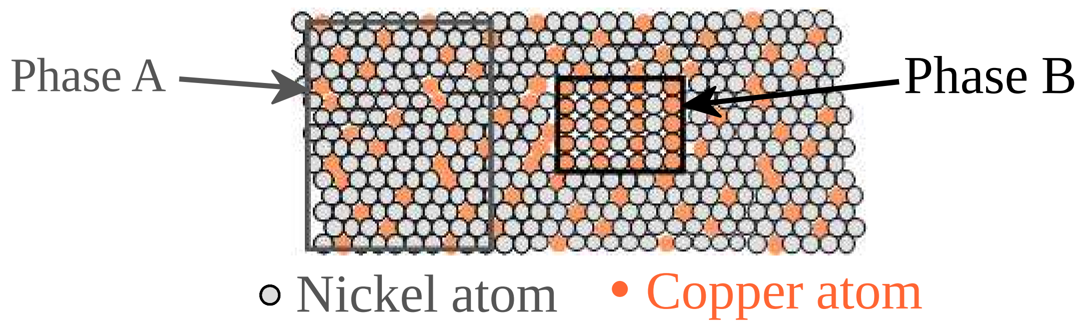
# Chapter 11: Phase Diagrams for Metallic Systems

## ISSUES TO ADDRESS...

- When we combine **two elements,** what equilibrium state do we get?

- In particular, if we specify...
  --a **composition** (e.g., wt% Cu - wt% Ni), and
  --a **temperature** (*T*)

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



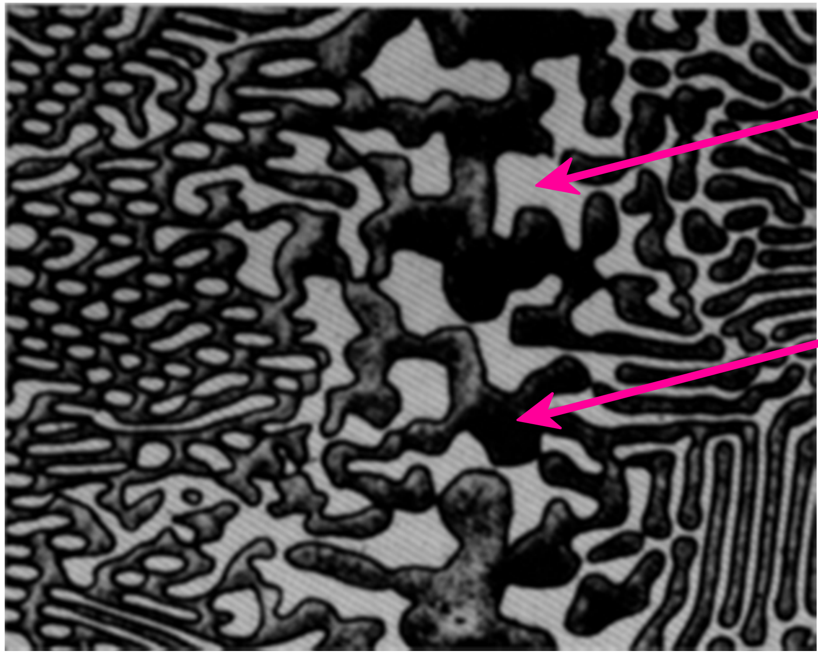
# Components and Phases

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

- Solute and Solvent:

The solute atoms occupy either substitutional or interstitial positions in the solvent lattice

Aluminum-Copper Alloy



β (lighter phase)

α (darker phase)

# Phase Equilibria: Solubility Limit

**Introduction**

- Solutions – solid solutions, single phase
- Mixtures – more than one phase

- Solubility Limit :
  Max concentration for which only a single phase solution occurs.

