Introduction to

Materials Science & Engineering

Chapter 9. Phase Diagrams

Contents

Issues to address

- When we combine two elements...

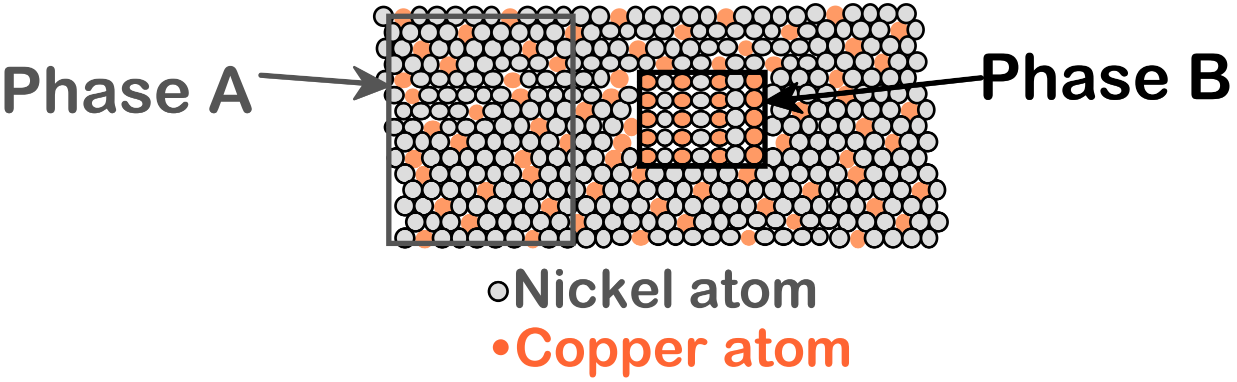
  → What equilibrium state do we get?

- In particular, if we specify...
  - √ Composition (e.g., atomic % Ge - atomic % Sn), and

    Temperature (*T*)

Then...

- √ How many phases do we get?
- √ What is the composition of each phase?
- √ How much of each phase do we get?

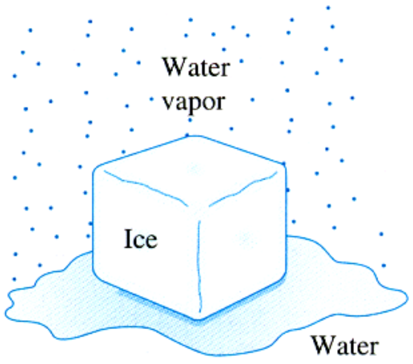


- Phase: chemically and structurally homogeneous region of material.
- Components: chemically distinct and essentially indivisible substance.
- Solubility limit - maximum concentration of solute that may dissolve in a solvent at a given temperature to form a solid solution.
- Precipitate - a solid phase that forms from the original matrix phase when the solubility limit is exceeded.
- Phase diagram - graphical representation of the phases present and the ranges in composition, temperature, and pressure over which the phases are stable.
- **Gibbs phase rule:** $F = C + 2 - P$
  - √ C: # components
  - √ P: # phases in equilibrium
  - √ F: degree of freedom (temperature, pressure, composition.)

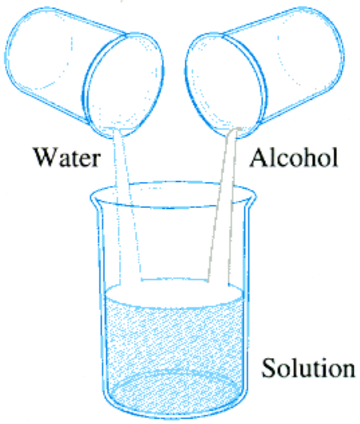
- Binary phase diagram - A phase diagram for a system with two components.
- Ternary phase diagram - A phase diagram for a system with three components.
- Isomorphous phase diagram - A phase diagram in which components display unlimited solid solubility.
- Liquidus temperature - The temperature at which the first solid begins to form during solidification.
- Solidus temperature - The temperature below which all liquid has completely solidified.
- Intermetallic compound - A compound formed of two or more metals that has its own unique composition, structure, and properties.
- Eutectic - A three-phase invariant reaction in which one liquid phase solidifies to produce two solid phases.
- Peritectic - A three-phase reaction in which a solid and a liquid combine to produce a second solid on cooling.

Contents

Phases & Solubility



(a)



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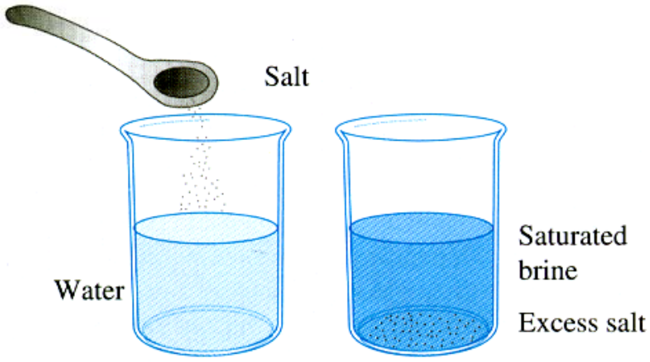

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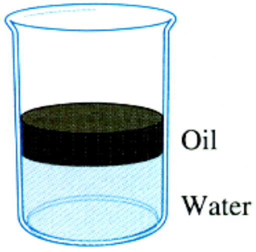


(d)

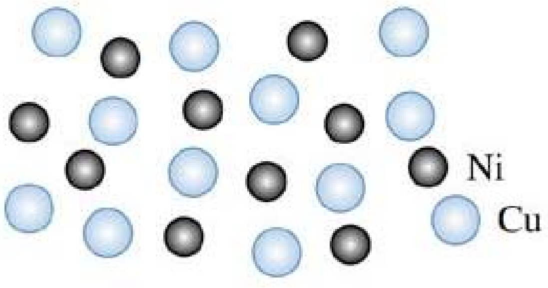
(a) The three forms of water – gas, liquid & solid – are each a phase.

(b) Water and alcohol have unlimited solubility.

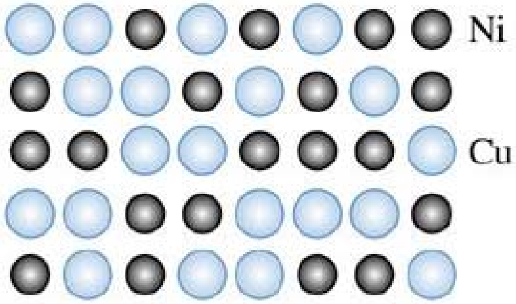
(c) Salt and water have limited solubility.

(d) Oil and water have virtually no solubility.

Solubility Limit



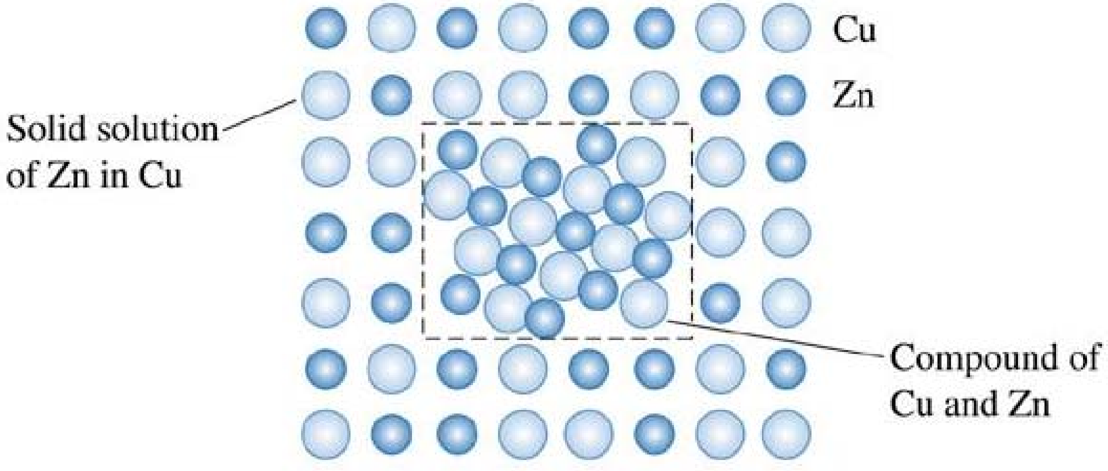
(a)



(b)

-Liquid copper-nickel are completely soluble.

- Solid copper-nickel are completely soluble, with copper and nickel atoms occupying random lattice sites.



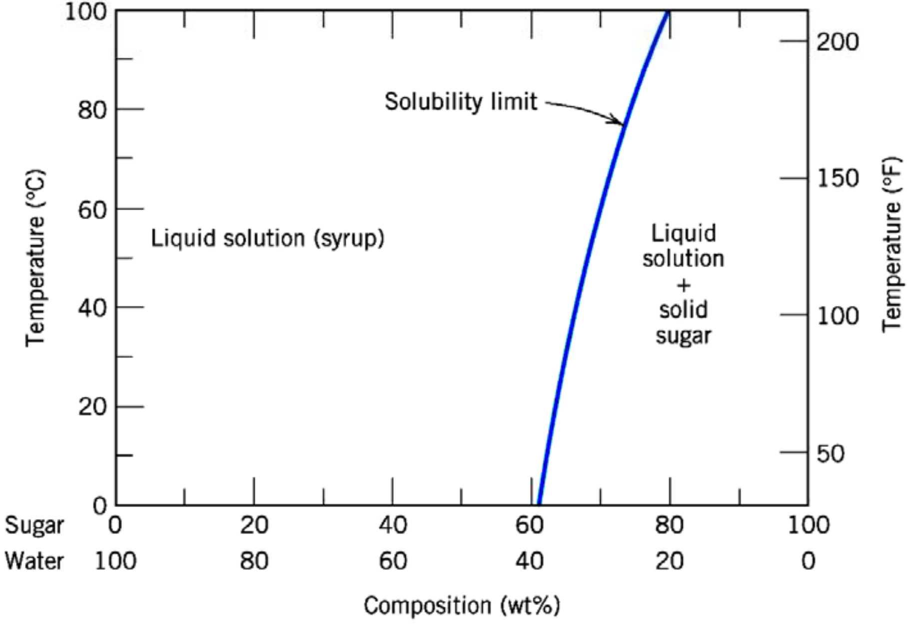
(c)

- In copper-zinc alloys containing more than 30 at. % Zn, a second phase forms because of the limited solubility of zinc in copper.

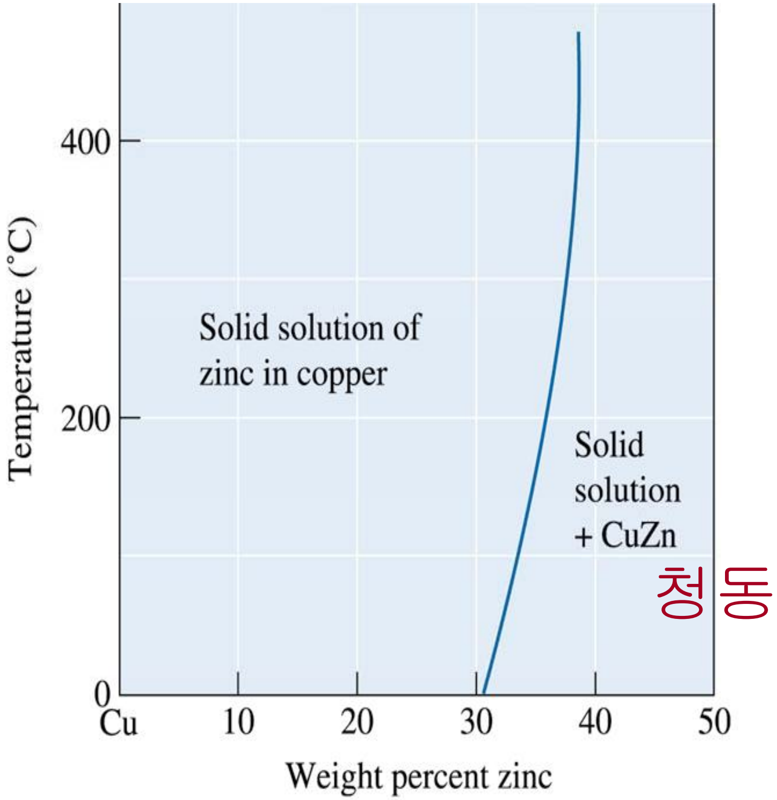
Solubility Limit

- Solubility limit - maximum concentration of solute that may dissolve in a solvent at a given temperature to form a solid solution.
- Precipitate - a new solid phase that forms when the solubility limit is exceeded.

