# Chemical Engineering 378

*Science of Materials Engineering*

Lecture 19

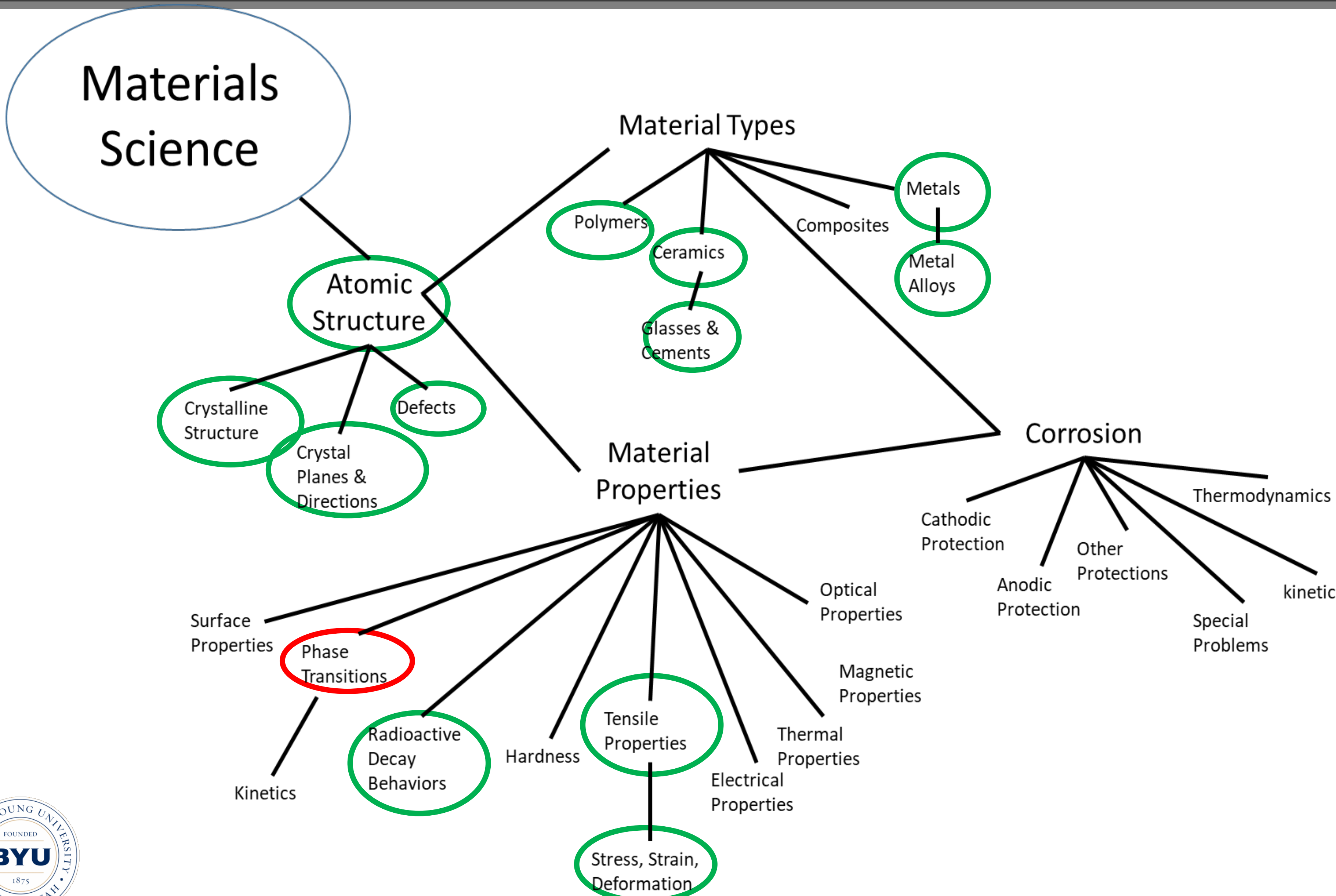
Phase Equilibrium

# Spiritual Thought

"I Testify that bad days come to an end, that faith always triumphs, and that heavenly promises are always kept."

-Jeffery R. Holland

# Materials Roadmap

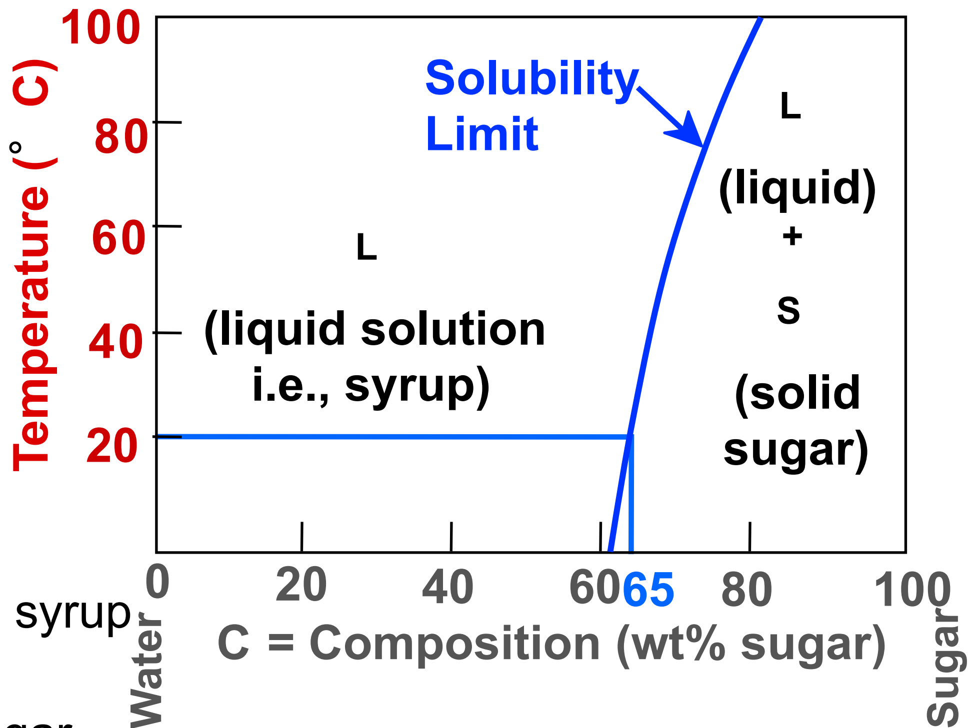


# Phase Equilibria: Solubility Limit

- **Solution** – solid, liquid, or gas solutions, single phase
- **Mixture** – more than one phase
- **Solubility Limit**:
  Maximum concentration for which only a single phase solution exists.

Adapted from Fig. 9.1, Callister & Rethwisch 10e.

Sugar/Water Phase Diagram




Question: What is the solubility limit for sugar in water at 20° C?

Answer: 65 wt% sugar.

