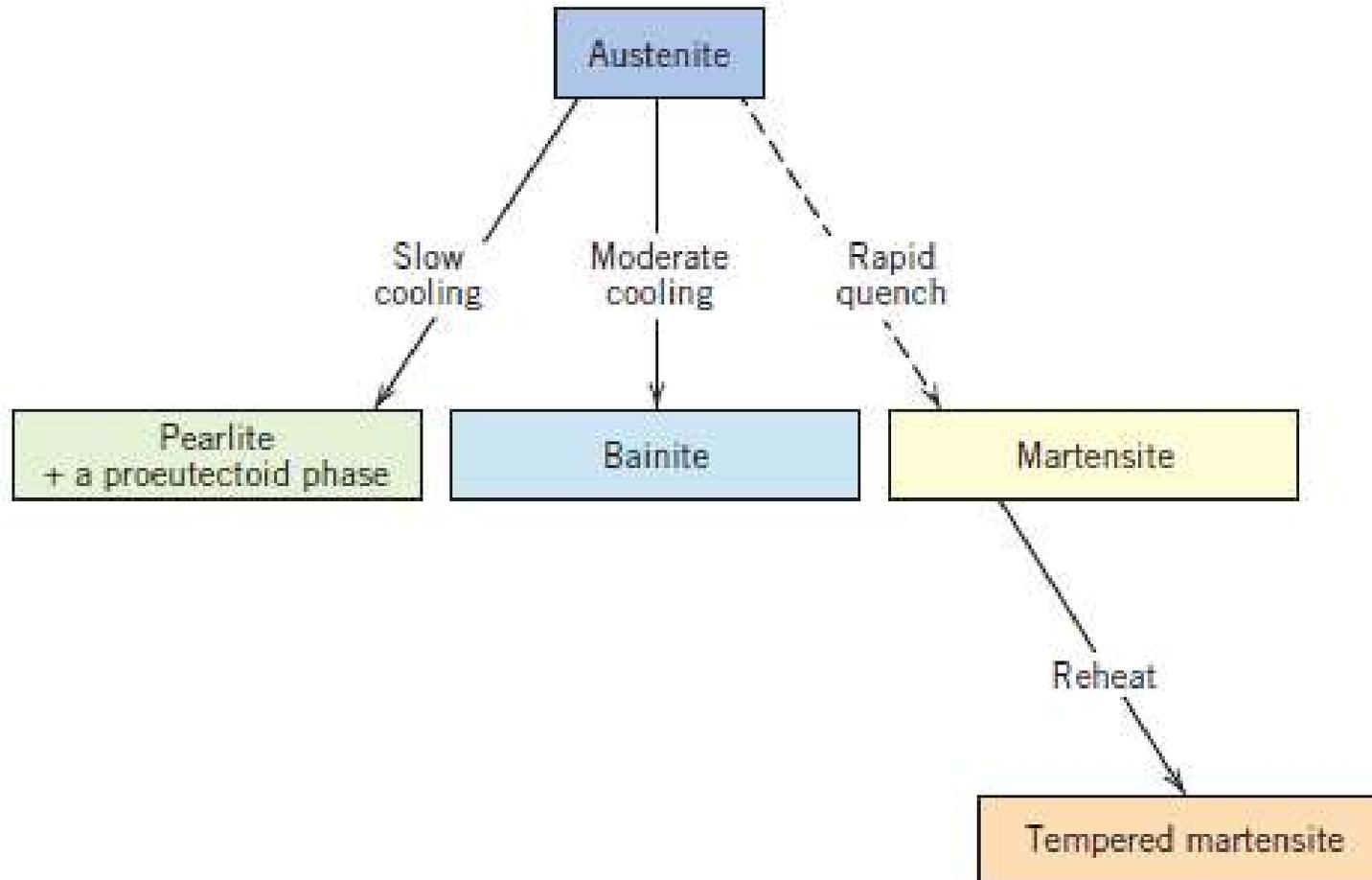
Martensite

“Martensitic transformation is **independent of time**; it is a function only of the temperature to which the alloy is quenched or rapidly cooled.