(Fig. 9-1)



$C_{12}H_{22}O_{11} - H_2O$



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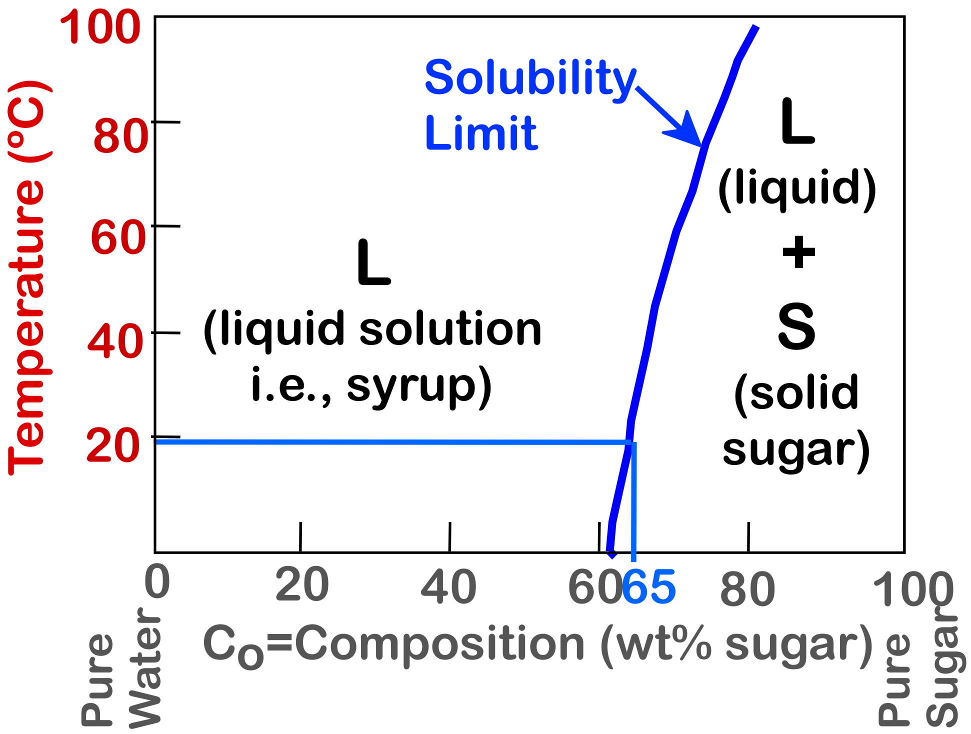
Solubility Limit

- Phase Diagram of Water - Sugar System



Question: What is the solubility limit at 20°C?

Answer: 65 wt. % sugar

If $C_o < 65$ wt. % sugar: syrup

If $C_o > 65$ wt. % sugar: syrup + sugar

- Solubility limit increases with *T*:

  e.g., if *T* = 100°C, solubility limit = 80 wt. % sugar

Components and Phases

- **Components:**

  The elements or compounds which are mixed initially

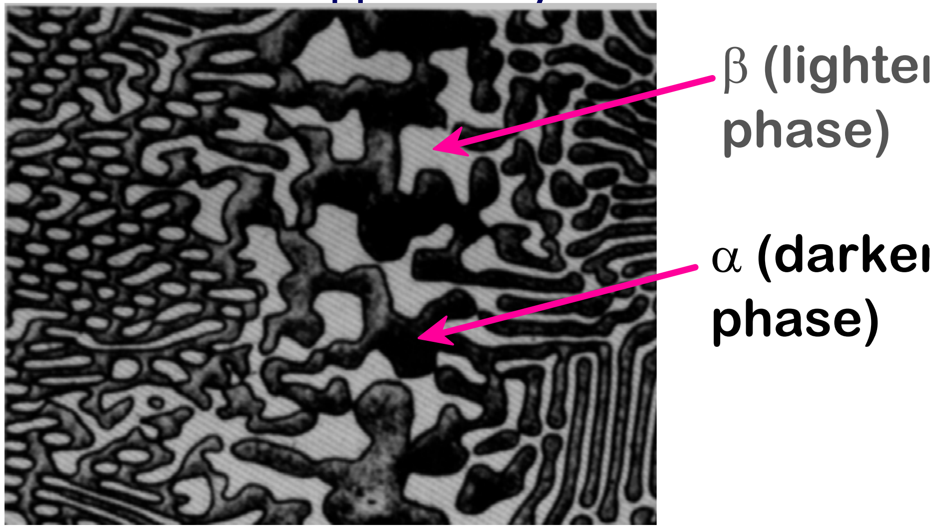
  (e.g., Al and Cu).

- **Phases:**

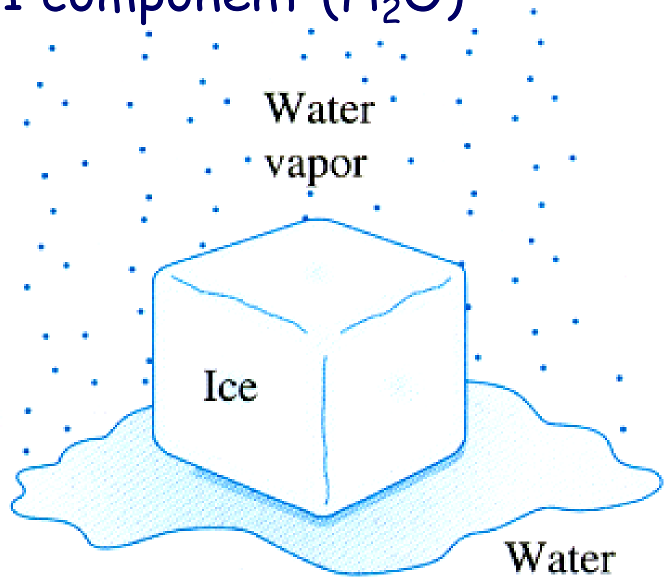
  The physically and chemically distinct material regions

  that result.

Aluminum-Copper Alloy



1 component (H_2O)



Contents

Fundamental Concepts

- Phase diagram: graphical representation of the phases present and the ranges in composition, temperature, and pressure over which the phases are stable.
- Gibbs phase rule: $F = C + 2 - P$ **(Eq. 9-16)**

  C: # components, P: # phases in equilibrium

  F: degree of freedom (temperature, pressure, composition.)

ex) H_2O, $C = 1$, $F = C + 2 - P = 3 - P$

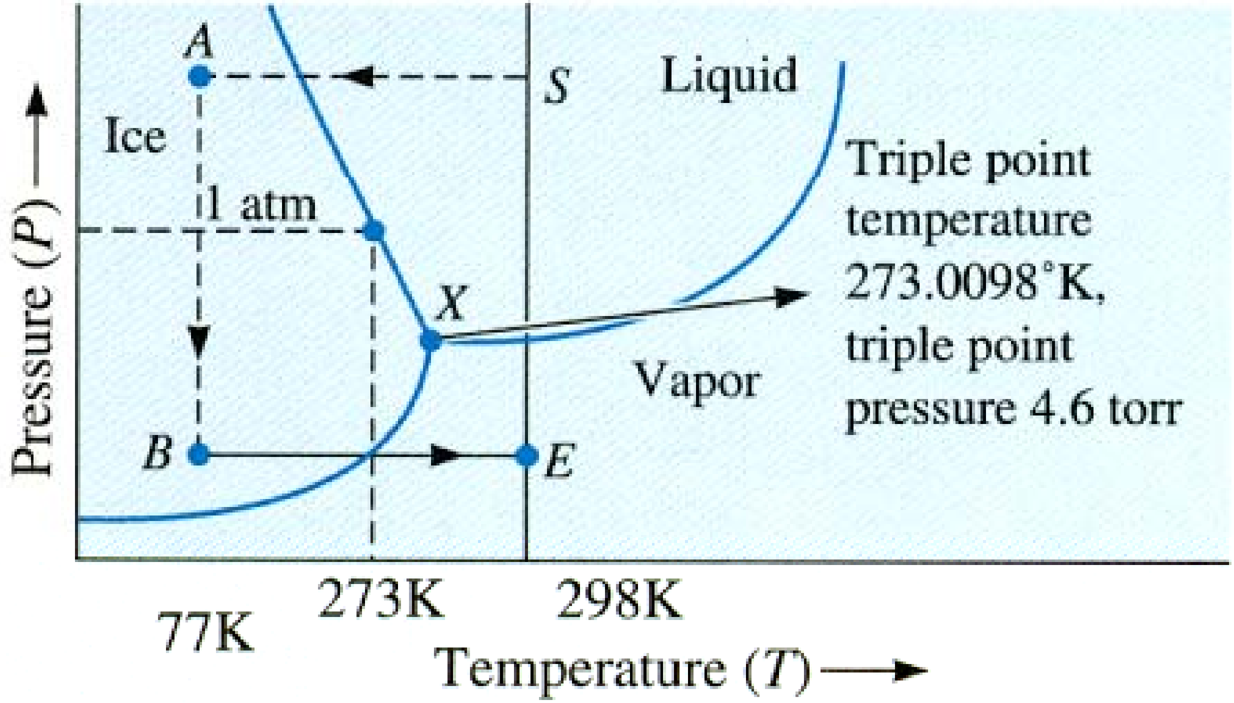
1 phase $F = 2$

2 phase $F = 1$

3 phase $F = 0$ (invariant)