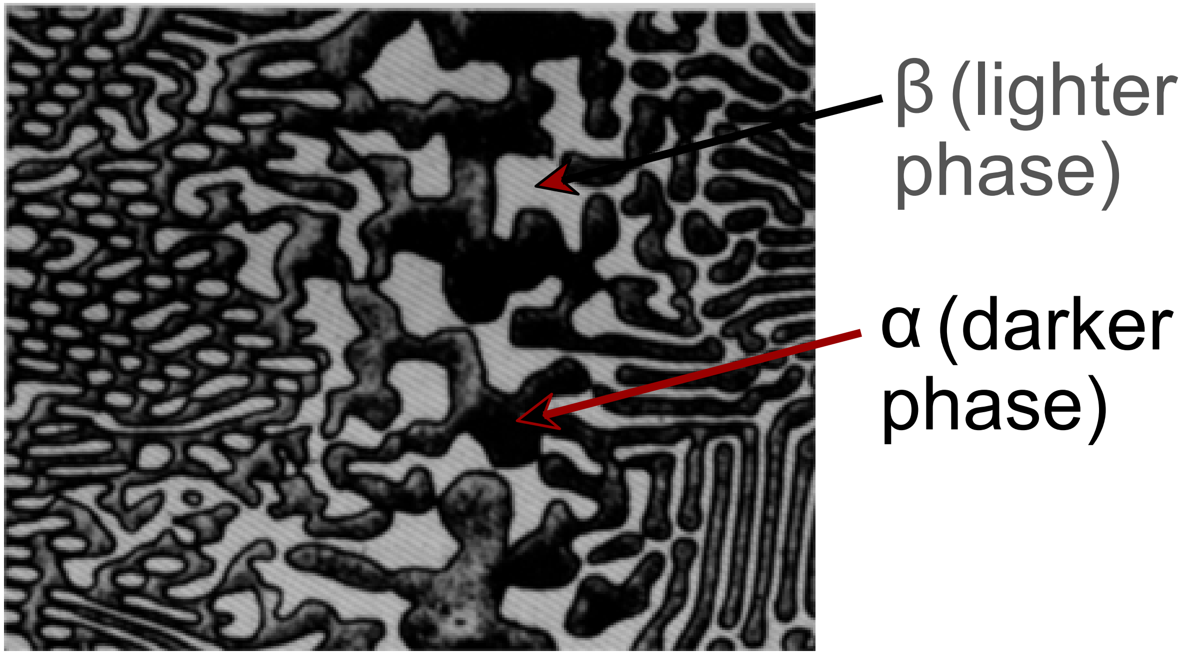
At 20° C, if C < 65 wt% sugar: syrup

At 20° C, if C > 65 wt% sugar: syrup + sugar

# Components and Phases

- Components:
  The elements or compounds which are present in the alloy (e.g., Al and Cu)
- Phases:
  The physically and chemically distinct material regions that form (e.g., α and β).

Aluminum-Copper Alloy




Adapted from chapter-opening photograph, Chapter 9, Callister, Materials Science & Engineering: An Introduction, 3e.

# Effect of Temperature & Composition

- Altering T can change # of phases: path A to B.
- Altering C can change # of phases: path B to D.

water-sugar system

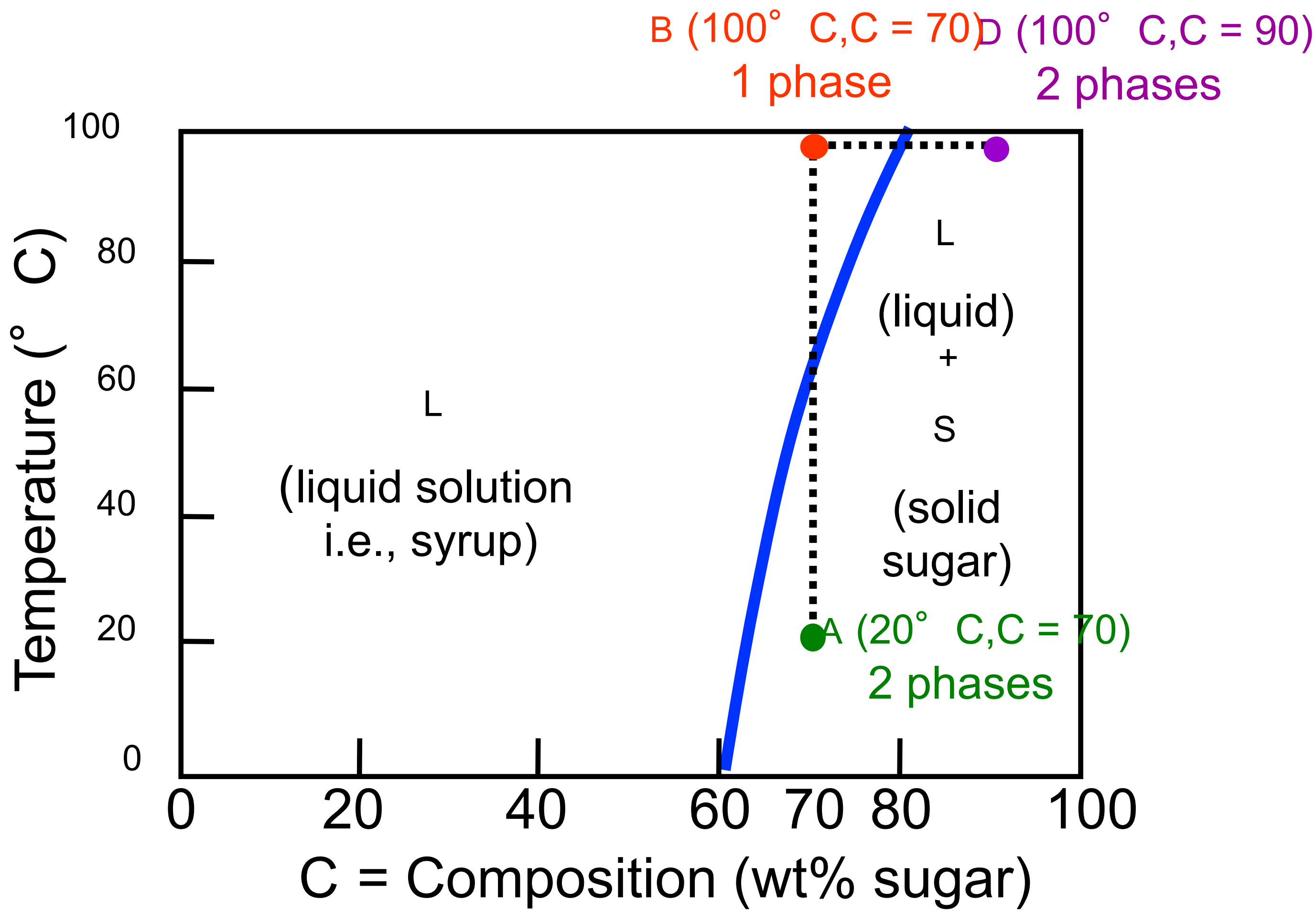



Fig. 9.1, Callister & Rethwisch 10e.

# Criteria for Solid Solubility

Simple system (e.g., Ni-Cu solution)

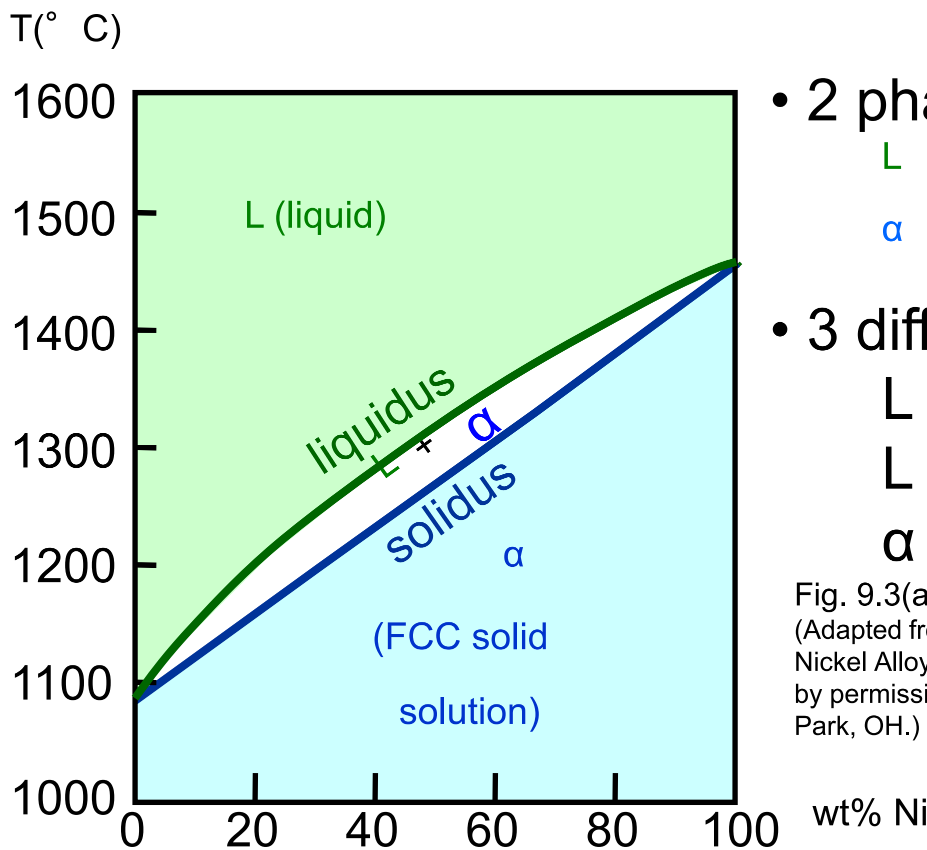
| | Crystal Structure | electroneg | *r* (nm) |
|---|---|---|---|
| Ni | FCC | 1.9 | 0.1246 |
| Cu | FCC | 1.8 | 0.1278 |

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.
- Ni and Cu are totally soluble in one another for all proportions.