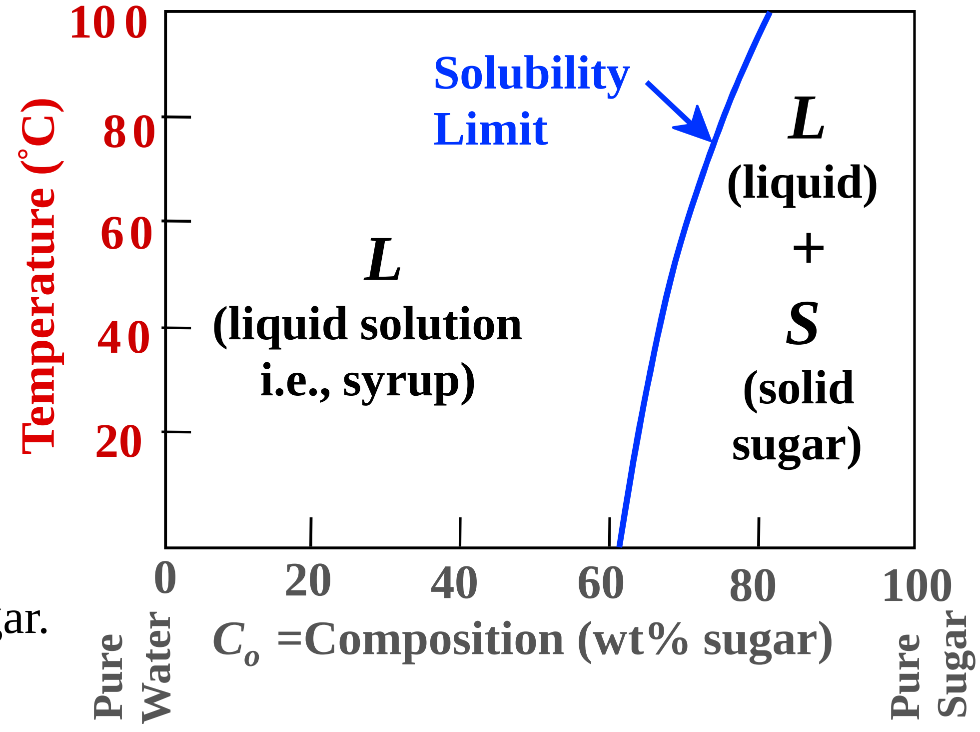
Question: What is the solubility limit at 20°C?

Answer: 65 wt% sugar.