* pressure constant → $F = C + 1 - P$

One-Component Phase Diagram

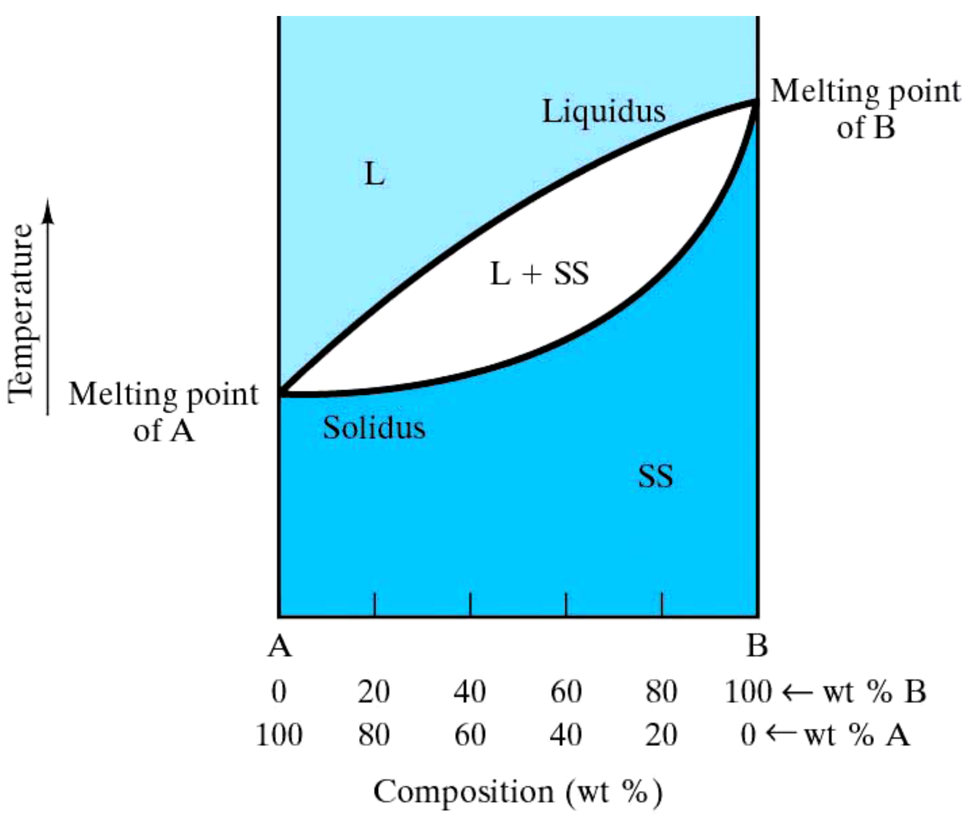


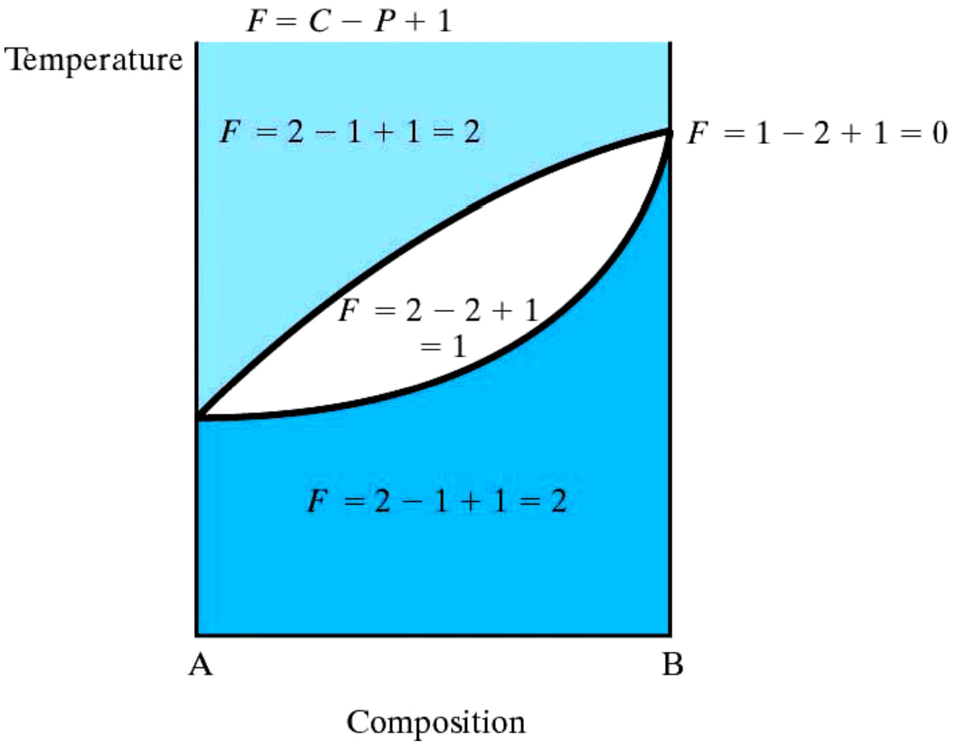
(Fig. 9-2)

Pressure-temperature diagram for H_2O. Notice the solid-liquid line sloping to the left. At normal pressure (1 atm or 760 torr), the melting temperature is 273 K.

Isomorphous Phase Diagram

Complete liquid and solid solutions





(Fig. 9-3)

Constant pressure:

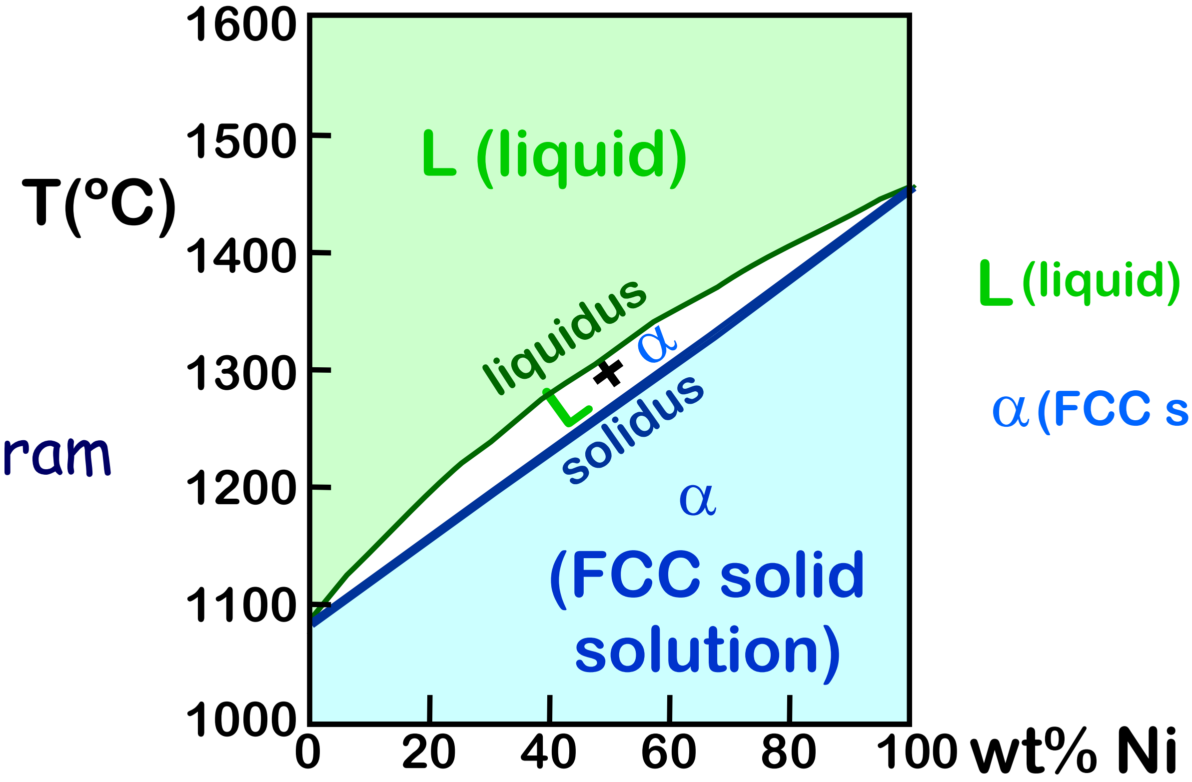
$F = C + 1 - P$, $C = 2$, $F = 3 - P$

Phase Diagrams

- Tell us about the phases as a function of T, C_o, and P
- For this course:
  - Binary systems: just 2 components
  - Independent variables: T and C_o (at P = 1 atm)

Cu-Ni

Phase diagram



L (liquid)

α (FCC solid solution)

Phase Diagrams: Number and Types of Phases

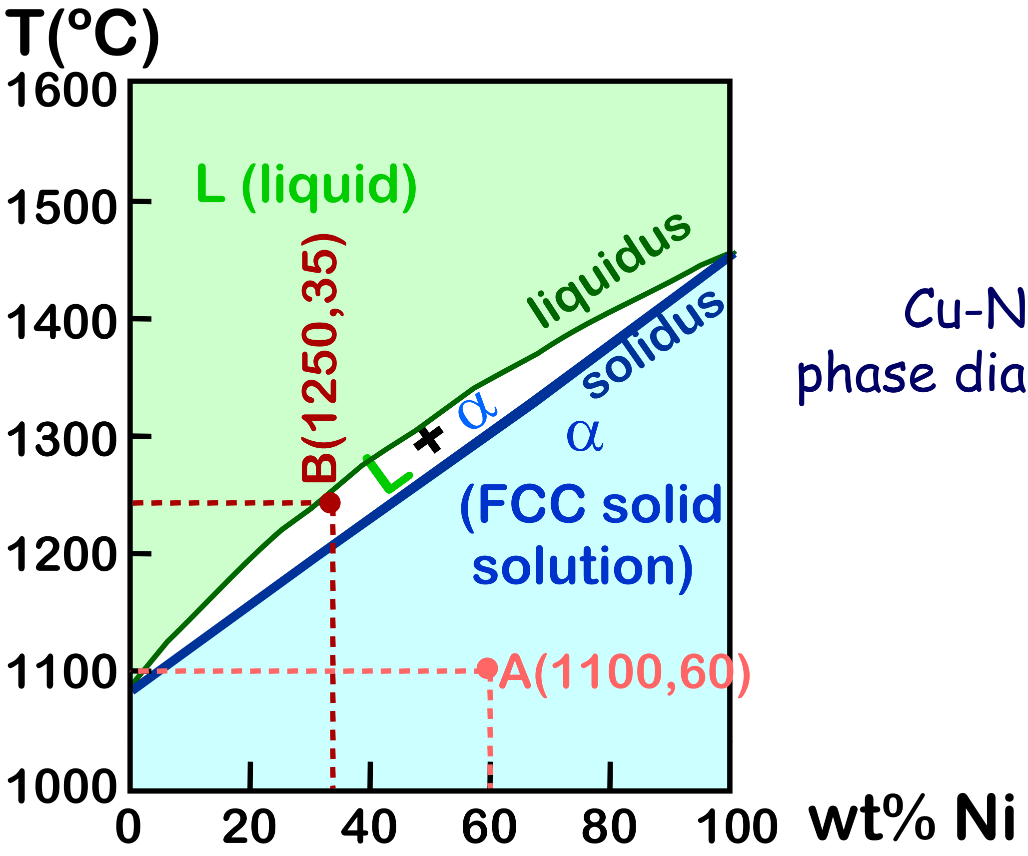
Rule 1: If we know *T* and C_o, then we know:

- the number and types of phases present.

Examples:

A(1100, 60):
1 phase: α

B(1250, 35):
2 phases: L + α



Cu-Ni
phase diagram

Phase Diagrams: Composition of Phases

Rule 2: If we know *T* and C_o, then we know:

- the composition of each phase.

Examples:

C_O = 35wt%Ni

At T_A:

Only Liquid (L)

$C_L = C_O$ (= 35wt% Ni)

At T_D:

Only Solid (α)

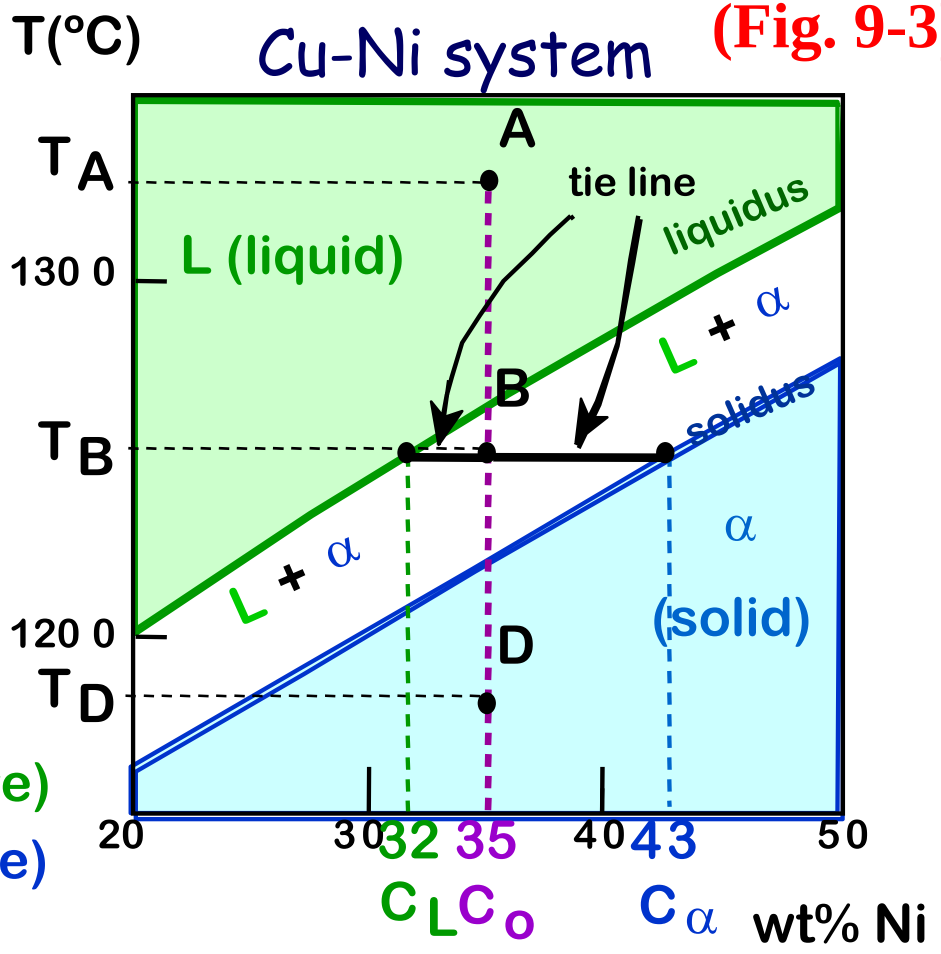
$C_\alpha = C_O$ (= 35wt% Ni)

At T_B:

Both α and L

$C_L = C_{liquidus}$ (= 32wt% Ni here)

$C_\alpha = C_{solidus}$ (= 43wt% Ni here)



(Fig. 9-3)

Phase Diagrams: Fractions of Phases

Rule 3: If we know *T* and C_o, then we know:
- the amount of each phase (given in wt. or at. %).