A transformation of this type is termed an **athermal transformation**”



“Consider an alloy of eutectoid composition that is very rapidly cooled from a temperature above 727C (1341F) to, say, 165C (330F). From the isothermal transformation Diagram, it may be noted that 50% of the austenite will immediately transform to martensite; as long as this temperature is maintained, there will be no further transformation”





MECHANICAL BEHAVIOR OF IRON-CARBON ALLOYS

Pearlite

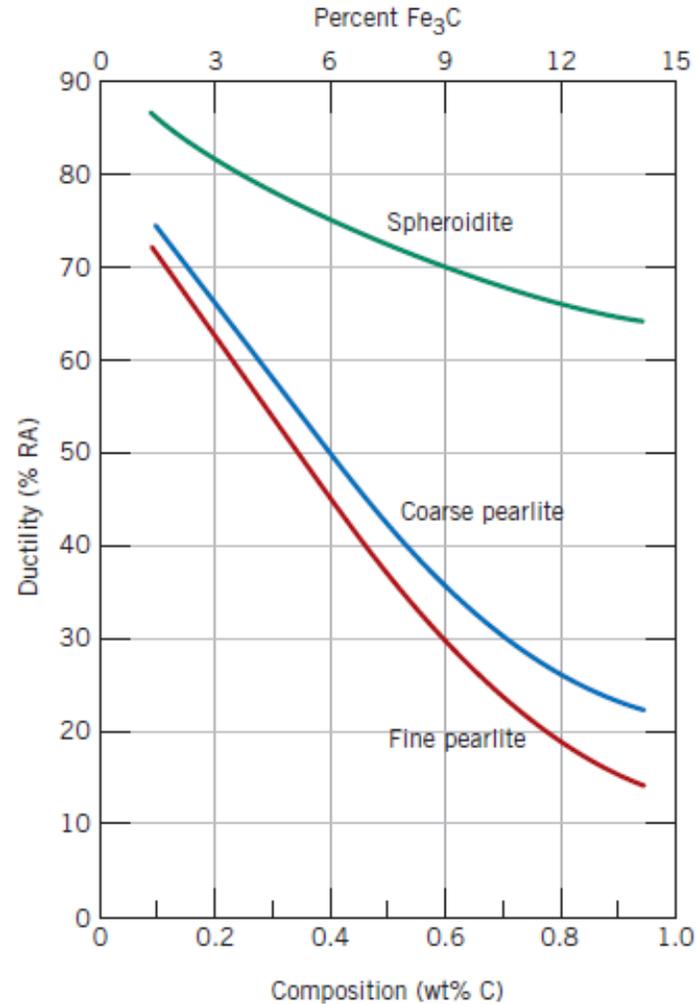




Table 10.2 Summary of Microstructures and Mechanical Properties for Iron–Carbon Alloys

<i>Microconstituent</i>	<i>Phases Present</i>	<i>Arrangement of Phases</i>	<i>Mechanical Properties (Relative)</i>
Spheroidite	α -Ferrite + Fe_3C	Relatively small Fe_3C spherelike particles in an α -ferrite matrix	Soft and ductile
Coarse pearlite	α -Ferrite + Fe_3C	Alternating layers of α -ferrite and Fe_3C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	α -Ferrite + Fe_3C	Alternating layers of α -ferrite and Fe_3C that are relatively thin	Harder and stronger than coarse pearlite, but not as ductile as coarse pearlite
Bainite	α -Ferrite + Fe_3C	Very fine and elongated particles of Fe_3C in an α -ferrite matrix	Hardness and strength greater than fine pearlite; hardness less than martensite; ductility greater than martensite
Tempered martensite	α -Ferrite + Fe_3C	Very small Fe_3C spherelike particles in an α -ferrite matrix	Strong; not as hard as martensite, but much more ductile than martensite
Martensite	Body-centered, tetragonal, single phase	Needle-shaped grains	Very hard and very brittle



End of the ME 221 Course