If $C_o$ < 65 wt% sugar: syrup

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

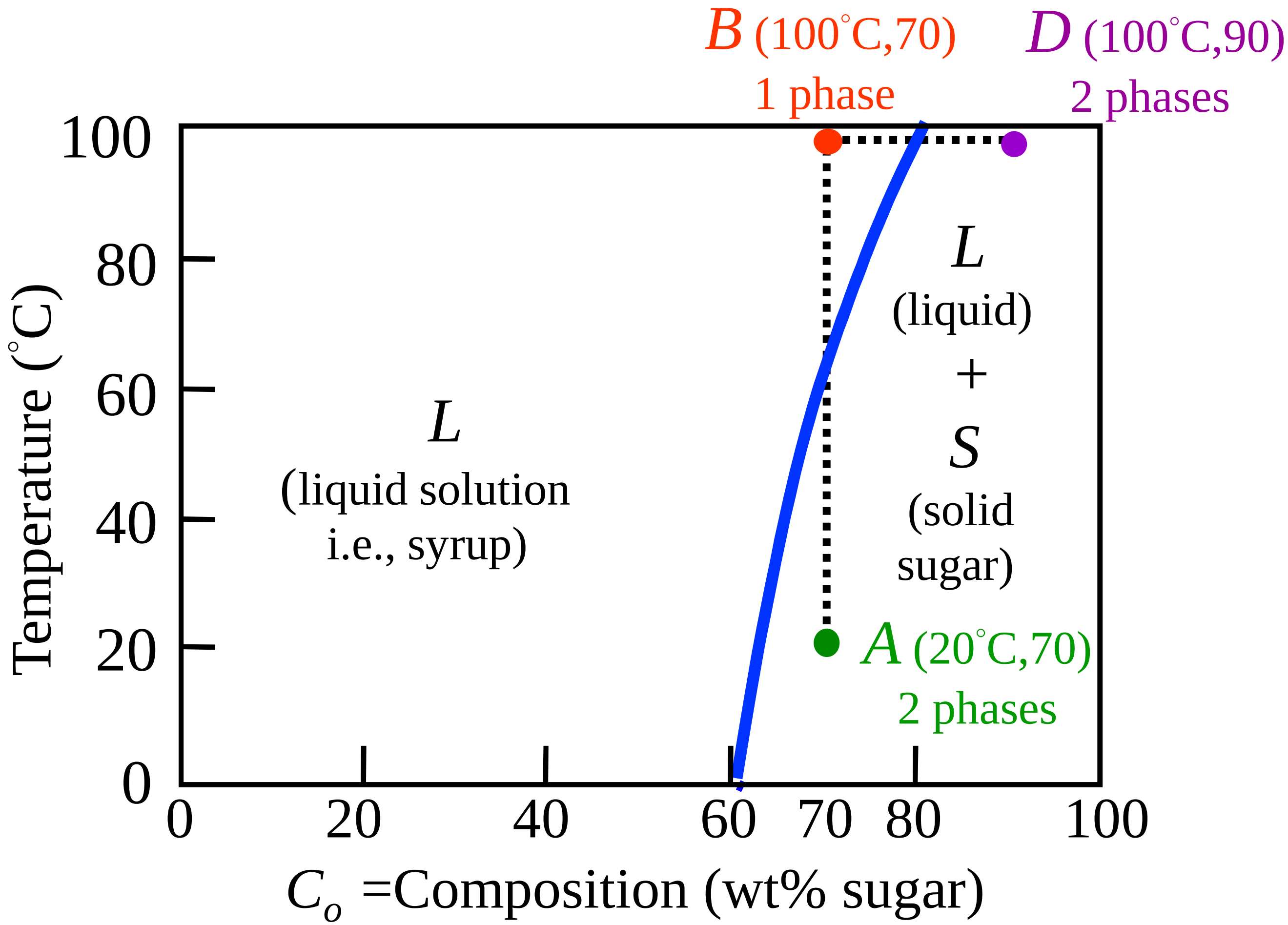
Sucrose/Water Phase Diagram



# Effect of *T* & Composition ($C_o$)

- Changing *T* can change # of phases: path *A* to *B*.
- Changing $C_o$ can change # of phases: path *B* to *D*.

water-sugar system




Adapted from Fig. 9.1, *Callister 7e.*

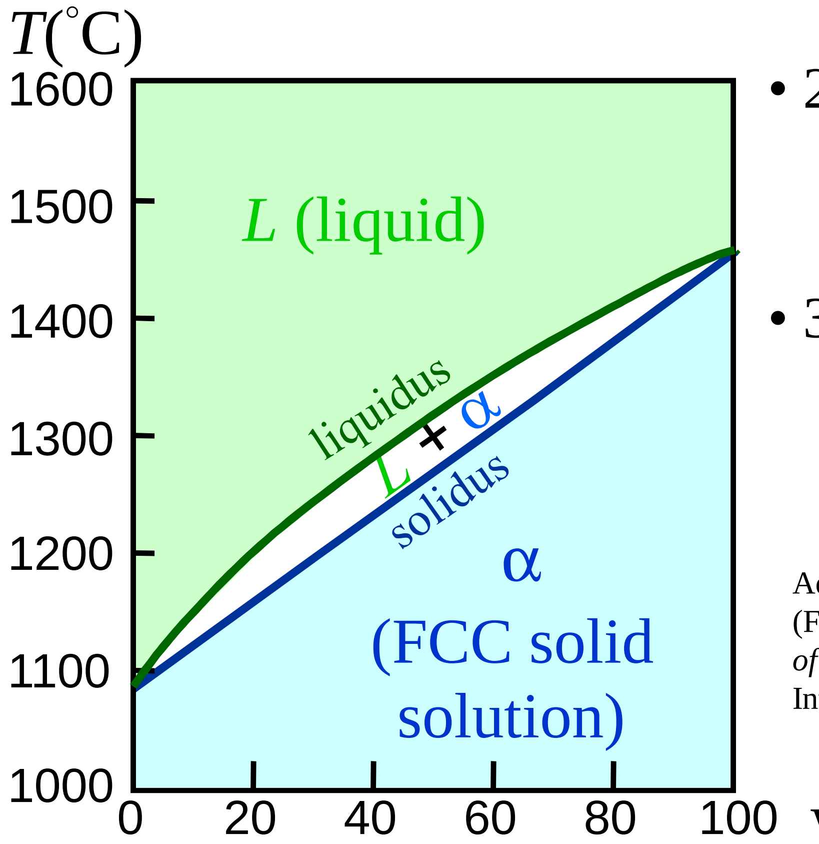
# Phase Diagrams

- Indicate phases as function of $T$, $C_o$, and $P$.
- For this course:

  -binary systems: just 2 components.

  -independent variables: $T$ and $C_o$ ($P$ = 1 atm is almost always used).