- Examples:

C_O = 35wt%Ni

At T_A: Only Liquid (L)

$W_L = 100\text{wt\%},\ W_\alpha = 0$

At T_D: Only Solid (α)

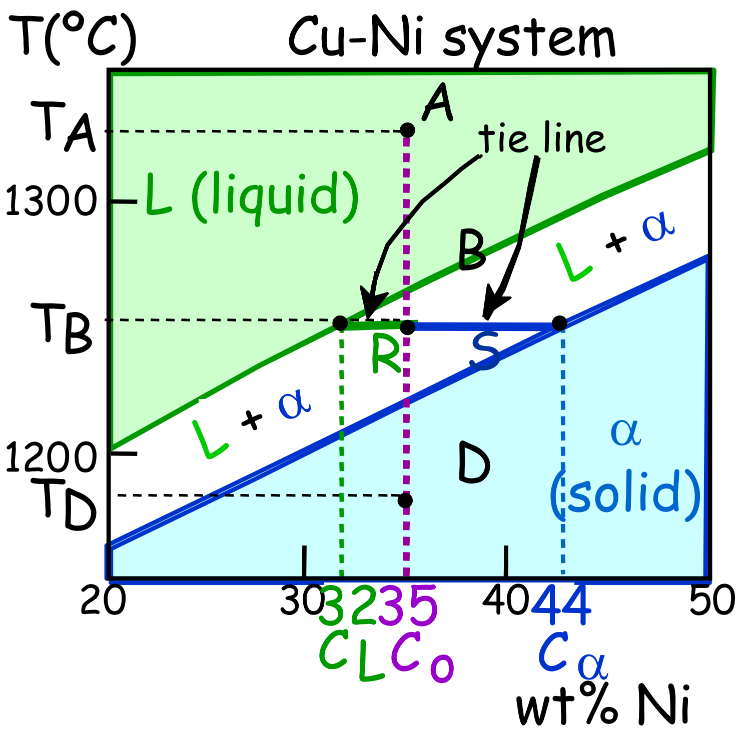
$W_L = 0,\ W_\alpha = 100\text{wt\%}$

At T_B: Both α and L

What would be W_L and W_α?

$$\boxed{W_L = \frac{S}{R+S}} = \frac{44-35}{44-32} = 75wt\%$$

$$\boxed{W_\alpha = \frac{R}{R+S}} = \frac{35-32}{44-32} = 25wt\%$$



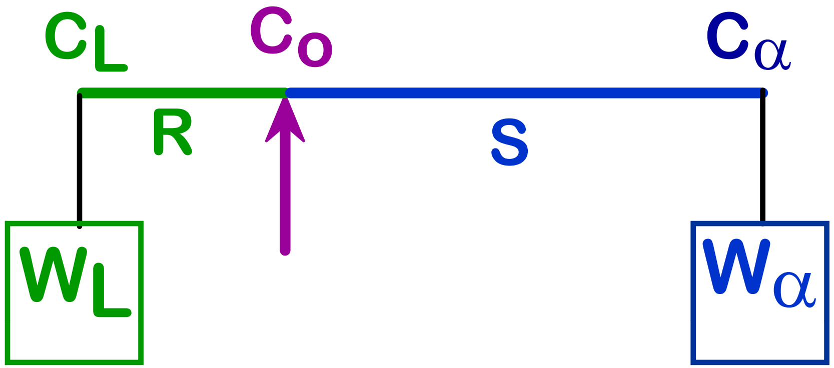
The Lever Rule (Proof)

- Sum of weight fractions: $W_L + W_\alpha = 1$ **(Example 9-1)**
- Conservation of mass (Ni): $C_o = W_L C_L + W_\alpha C_\alpha$
- Combine above equations:

$$\boxed{W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{S}{R+S}}$$

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

- A geometric interpretation:



moment equilibrium:

$$\underset{\substack{\nwarrow \\ \boxed{1 - W_\alpha}}}{\boxed{W_L}} R = W_\alpha S$$

solving gives Lever Rule

Contents

Cooling in a Cu-Ni Binary (equilibrium)

- Phase diagram: Cu-Ni system.
- System is:
  - binary

    2 components: Cu and Ni
  - isomorphous

    complete solubility

A phase field extends

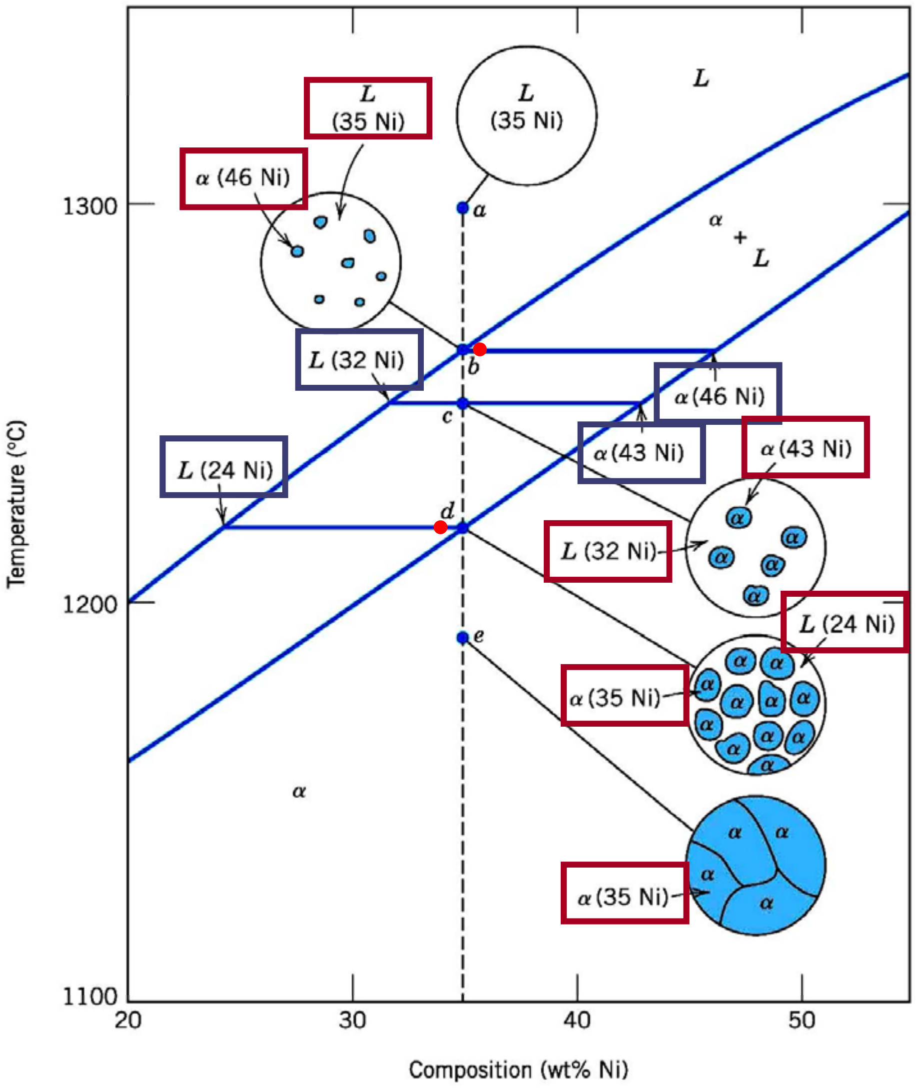
From 0 to 100 wt. % Ni

- Consider

  C_o = 35 wt. % Ni

What would be the microstructures?

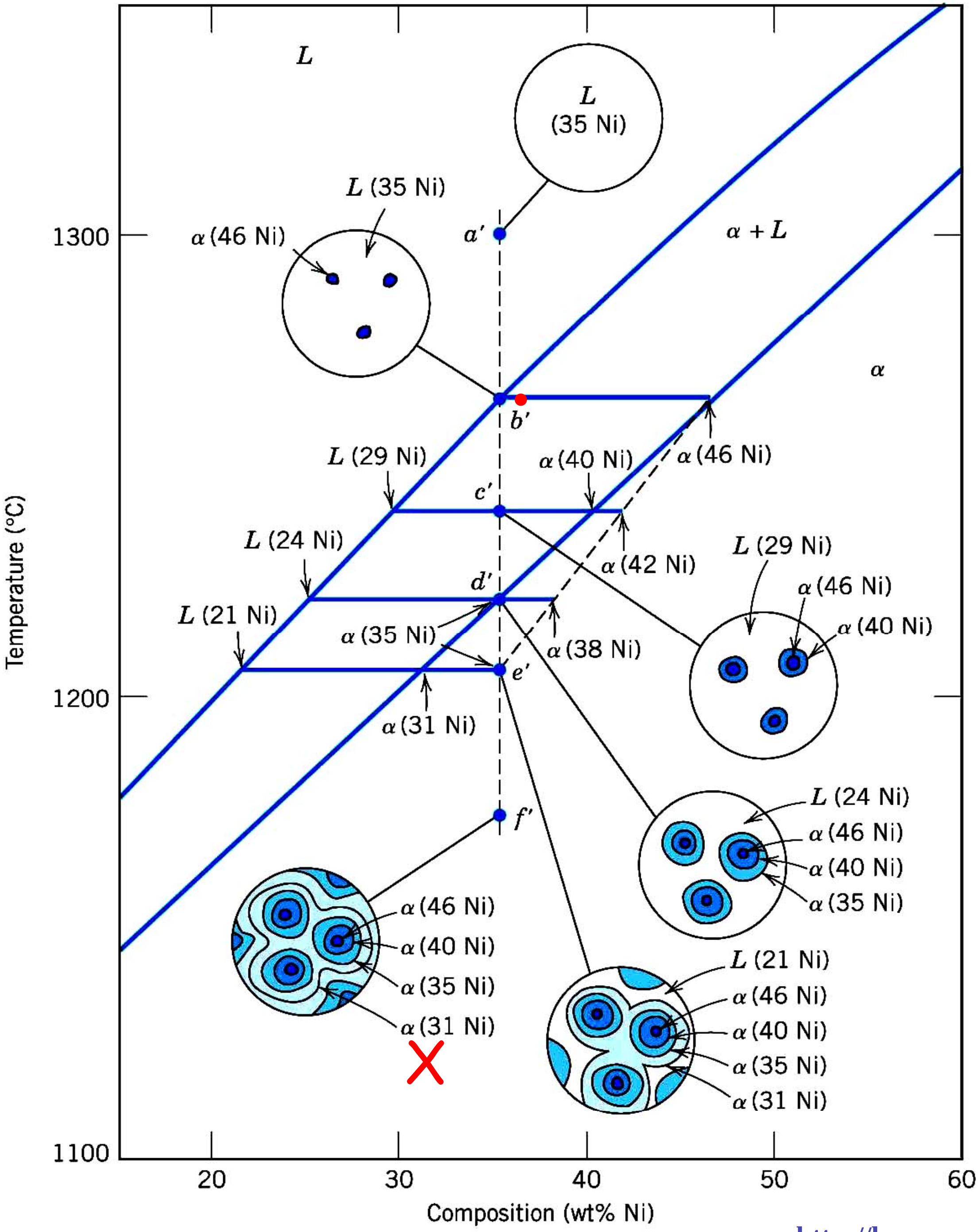
(Fig. 9-4 incorrect)



Cooling in Cu-Ni (nonequilibrium)

(skip)

(Fig. 9-5)



- Consider
  C_0 = 35 wt. % Ni.