# Phase Diagrams

- Indicate phases as a function of T, C, and P.
- For this course:
  - binary systems: just 2 components.
  - independent variables: T and C (P = 1 atm is almost always used).

**Phase Diagram** for Cu-Ni system




- 2 phases:
  - L (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - L
  - L + α
  - α

Fig. 9.3(a), Callister & Rethwisch 10e. (Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

# Isomorphous Binary Phase Diagram

- Phase diagram:
  Cu-Ni system.
- System is:
  -- binary
  i.e., 2 components:
  Cu and Ni.
  -- isomorphous
  i.e., complete
  solubility of one
  component in
  another; α phase
  field extends from
  0 to 100 wt% Ni.

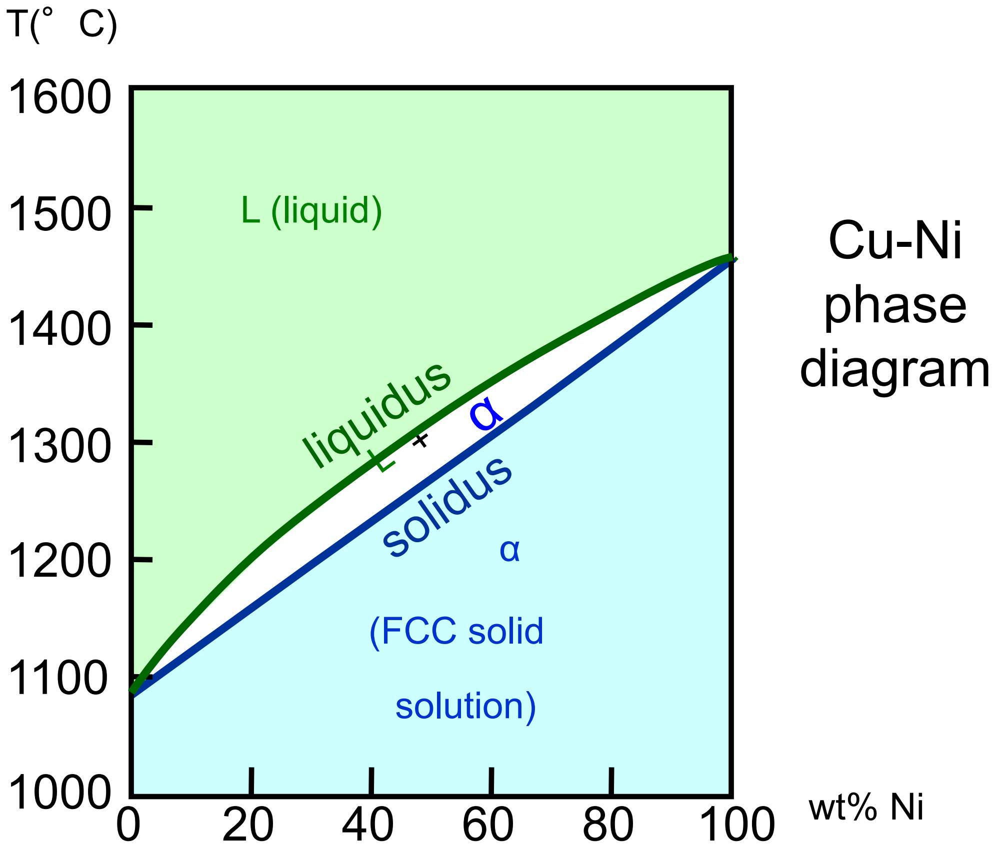


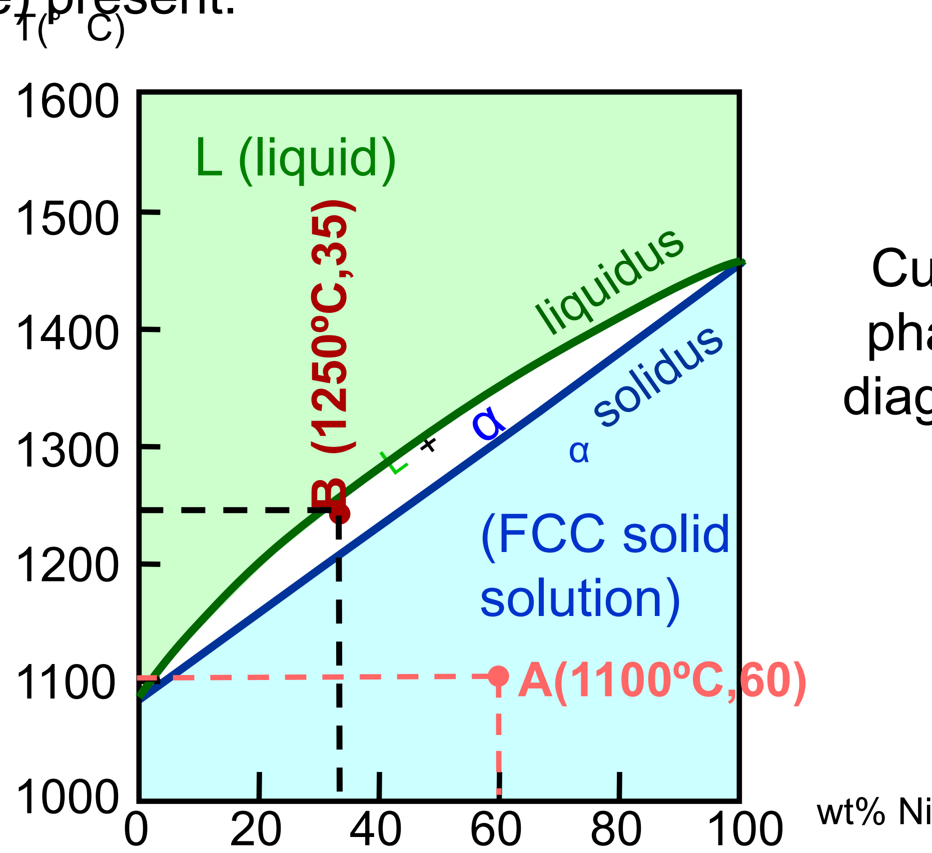

Fig. 9.3(a), Callister & Rethwisch 10e.
(Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

# Phase Diagrams:
## Determination of phase(s) present

- Rule 1: If we know T and $C_o$, then we know:
  - -- which phase(s) is (are) present.
- Examples:

A(1100° C, 60 wt% Ni):
1 phase: α

B(1250° C, 35 wt% Ni):
2 phases: L + α




Cu-Ni phase diagram

Fig. 9.3(a), Callister & Rethwisch 10e.
(Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

# Phase Diagrams:
## Determination of phase compositions



- Rule 2: If we know T and $C_0$, then we can determine:
  -- the composition of each phase.

- Examples:

Consider $C_0$ = 35 wt% Ni

At $T_A$ = 1320° C:
Only Liquid (L) present
$C_L = C_0$ ( = 35 wt% Ni)

At $T_D$ = 1190° C:
Only Solid (α) present
$C_\alpha = C_0$ ( = 35 wt% Ni)

At $T_B$ = 1250° C:
Both α and L present
$C_L = C_{liquidus}$ ( = 32 wt% Ni)
$C_\alpha = C_{solidus}$ ( = 43 wt% Ni)