- Phase Diagram for Cu-Ni system




- 2 phases:

  $L$ (liquid)

  $\alpha$ (FCC solid solution)

- 3 phase fields:

  $L$

  $L + \alpha$

  $\alpha$

Adapted from Fig. 9.3(a), *Callister 7e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

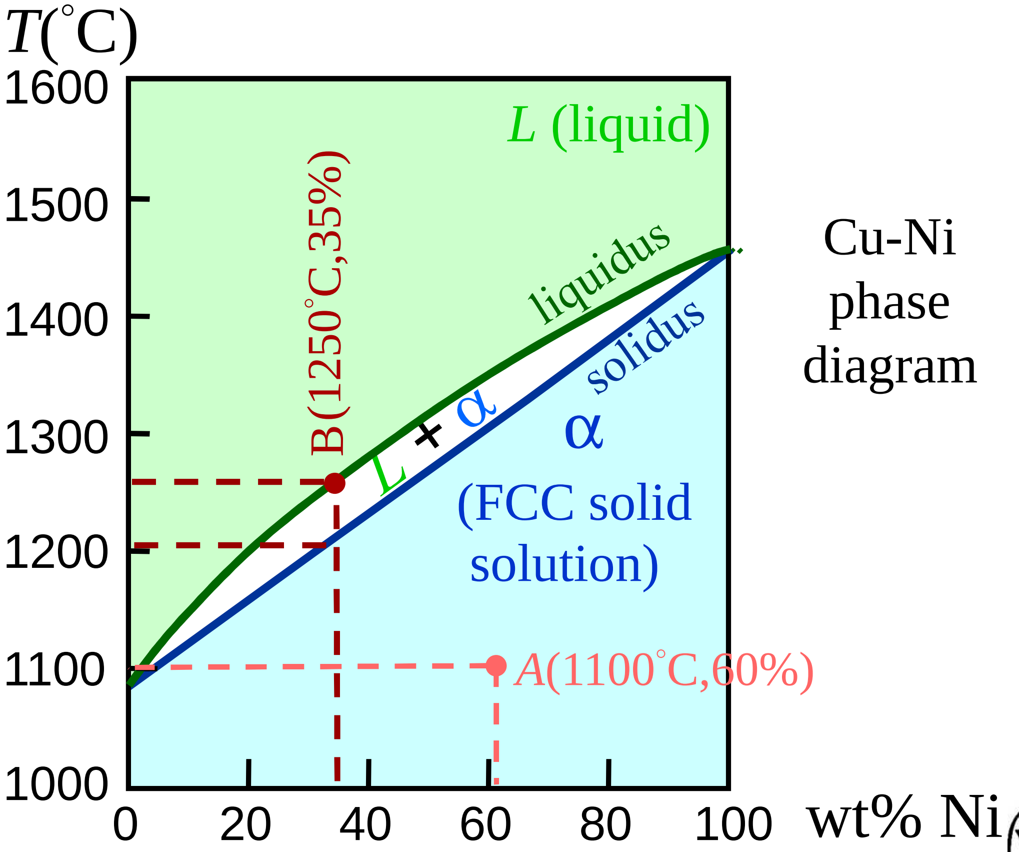
# Phase Diagrams: numbers(#) and types of phases

- Rule 1: If we know *T* and $C_o$, then we know:
  --the # and types of phases present.

- Examples:

  *A*(1100°C, 60):
  1 phase: α

  *B*(1250°C, 35):
  2 phases: *L* + α




Cu-Ni phase diagram

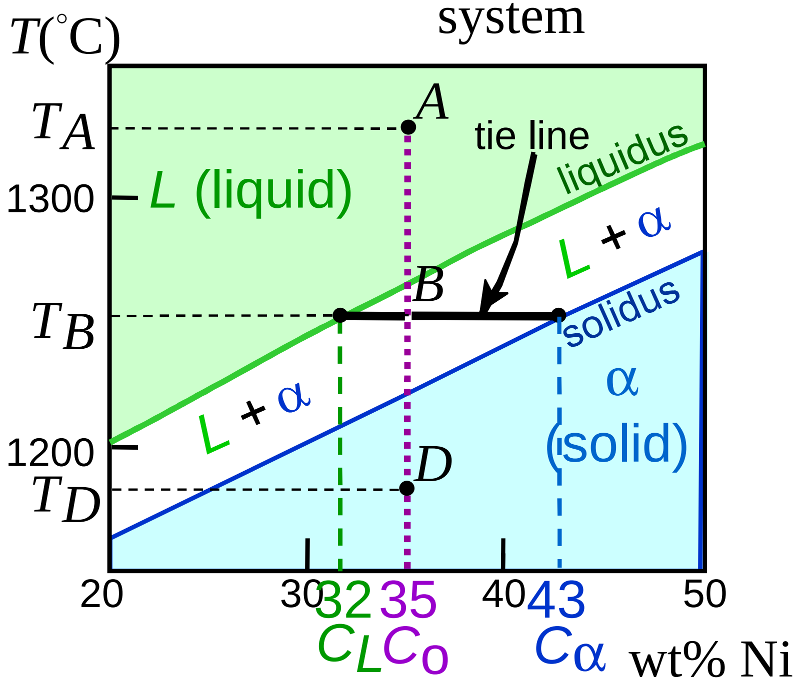
Adapted from Fig. 9.3(a), *Callister 7e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991).