Contents

Binary Eutectic Systems

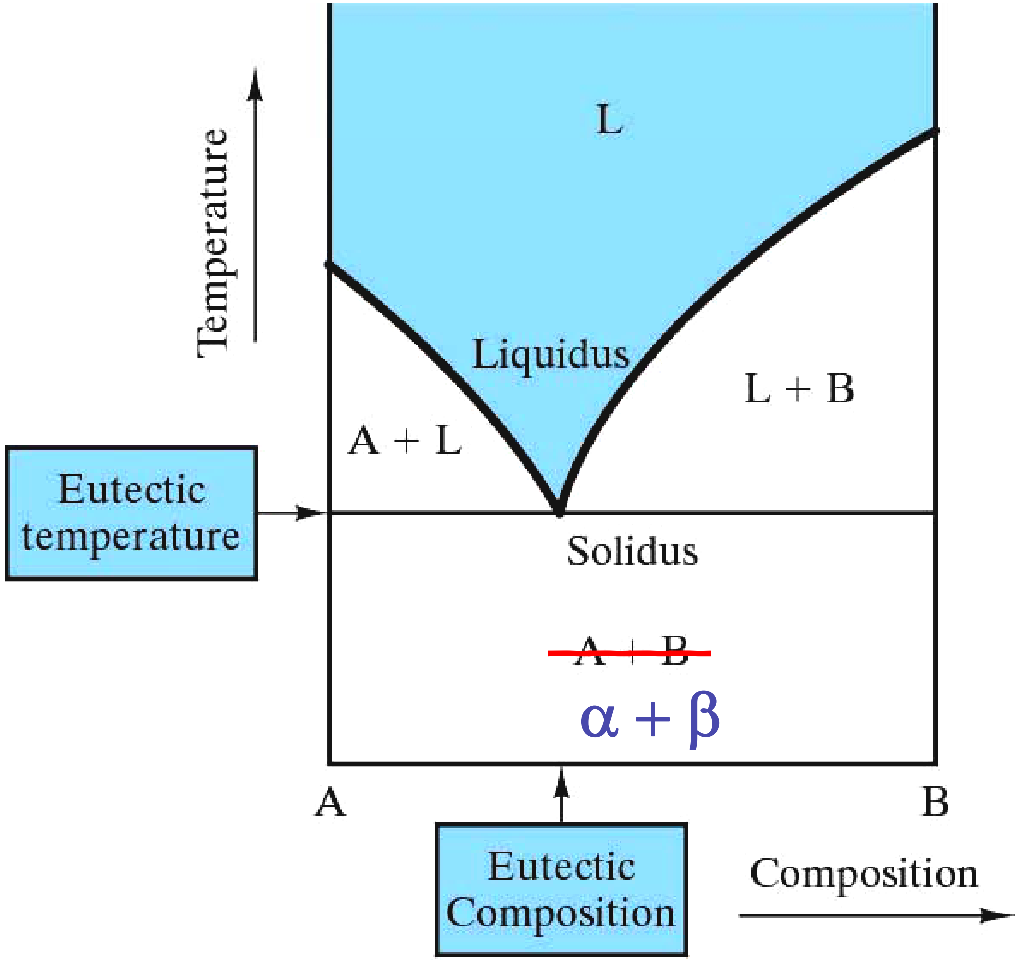
Greek - Easily melting

A special composition with an easy melting *T* **(Fig. 9-7)**

2 components

Eutectic reaction

$L \rightarrow \alpha + \beta$



Binary Eutectic Systems

2 components

It has a special composition with a minimum melting *T*.

Ex.: Cu-Ag system

3 single phase regions (L,α, β)

Limited solubility:

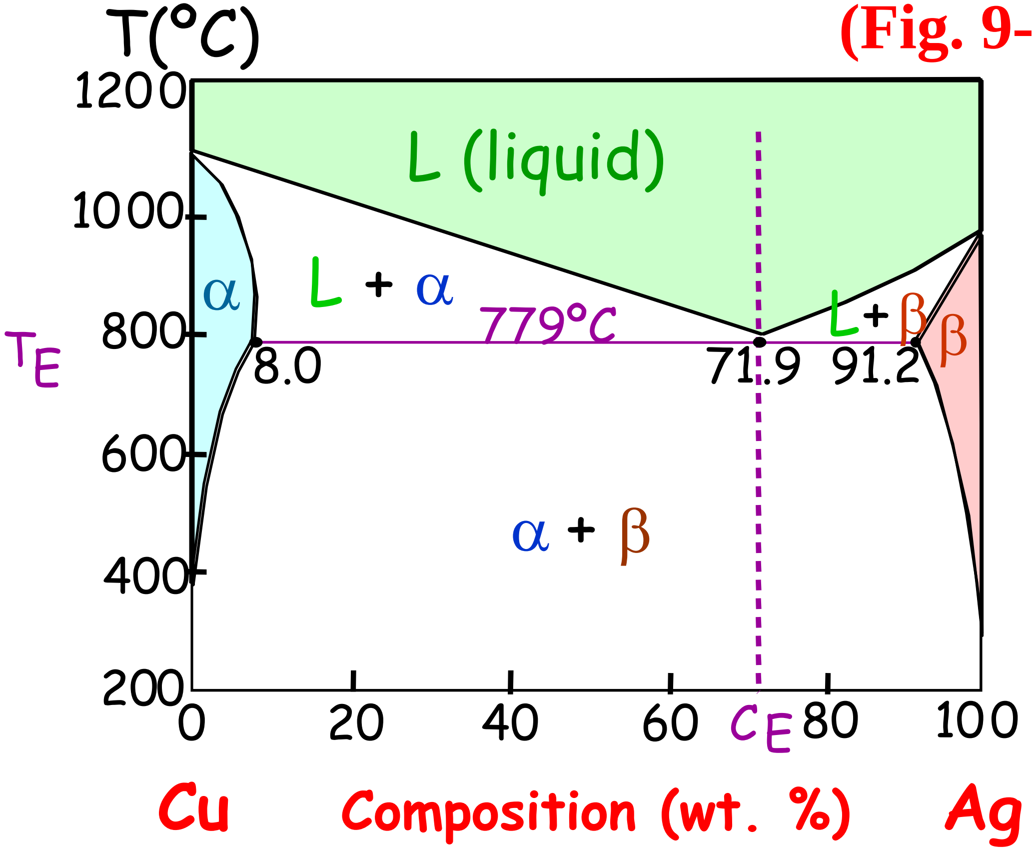
α: mostly Cu

β: mostly Ag

T_E: No liquid below T_E

C_E: Min. melting *T* composition

(Fig. 9-7)



Example: Pb-Sn Eutectic System

For a 40 wt. % Sn – 60 wt. % Pb alloy at 150°C, find...

- the phases present: $\alpha + \beta$
- the compositions of the phases:

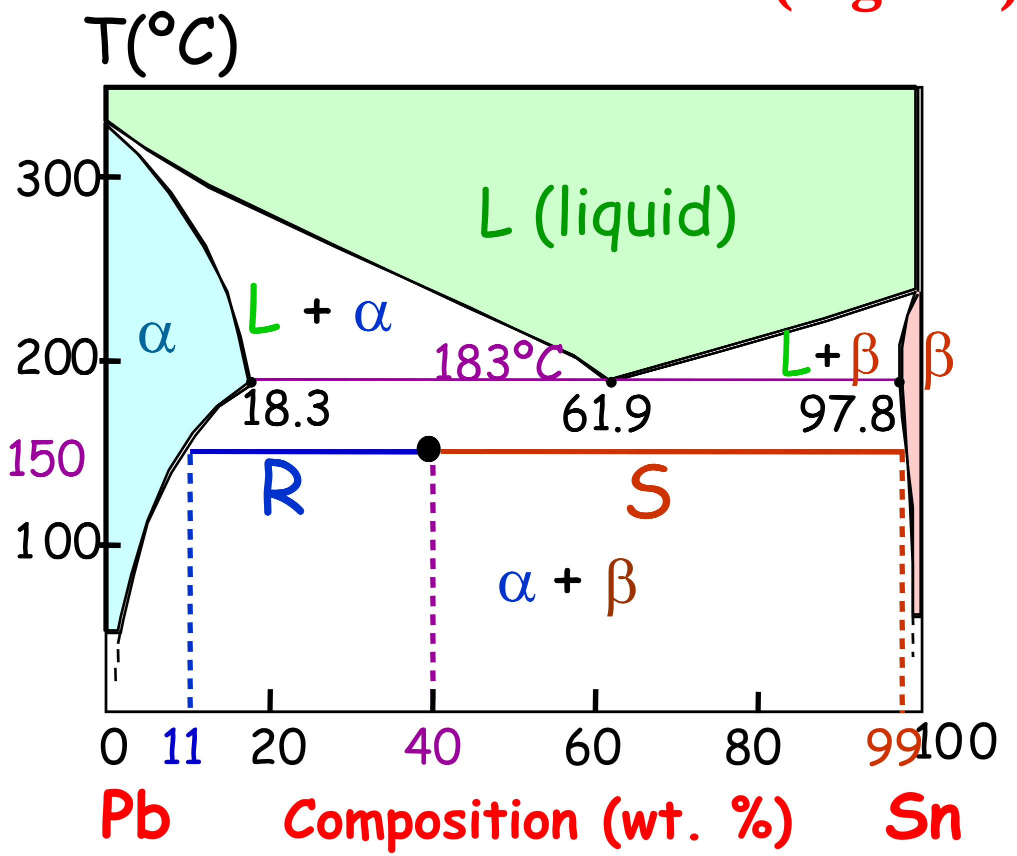
  C_α = 11 wt. % Sn

  C_β = 99 wt. % Sn
- the relative amounts of each phase:

$$W_\alpha = \frac{59}{88} = 67\,\mathrm{wt}\,\%$$

$$W_\beta = \frac{29}{88} = 33\,\mathrm{wt}\,\%$$

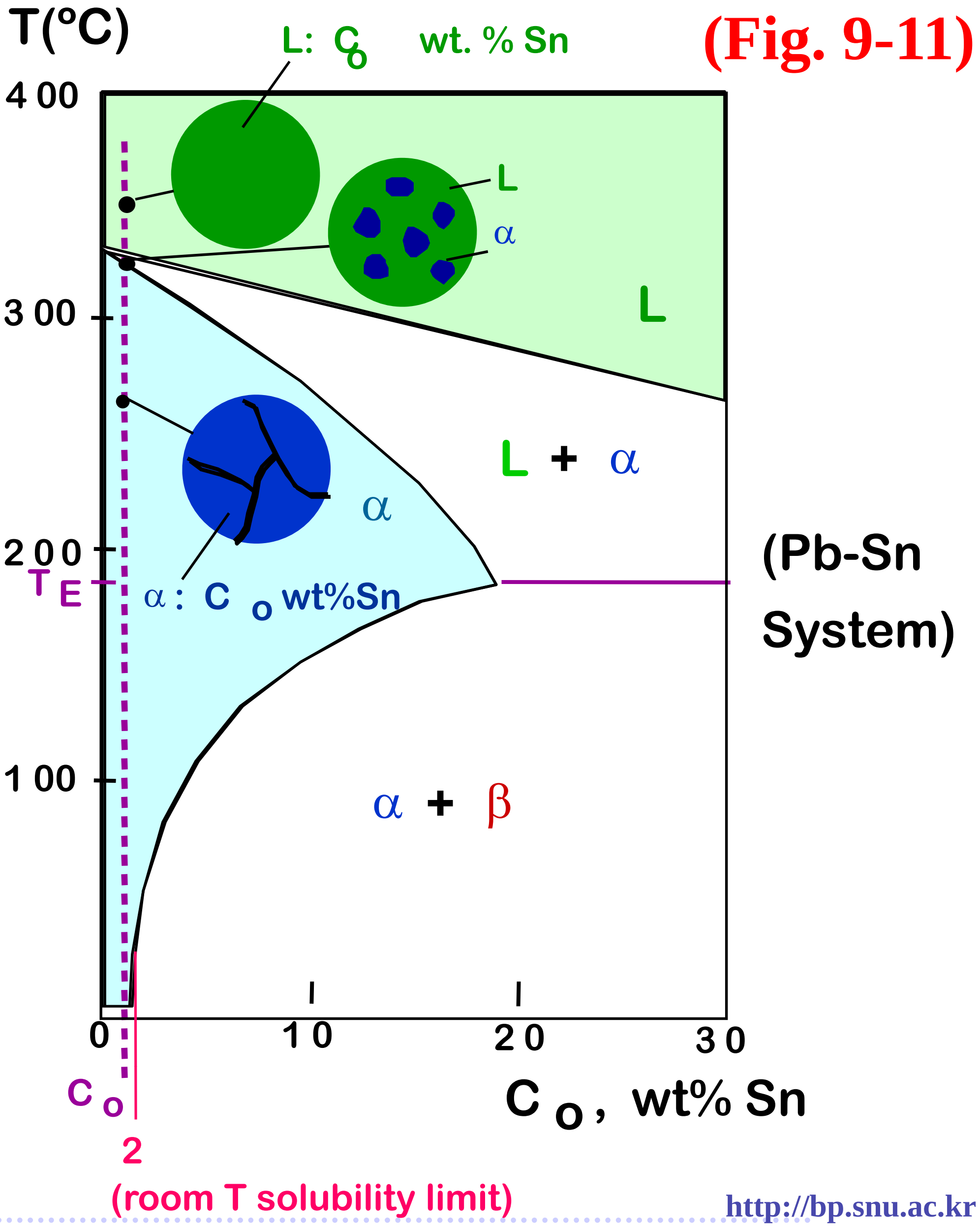
(Fig. 9-8)
(Fig. 9-9)