Cu-Ni system

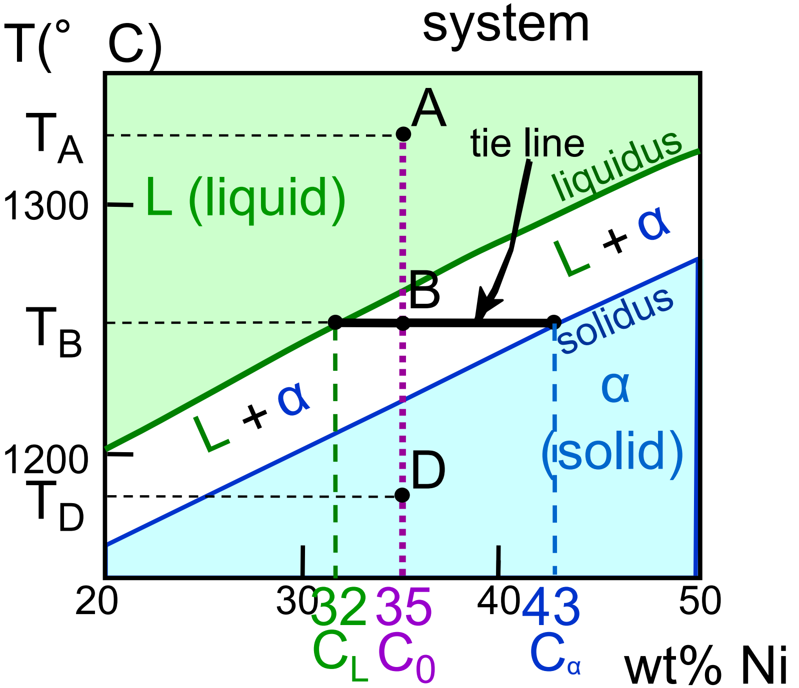



Fig. 9.3(b), Callister & Rethwisch 10e.
(Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

# Phase Diagrams:
## Determination of phase weight fractions

- Rule 3: If we know T and $C_0$, then can determine:
  -- the weight fraction of each phase.
- Examples:

Consider $C_0$ = 35 wt% Ni

At $T_A$ : Only Liquid (L) present

$W_L = 1.00, W_\alpha = 0$

At $T_D$ : Only Solid ( α ) present

$W_L = 0, W_\alpha = 1.00$

At $T_B$ : Both α and L present

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 0.73$$

$$W_\alpha = \frac{R}{R+S} = 0.27$$

Cu-Ni system

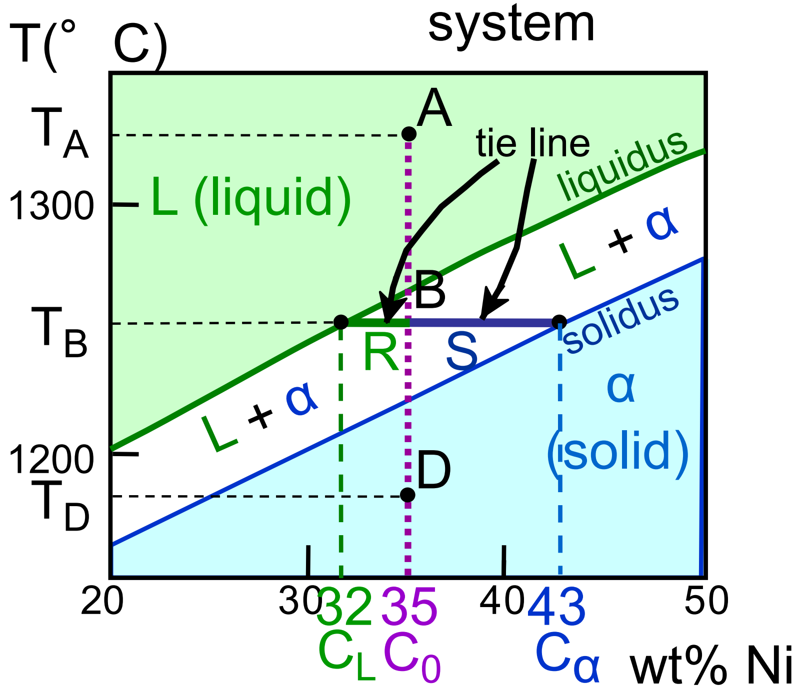
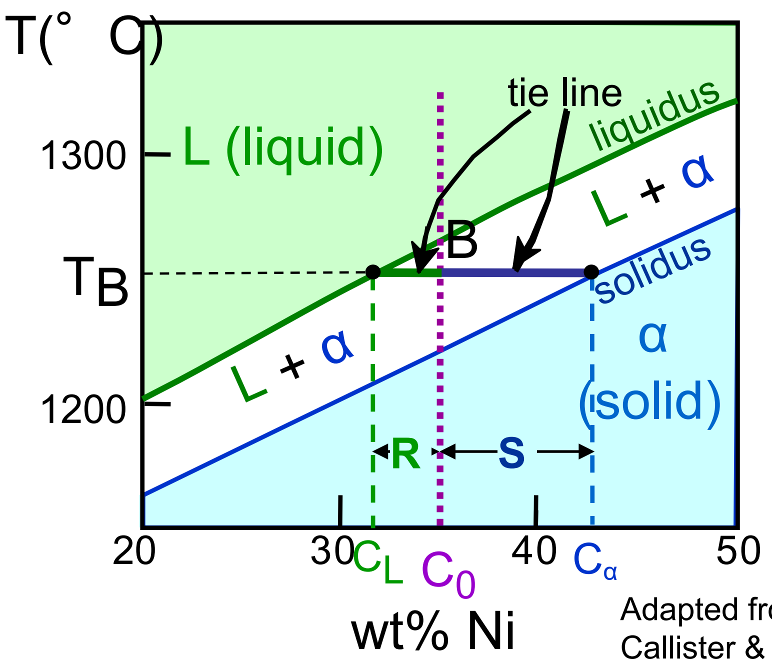



Fig. 9.3(b), Callister & Rethwisch 10e. (Adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

# The Lever Rule

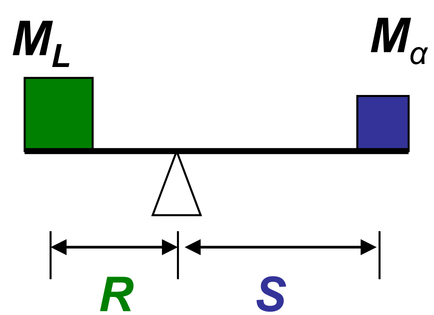
- Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm




Adapted from Fig. 9.3(b), Callister & Rethwisch 10e.

What fraction of each phase?

Think of the tie line as a lever (teeter-totter)