# Phase Diagrams:
## composition of phases

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

- Examples:
  $C_o$ = 35 wt% Ni
  At $T_A$ = 1320°C:
  Only Liquid ($L$)
  $C_L = C_o$ ( = 35 wt% Ni)
  At $T_D$ = 1190°C:
  Only Solid ( α )
  $C_\alpha = C_o$ ( = 35 wt% Ni )
  At $T_B$ = 1250°C:
  Both α and $L$
  $C_L = C_{\text{liquidus}}$ ( = 32 wt% Ni here)
  $C_\alpha = C_{\text{solidus}}$ ( = 43 wt% Ni here)

Cu-Ni system




Adapted from Fig. 9.3(b), *Callister 7e.* (Fig. 9.3(b) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)

# Phase Diagrams:
## weight fractions of phases

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

$C_o$ = 35 wt% Ni

At $T_A$: Only Liquid (L)

$W_L$ = 100 wt%, $W_\alpha$ = 0

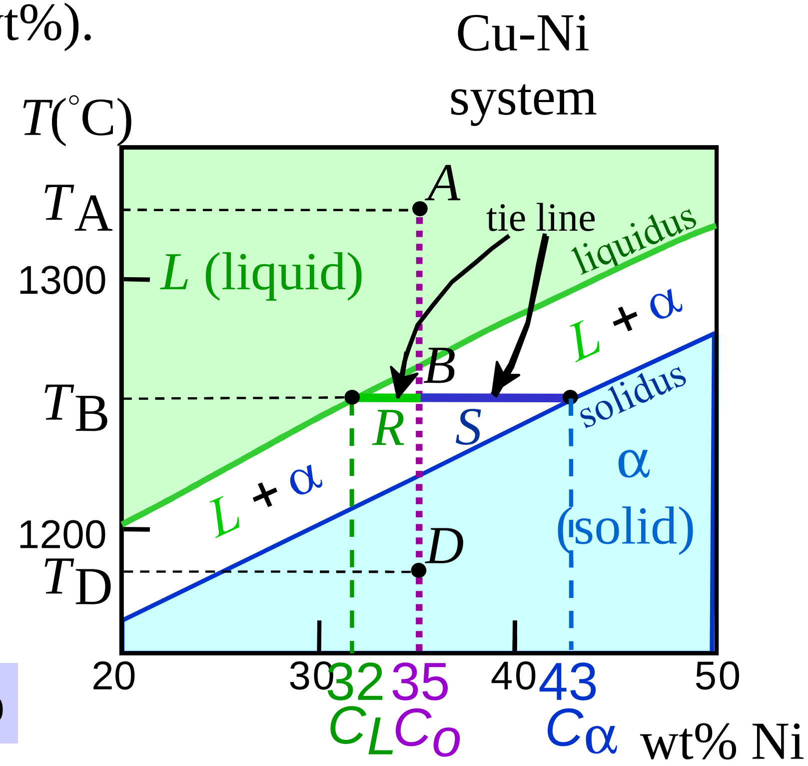
At $T_D$: Only Solid ( α )