Microstructures in Eutectic Systems - I

- $C_o < 2$ wt. % Sn
- Result →

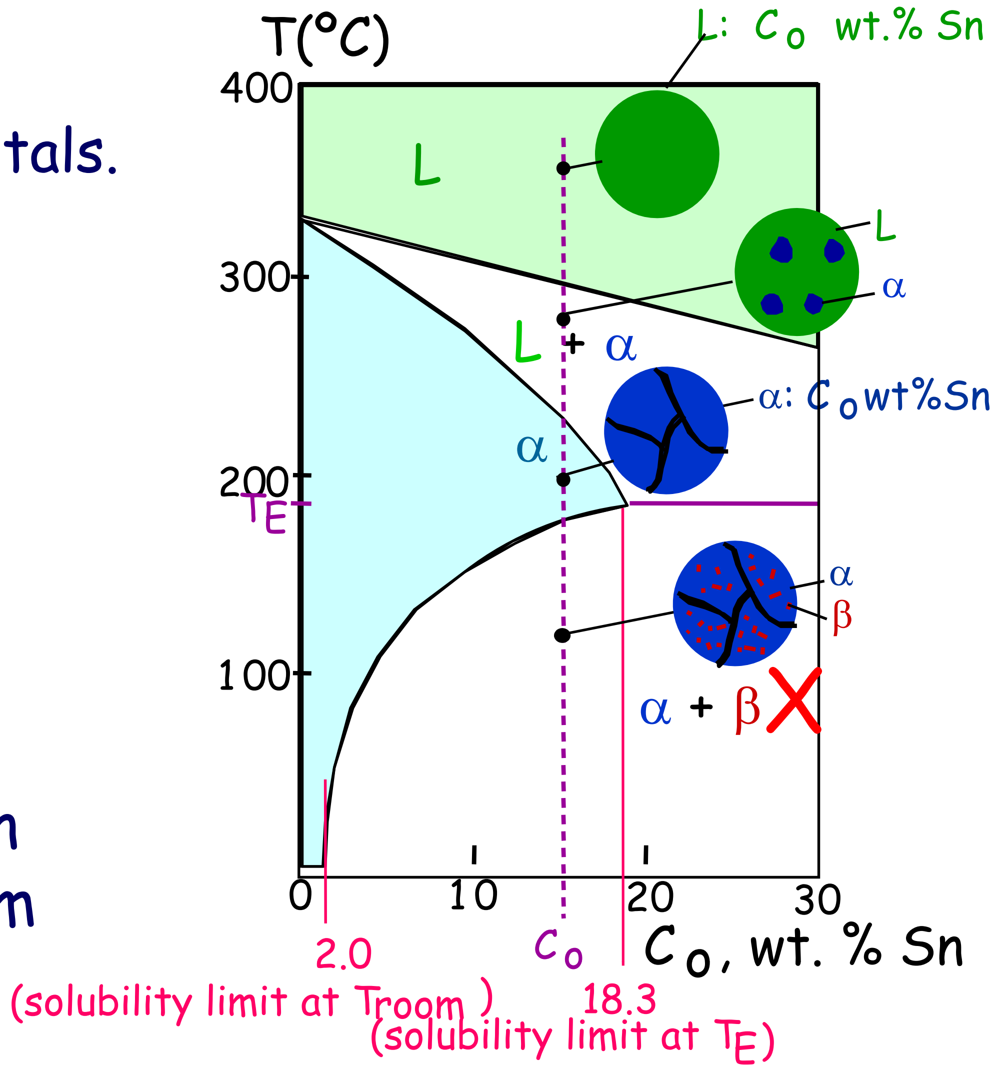
  polycrystal of α grains



Microstructures in Eutectic Systems - II

- 2 wt. % Sn < C_o < 18.3 wt. % Sn
- Result → α polycrystal
  with fine β crystals.

(Fig. 9-12)

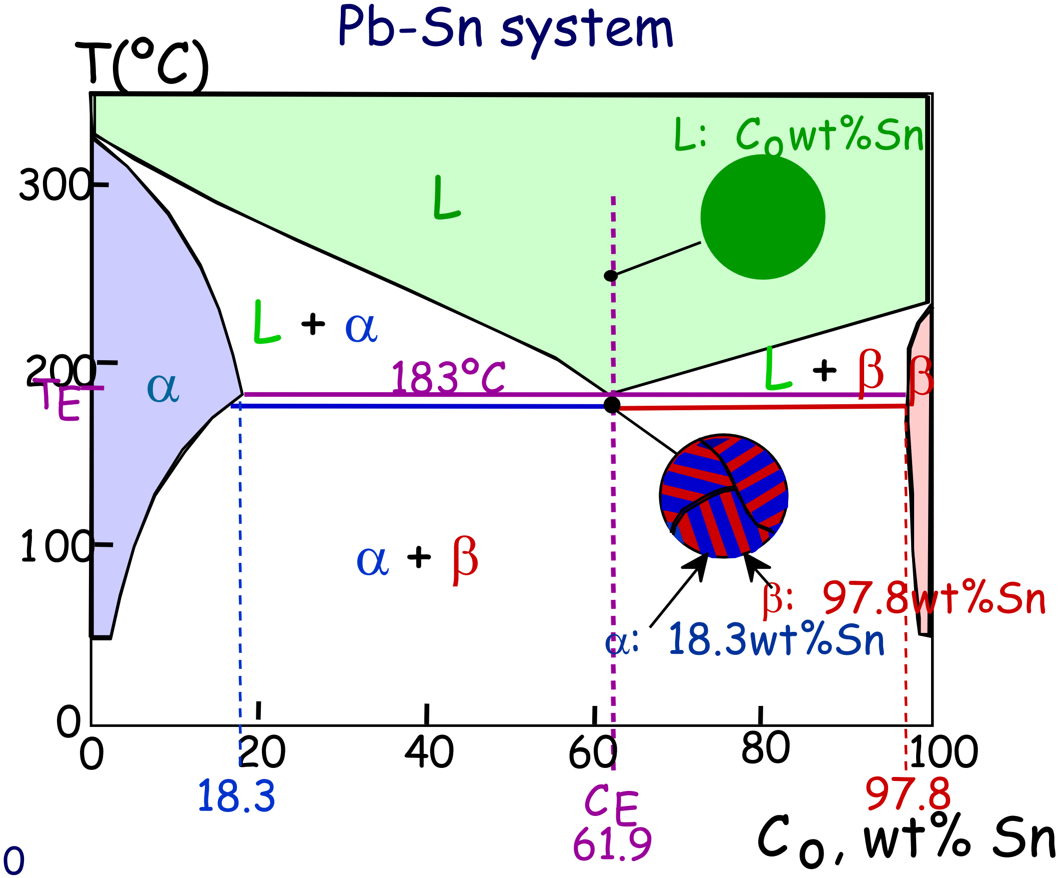


Pb-Sn
system

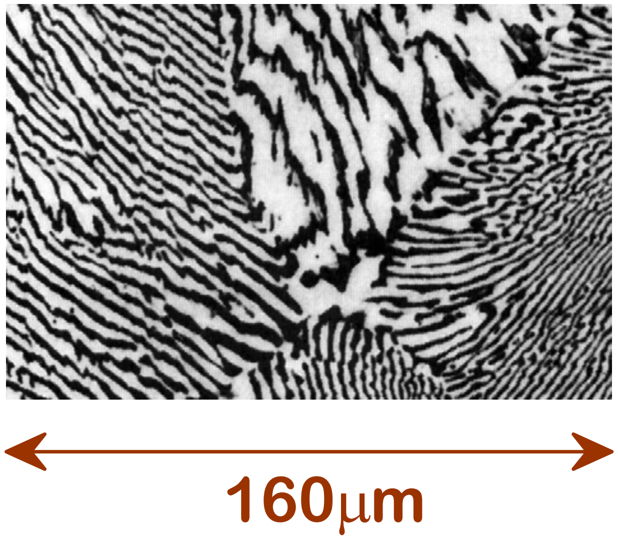
Microstructures in Eutectic Systems - III

- $C_o = C_E$
- Result → Eutectic microstructure --- alternating layers of α and β crystals.

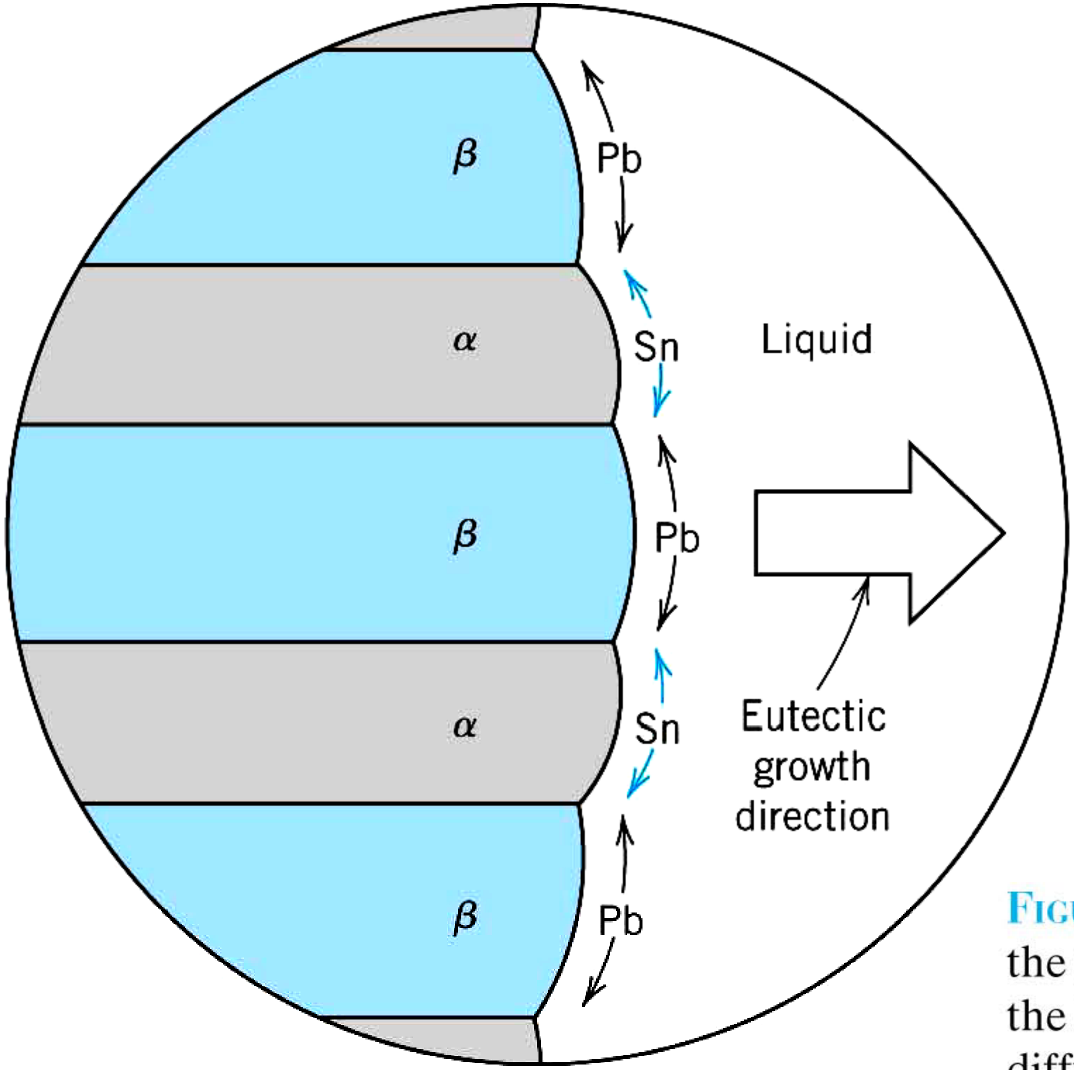
(Fig. 9-13)