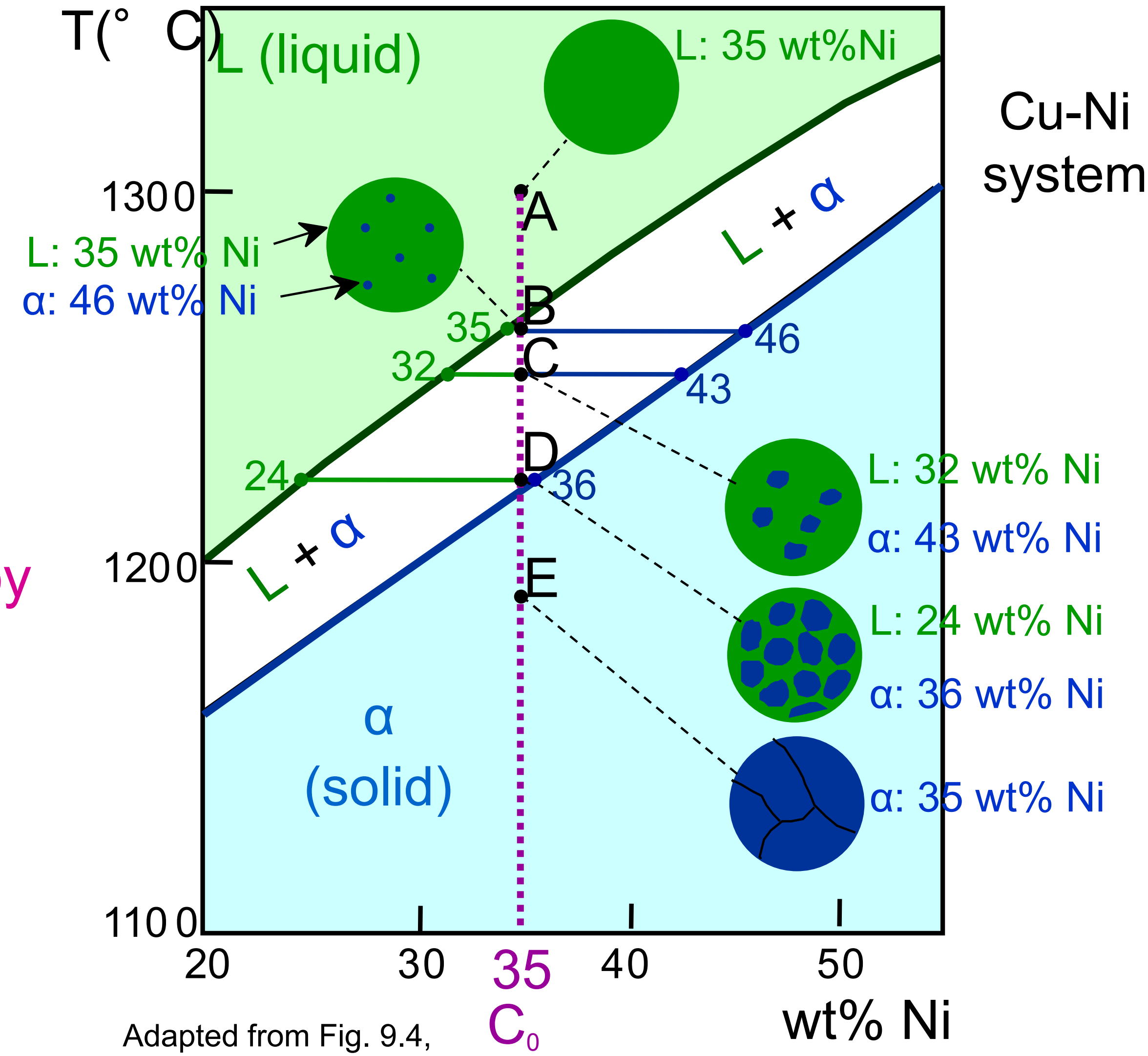

$$M_\alpha \text{ x } S = M_L \text{ x } R$$

$$W_L = \frac{M_L}{M_L + M_\alpha} = \frac{S}{R+S} = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

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

# Ex: Cooling of a Cu-Ni Alloy

- Phase diagram: Cu-Ni system.
- Consider microstuctural changes that accompany the cooling of a $C_0$ = 35 wt% Ni alloy

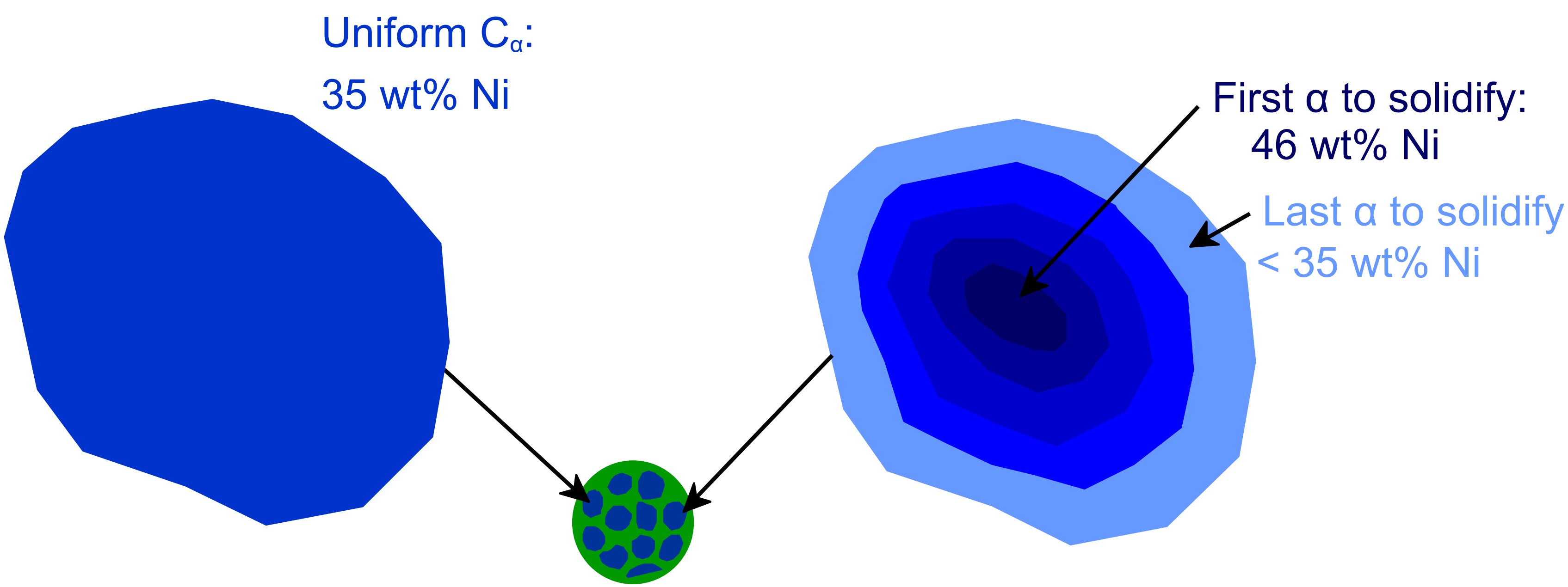



Adapted from Fig. 9.4, Callister & Rethwisch 10e.

# Cored vs Equilibrium Structures

- $C_\alpha$ changes as we solidify.
- Cu-Ni case: First α to solidify has $C_\alpha$ = 46 wt% Ni.
  Last α to solidify has $C_\alpha$ = 35 wt% Ni.

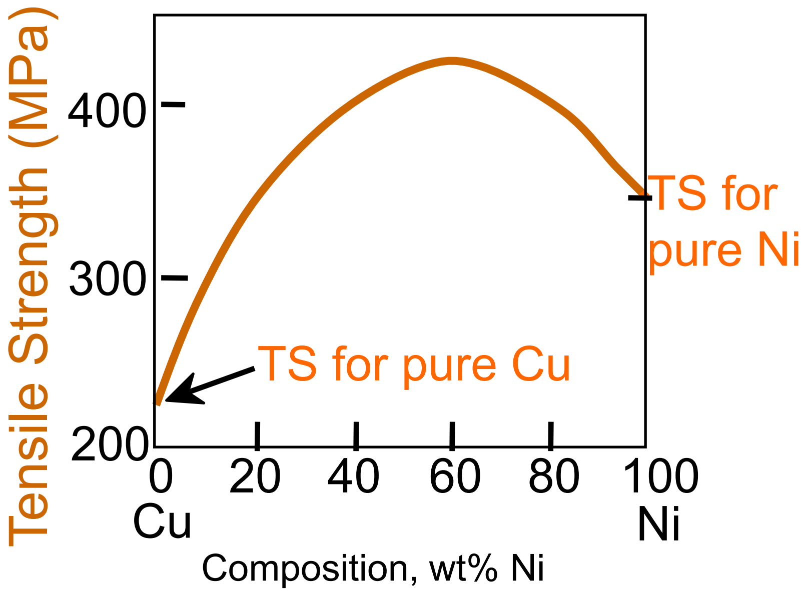
- Slow rate of cooling:
  Equilibrium structure
- Fast rate of cooling:
  Cored structure



# Mechanical Properties: Cu-Ni System

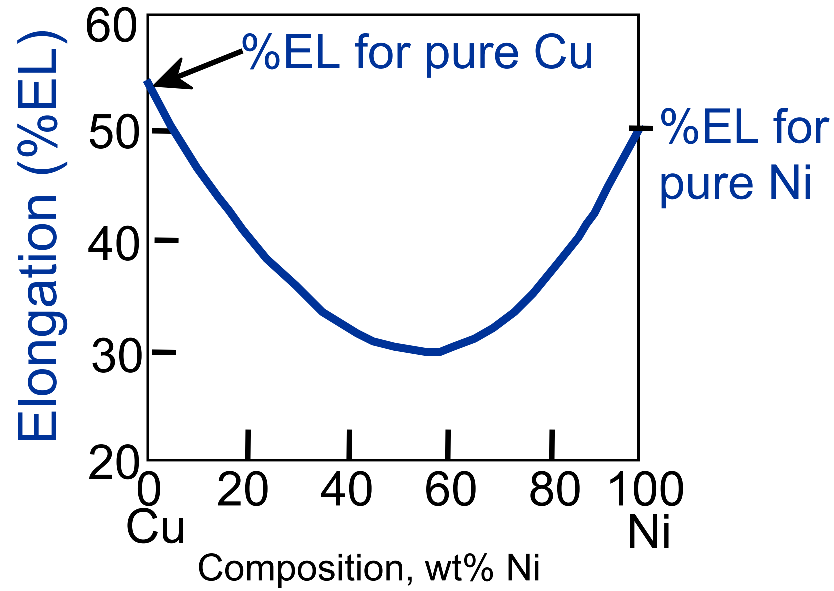
- Effect of solid solution strengthening on:

-- Tensile strength (TS)




Adapted from Fig. 9.6(a), Callister & Rethwisch 10e.