$W_L$ = 0, $W_\alpha$ = 100 wt%

At $T_B$: Both α and $L$

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 73\,wt\%$$

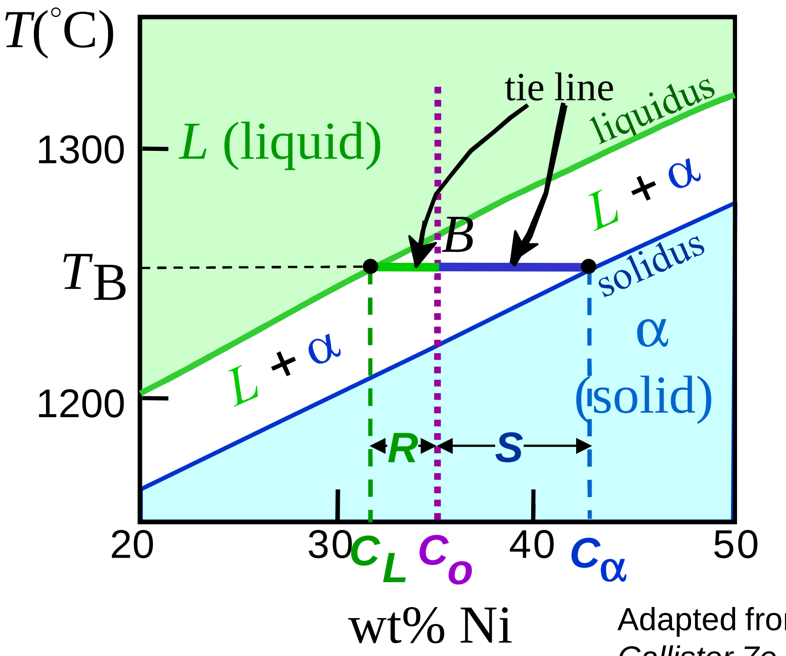
$$W_\alpha = \frac{R}{R+S} = 27\text{ wt\%}$$




Adapted from Fig. 9.3(b), *Callister 7e.* (Fig. 9.3(b) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)

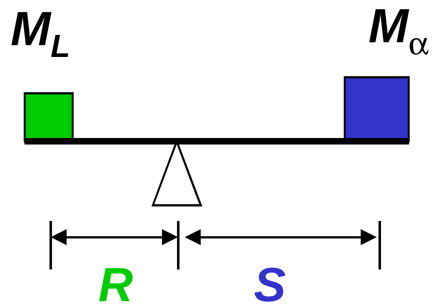
# The Lever Rule

- Tie line – connects the phases in equilibrium with each other - essentially an isotherm




Adapted from Fig. 9.3(b), *Callister 7e.*

How much of each phase?
Think of it as a lever (teeter-totter)




$$M_\alpha \cdot S = M_L \cdot R$$

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

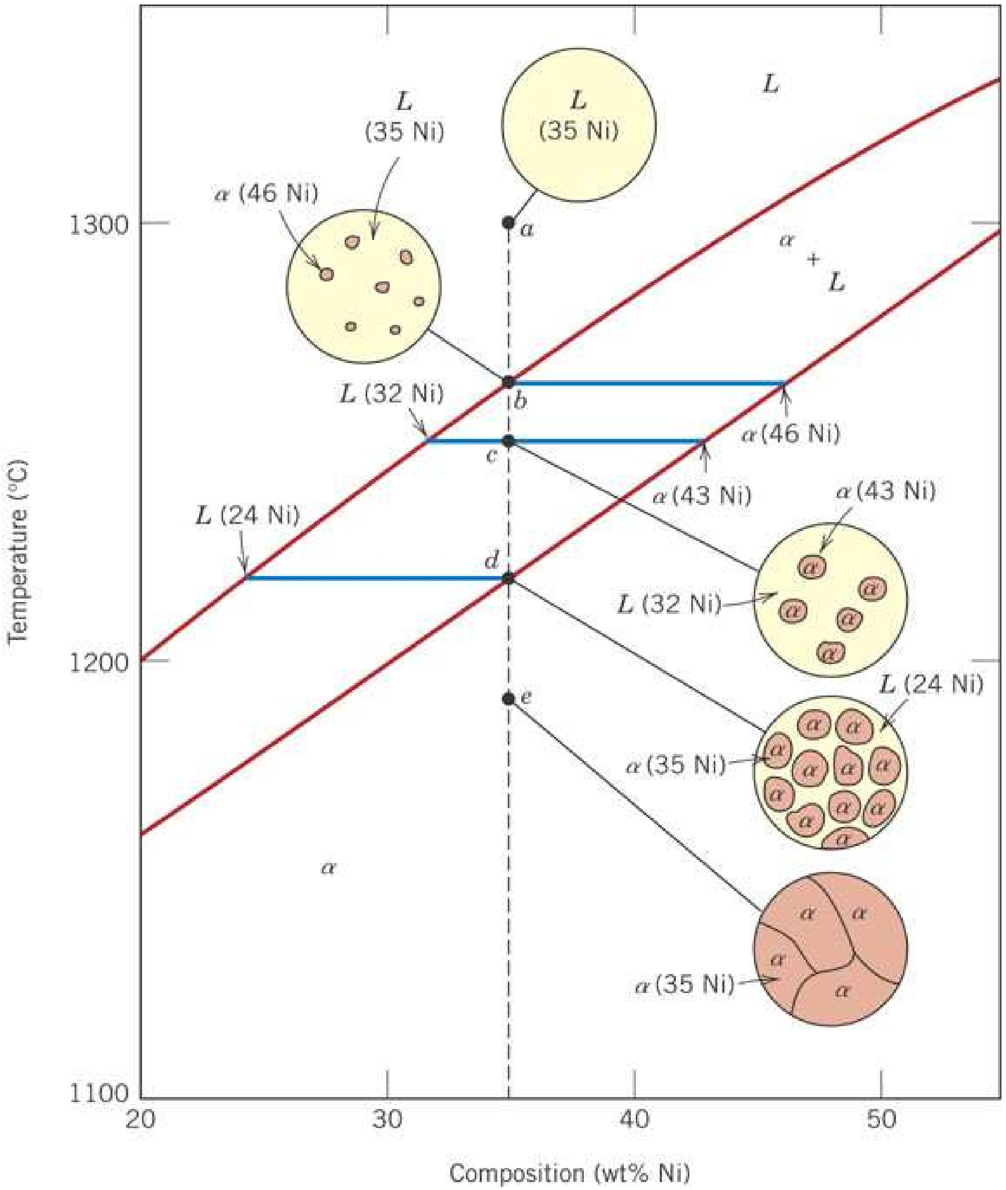
$$W_\alpha = \frac{R}{R+S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