(Fig. 9-14)



Formation of Eutectic Lamellar Structure



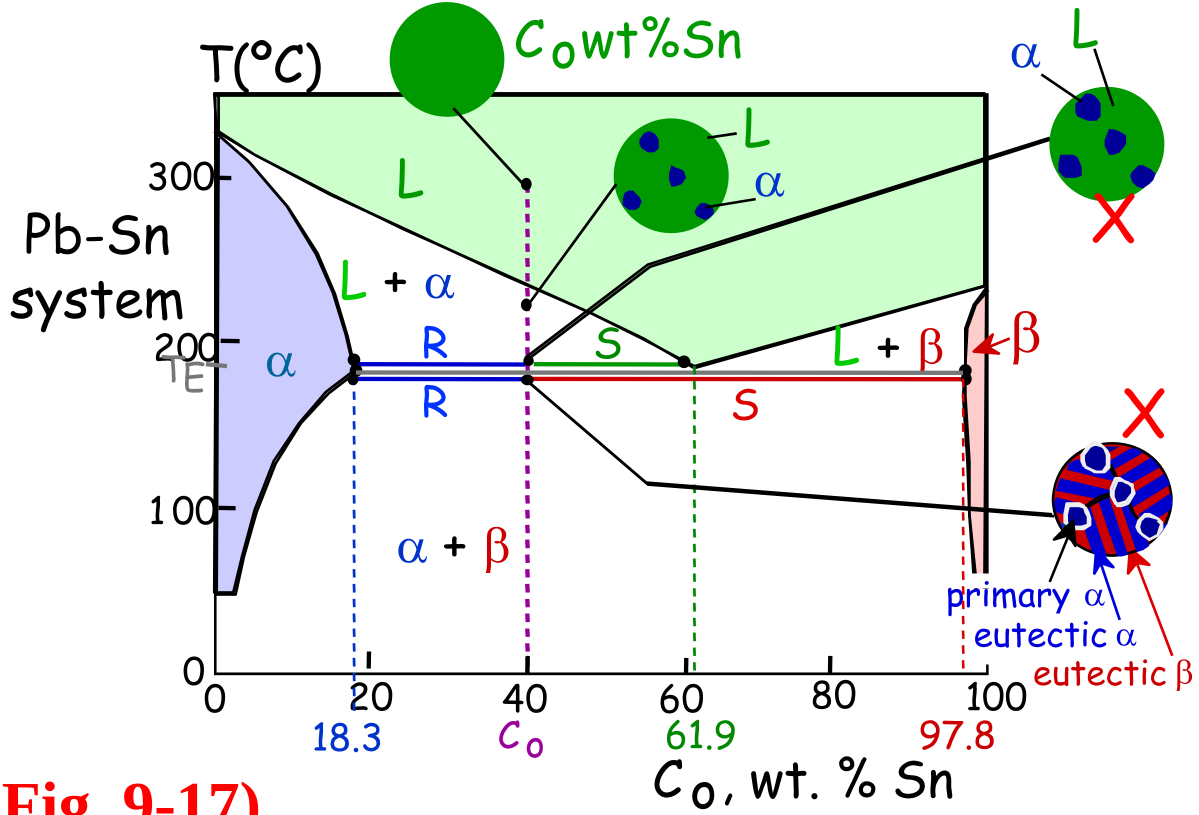
(Fig. 9-15)

FIGURE 9.13 Schematic representation of the formation of the eutectic structure for the lead–tin system. Directions of diffusion of tin and lead atoms are indicated by colored and black arrows, respectively.

Microstructures in Eutectic Systems

- 18.3 wt. % Sn < C_o < 61.9 wt. % Sn
- Result: α crystals and an eutectic microstructure

(Fig. 9-16)



(Fig. 9-17)

Just above T_E :

C_α = 18.3 wt. % Sn

C_L = 61.9 wt. % Sn

$W_\alpha = \frac{S}{R + S}$ =50 wt. %

$W_L = (1-W_\alpha)$ =50 wt. %

Just below T_E :

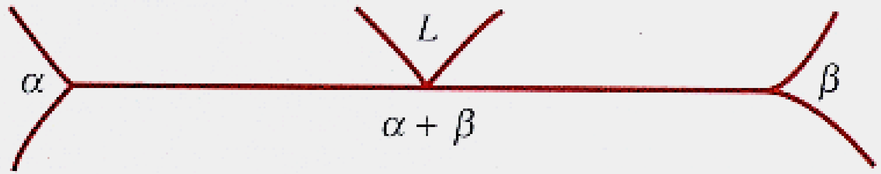
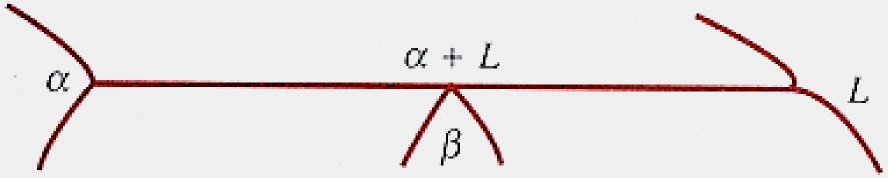
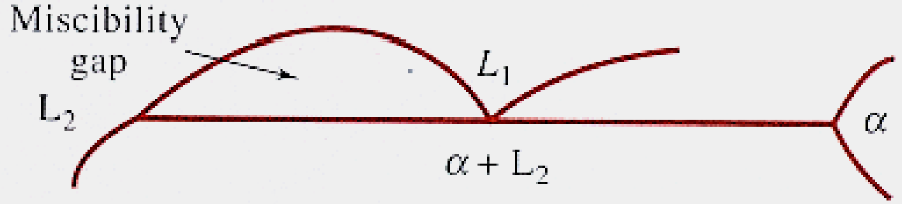
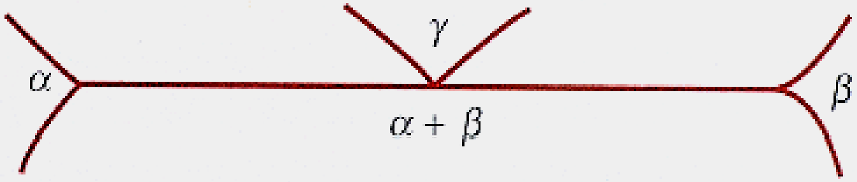
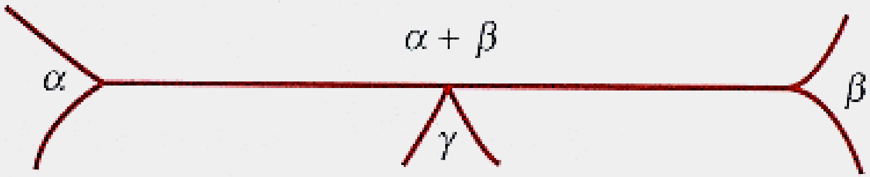
C_α = 18.3 wt. % Sn

C_β = 97.8 wt. % Sn

$W_\alpha = \frac{S}{R + S}$ =73 wt. %

W_β = 27 wt. %

Invariant Reactions

Eutectic	$L \rightarrow \alpha + \beta$	
Peritectic	$\alpha + L \rightarrow \beta$	
Monotectic	$L_1 \rightarrow L_2 + \alpha$	
Eutectoid	$\gamma \rightarrow \alpha + \beta$	
Peritectoid	$\alpha + \beta \rightarrow \gamma$	

Other Examples

(Fig. 9-20)

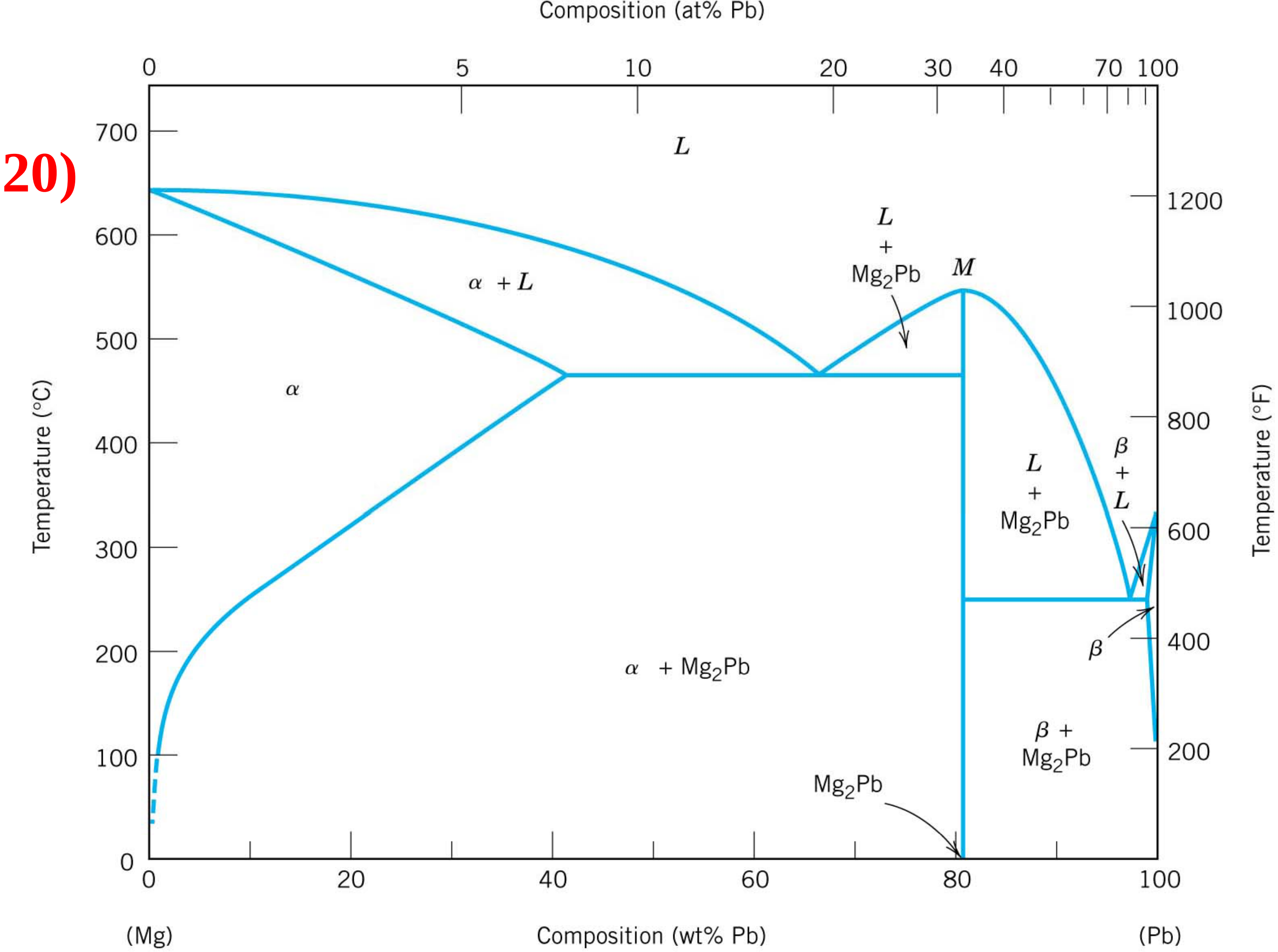
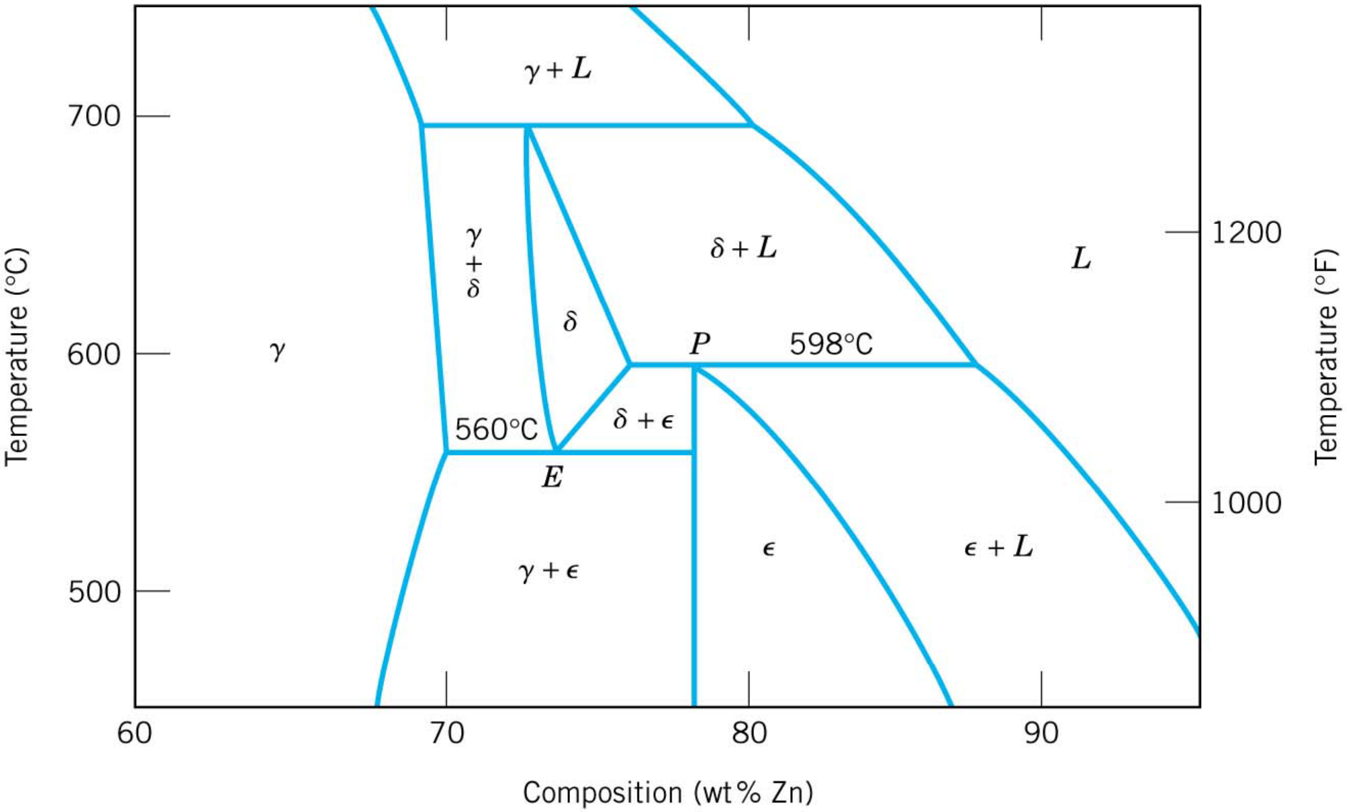