-- Ductility (%EL)




Adapted from Fig. 9.6(b), Callister & Rethwisch 10e.

# Binary-Eutectic Systems

2 components

has a special composition with a min. 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 $T_E$
- $C_E$ : Composition at temperature $T_E$

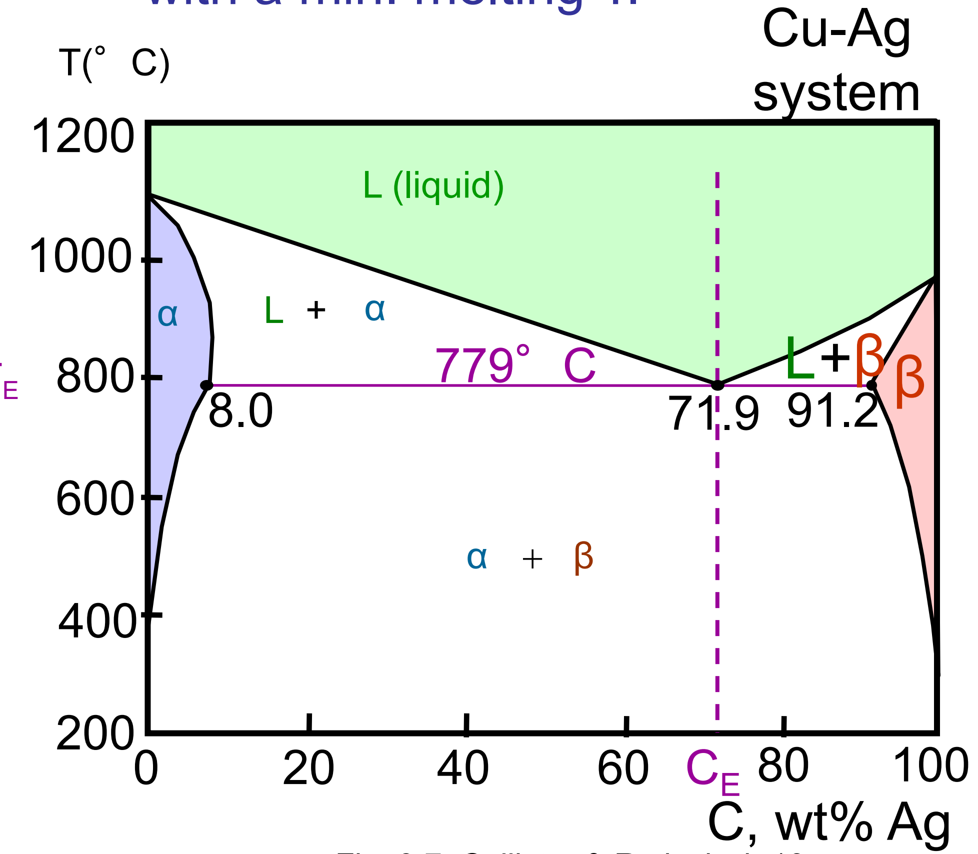



Fig. 9.7, Callister & Rethwisch 10e [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.].

- **Eutectic reaction**

$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

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

# EX 1: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 150° C, determine:
  -- the phases present

  **Answer:** α + β

  -- the phase compositions

  **Answer:** $C_\alpha$ = 11 wt% Sn
  $C_\beta$ = 99 wt% Sn

  -- the relative amount of each phase

  **Answer:**

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{99-40}{99-11} = \frac{59}{88} = 0.67$$

$$W_\beta = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{40-11}{99-11} = \frac{29}{88} = 0.33$$

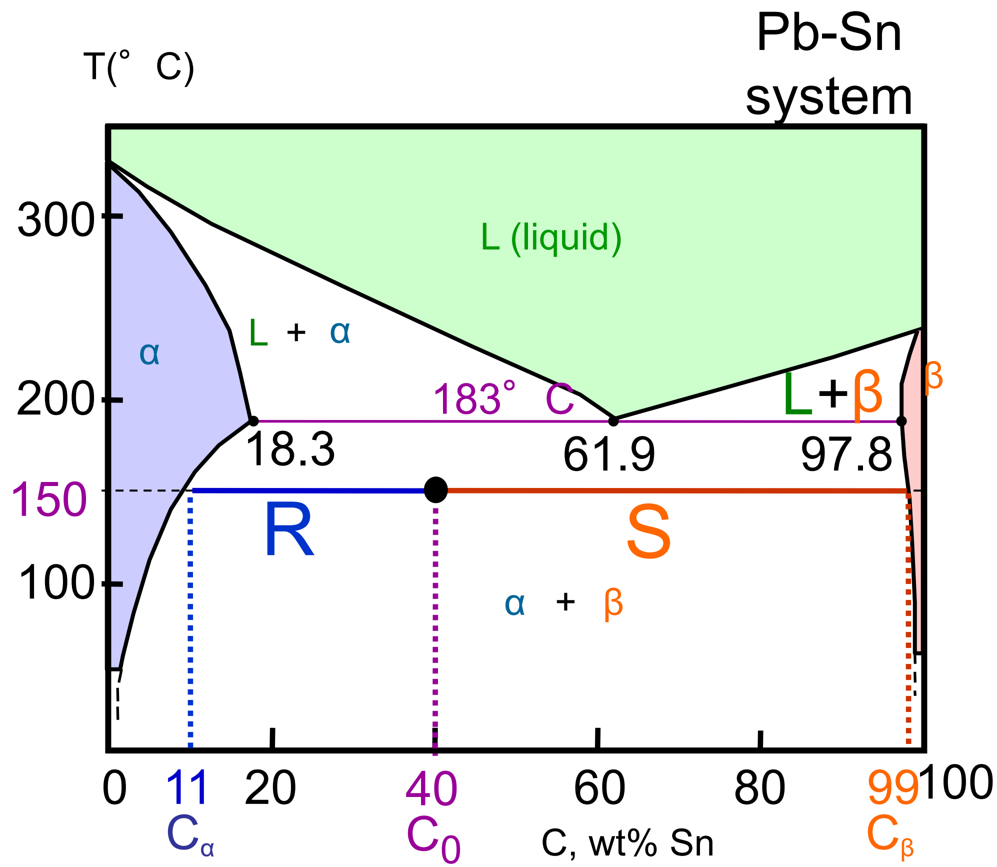



Fig. 9.8, Callister & Rethwisch 10e.
[Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