# Equilibrium Cooling in a Cu-Ni Binary

- 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; a phase field extends from 0 to 100 wt% Ni.

- Consider
  $C_o$ = 35 wt%Ni.



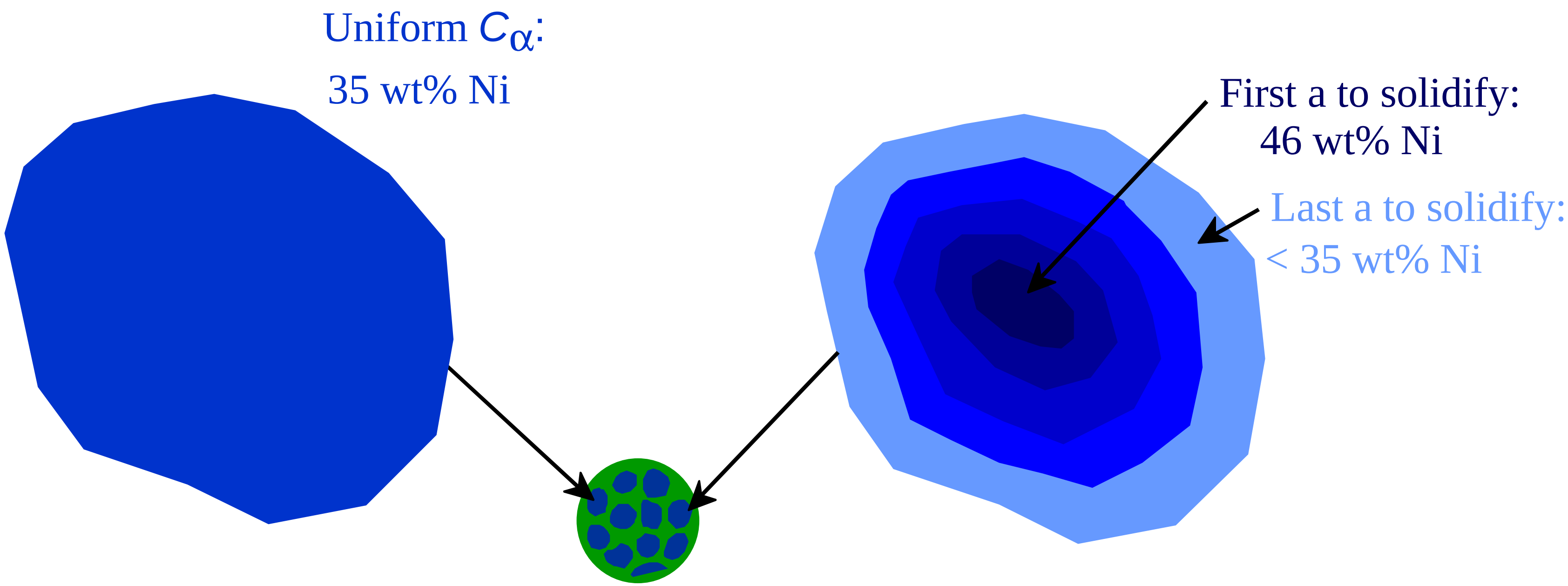

Cu-Ni system