FIGURE 9.18 The magnesium–lead phase diagram. [Adapted from *Phase Diagrams of Binary Magnesium Alloys,* A. A. Nayeb-Hashemi and J. B. Clark (Editors), 1988. Reprinted by permission of ASM International, Materials Park, OH.]

Other Examples

(Fig. 9-21)

FIGURE 9.19 A region of the copper–zinc phase diagram that has been enlarged to show eutectoid and peritectic invariant points, labeled *E* (560°C, 74 wt% Zn) and *P* (598°C, 78.6 wt% Zn), respectively. [Adapted from *Binary Alloy Phase Diagrams,* 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



Other Examples

(Fig. 9-22)

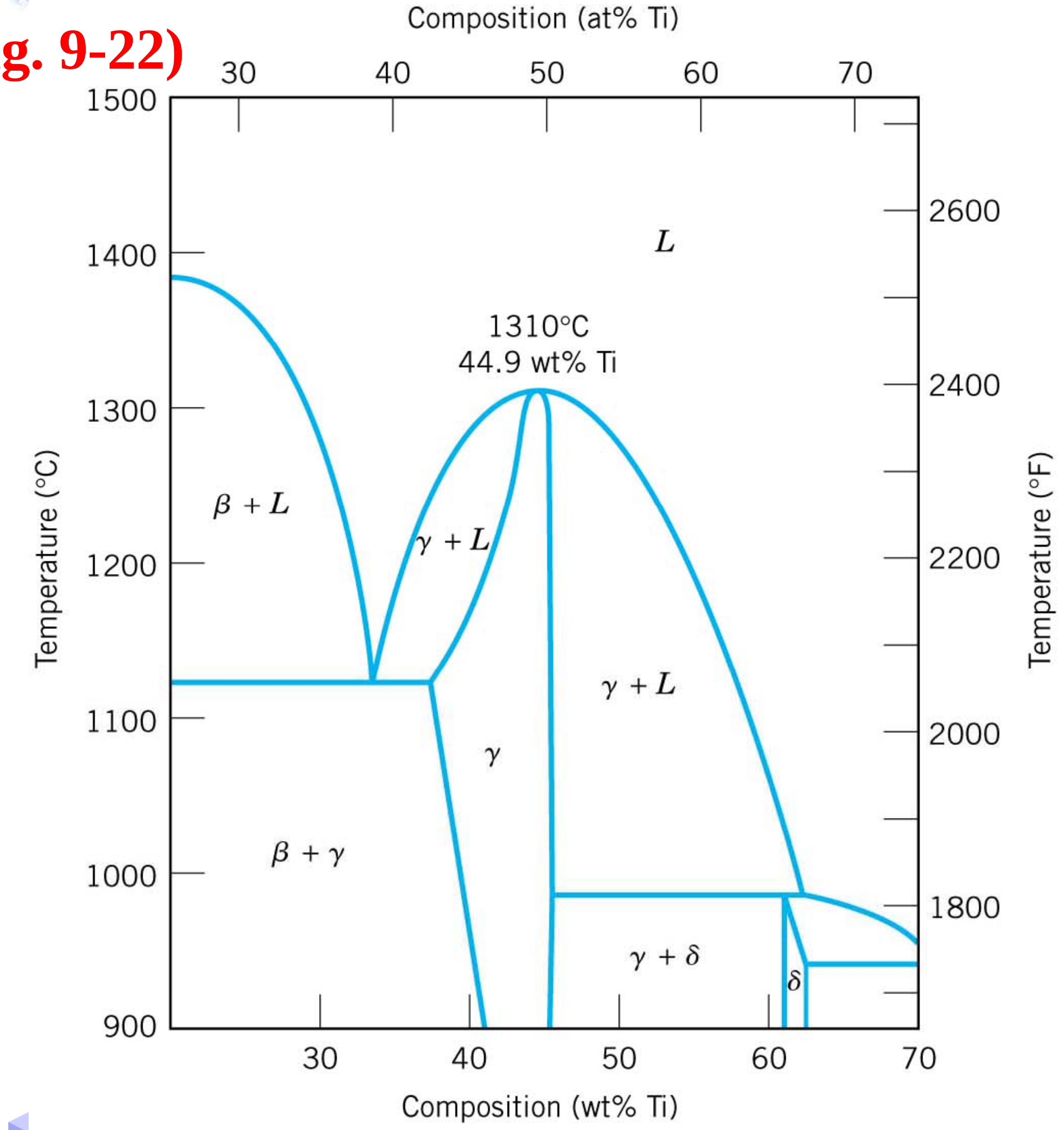


FIGURE 9.20 A portion of the nickel–titanium phase diagram on which is shown a congruent melting point for the γ-phase solid solution at 1310°C and 44.9 wt% Ti. [Adapted from *Phase Diagrams of Binary Nickel Alloys,* P. Nash (Editor), 1991. Reprinted by permission of ASM International, Materials Park, OH.]

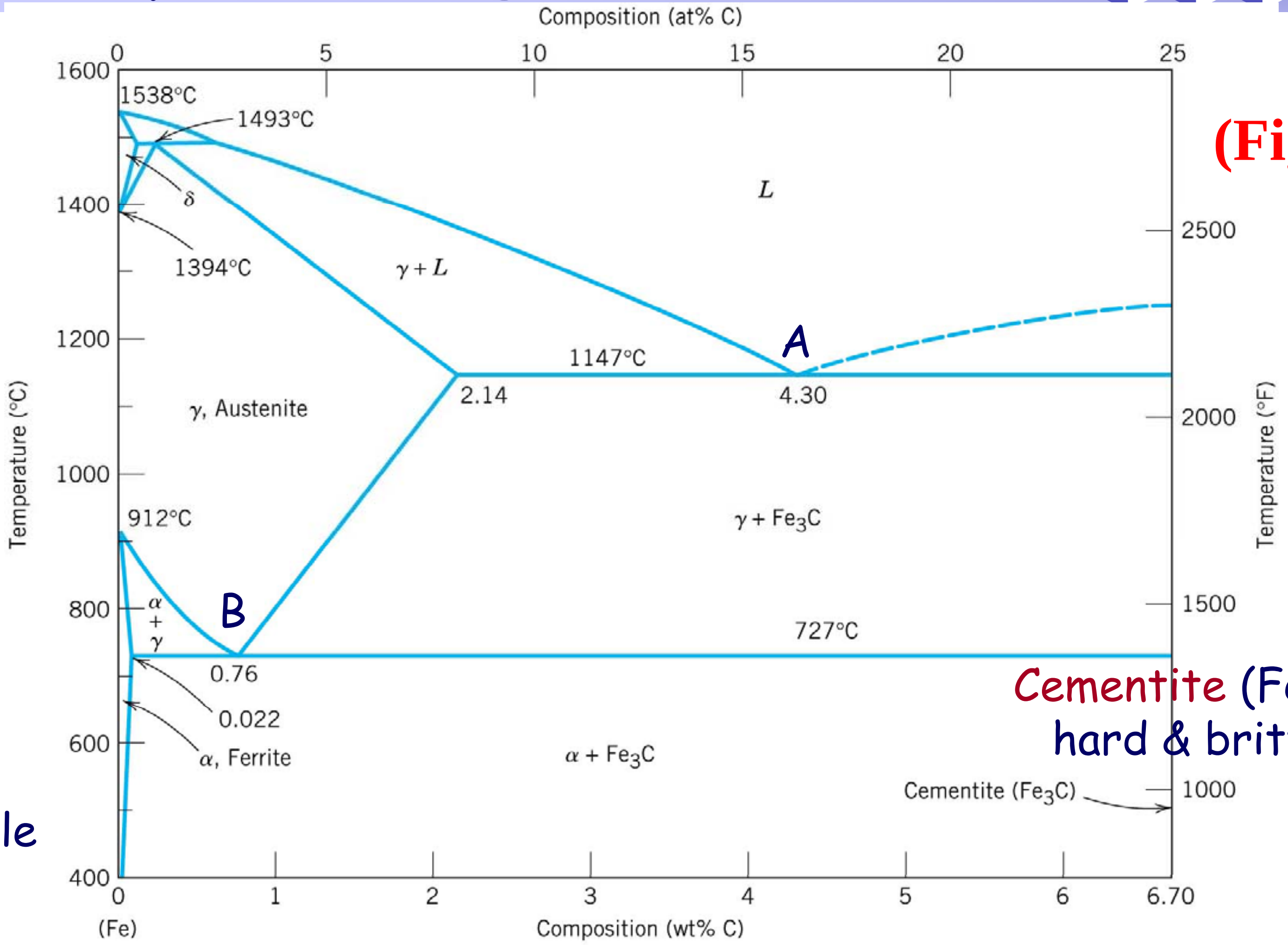
Contents

Fe-C phase diagram

(Fig. 9-24)

γ iron
Austenite
(FCC)

α iron
Ferrite
(BCC)
soft & ductile



Cementite (Fe_3C)
hard & brittle

A; eutectic

B; eutectoid

C concentration 0.008w% 2.14w% 6.7w%

iron steel cast iron

Summary

- Phase diagrams are useful tools to determine:

  √ The number and types of phases.

  √ The at. % or wt. % of each phase.

  √ The fraction of each phase.

  For the given *T* and composition of the system.

- Binary alloys allow various ranges of microstructures.

- Problems from Chap. 9   http://bp.snu.ac.kr

Prob. 9-3	Prob. 9-4	Prob. 9-5	Prob. 9-8
Prob. 9-9	Prob. 9-11	Prob. 9-12	Prob. 9-17
Prob. 9-27	Prob. 9-28	Prob. 9-36	Prob. 9-45