# EX 2: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220° C, determine:
  - -- the phases present:

  **Answer:** α + L

  - -- the phase compositions

  **Answer:** $C_\alpha$ = 17 wt% Sn
  $C_L$ = 46 wt% Sn

  - -- the relative amount of each phase

  **Answer:**

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 0.21$$

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$

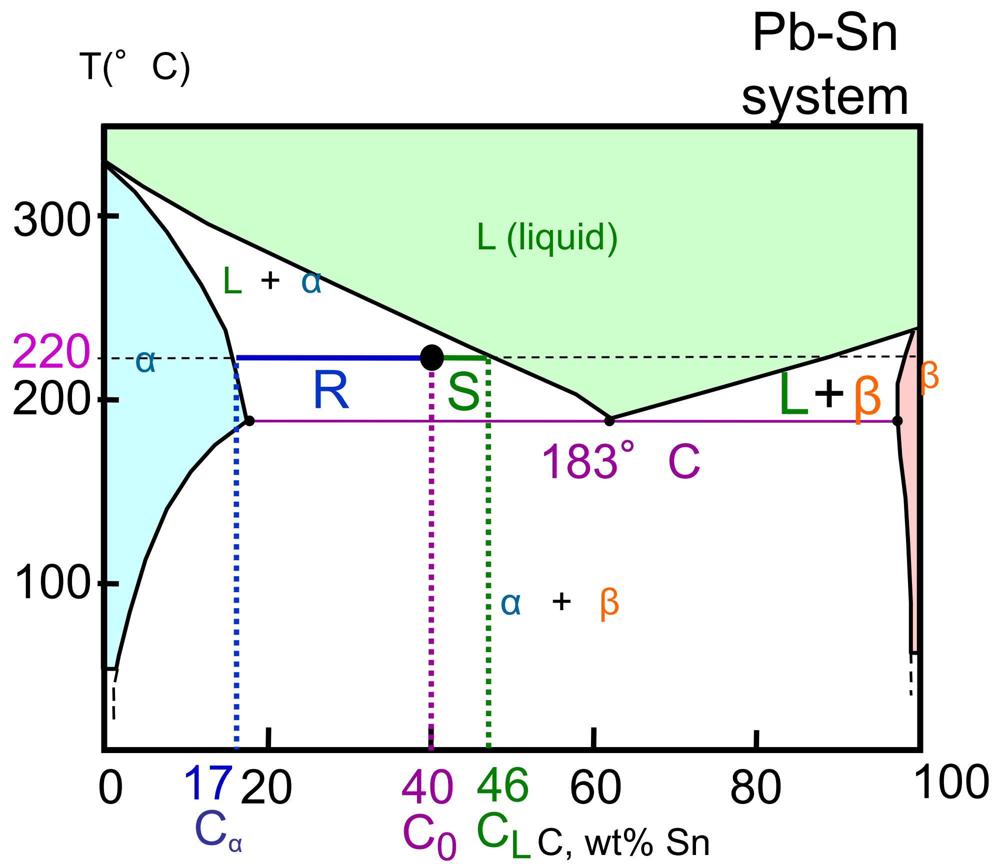



Fig. 9.8, Callister & Rethwisch 10e.
[Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

# Microstructural Developments in Eutectic Systems I

- For alloys for which
  $C_0 < 2$ wt% Sn
- Result: at room temperature
  -- polycrystalline with grains of α phase having composition $c_0$

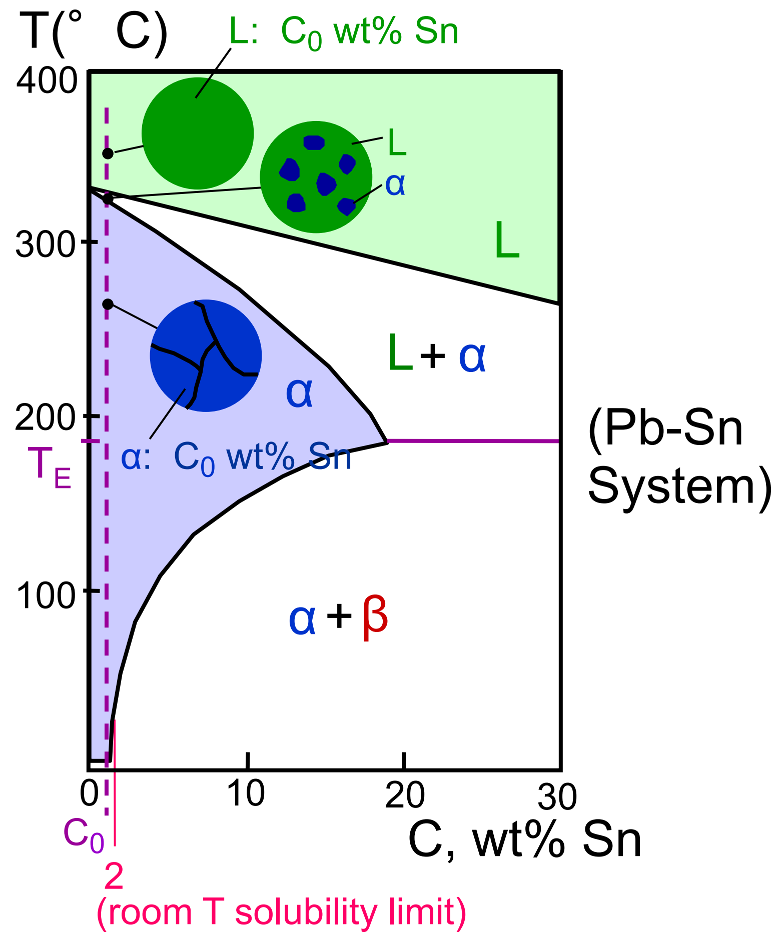



Fig. 9.11, Callister & Rethwisch 10e.

# Microstructural Developments in Eutectic Systems II

- For alloys for which
  2 wt% Sn < $C_0$ < 18.3 wt% Sn
- Result:
  at temperatures in α + β range
  -- polycrystalline with α grains
  and small β-phase particles

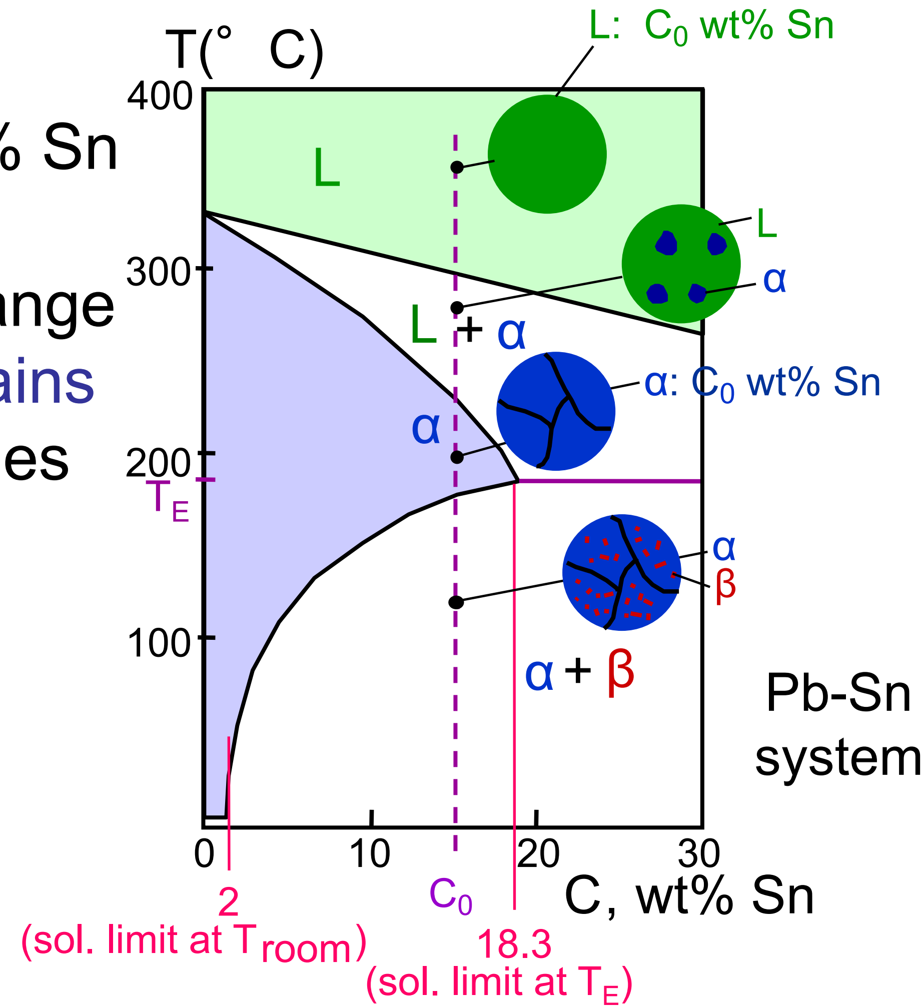



Fig. 9.12, Callister & Rethwisch 10e.

# Microstructural Developments in Eutectic Systems III

- For alloy of composition $C_0 = C_E$
- Result: Eutectic microstructure (lamellar structure)
  -- alternating layers (lamellae) of α and β phases.

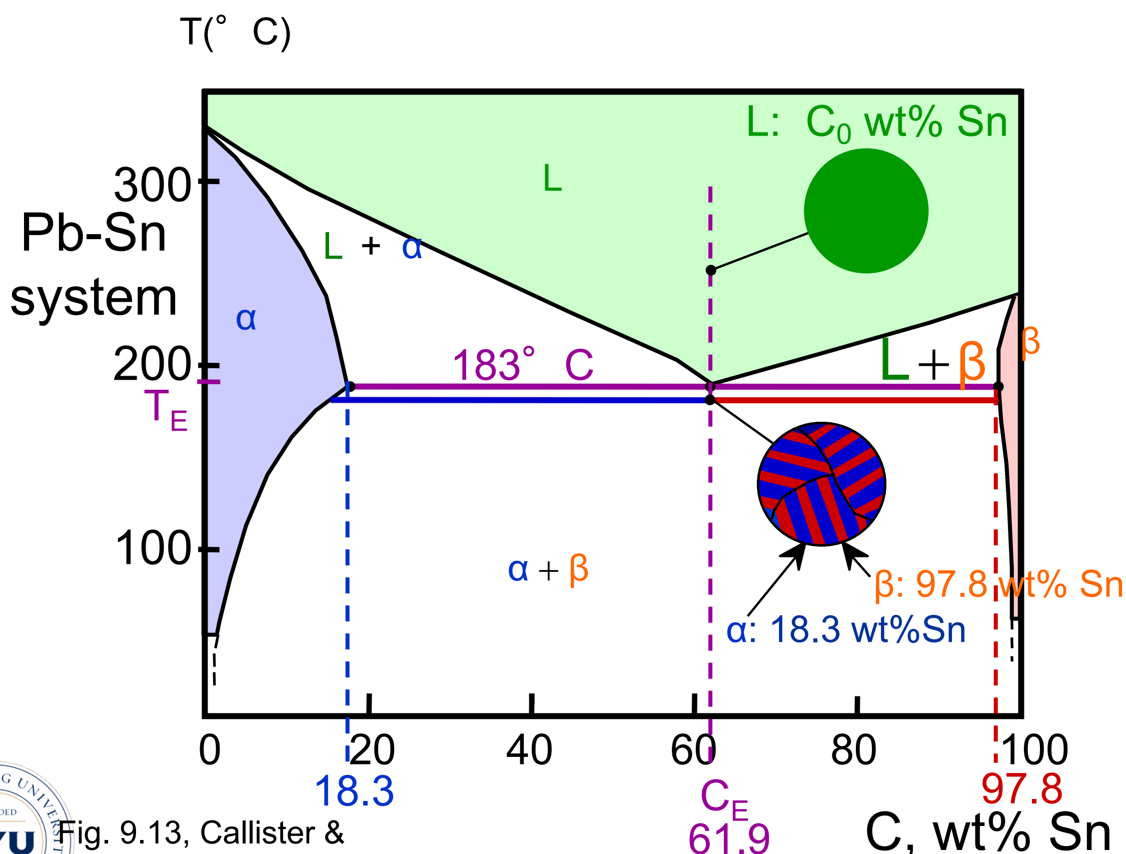



Fig. 9.13, Callister & Rethwisch 10e.

Micrograph of Pb-Sn eutectic microstructure

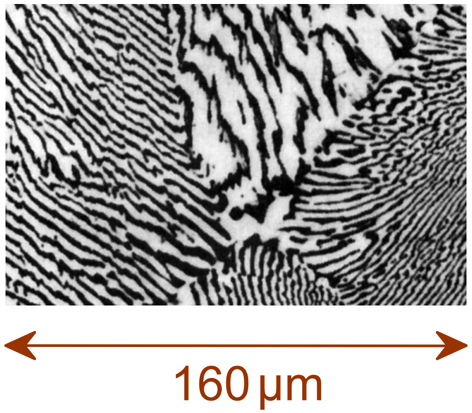
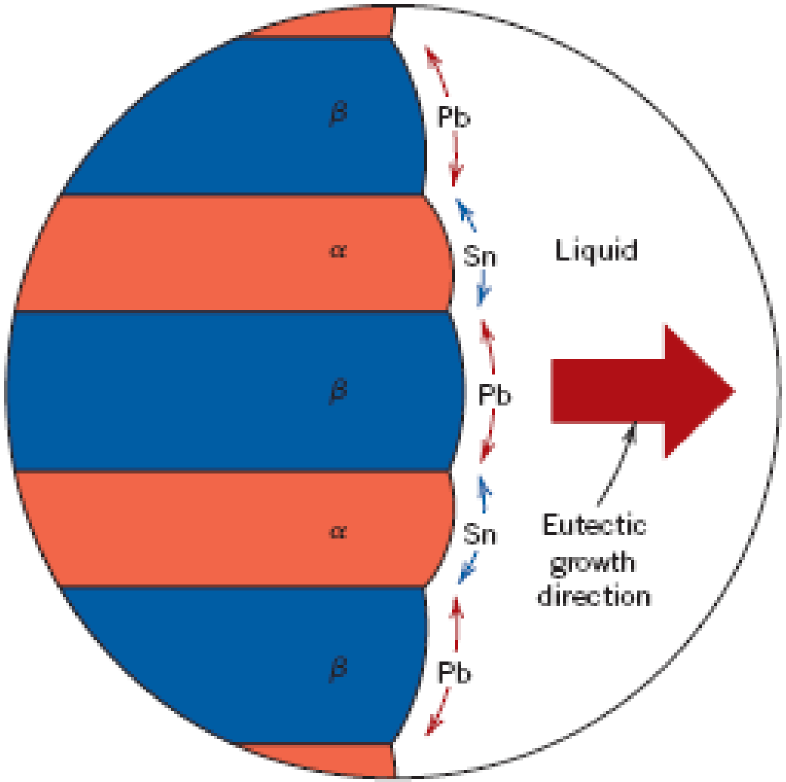
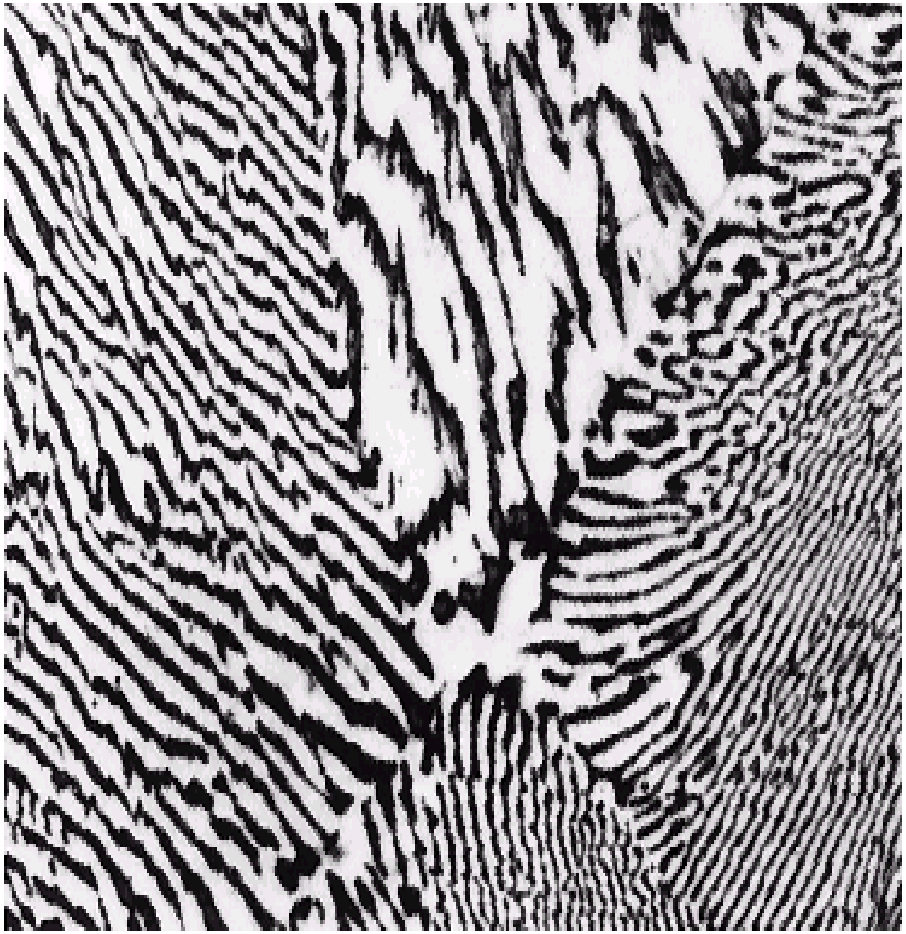



Fig. 9.14, Callister & Rethwisch 10e.
(From Metals Handbook, 9th edition, Vol. 9, Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

# Lamellar Eutectic Structure



Figs. 9.14 & 9.15, Callister & Rethwisch 10e.
(Fig. 9.14 from Metals Handbook, 9th edition, Vol. 9, Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.)