# Cored vs Equilibrium Structures

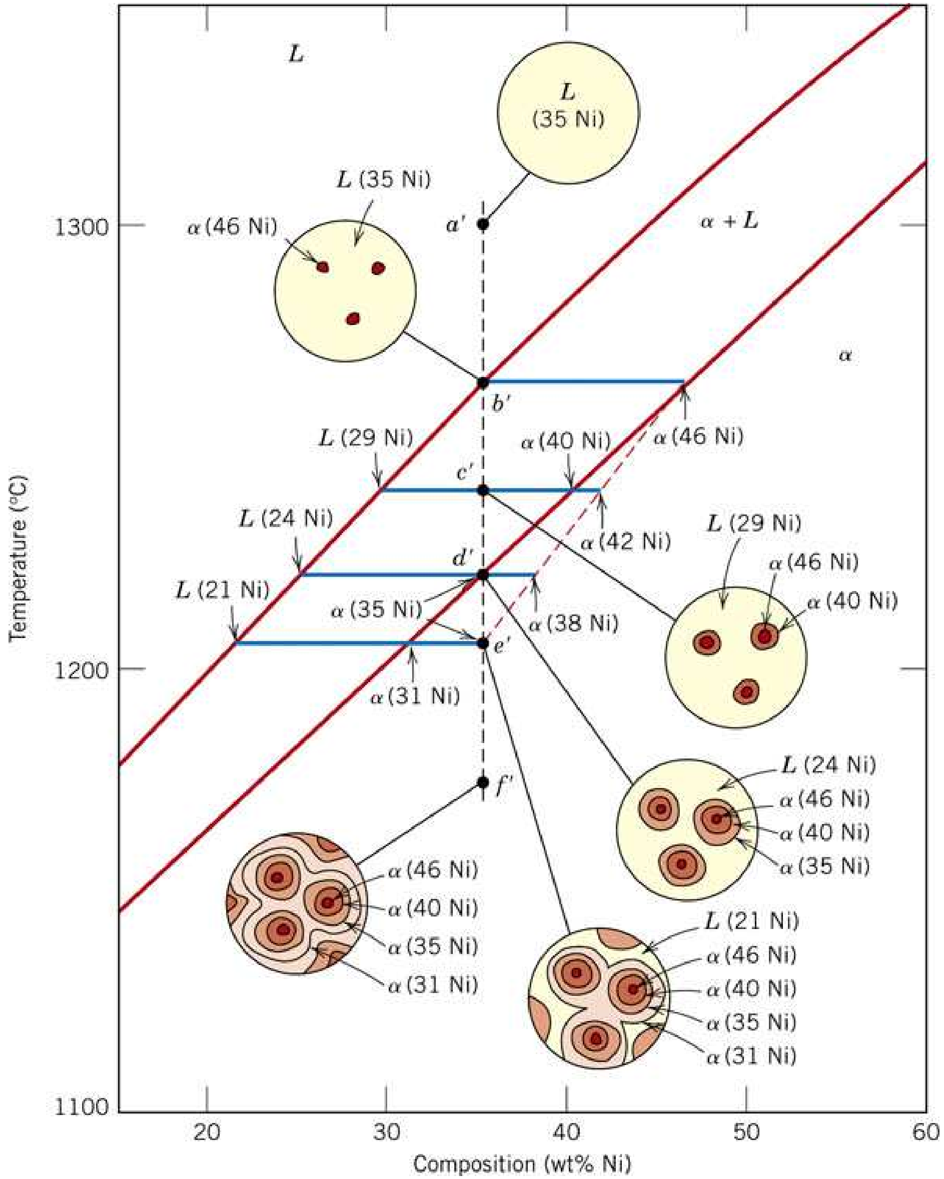
- $C_\alpha$ changes as we solidify.
- Cu-Ni case: First α to solidify has $C_\alpha$ = 46 wt% Ni.
  Last α to solidify has $C_\alpha$ = 35 wt% Ni.

- **Slow rate** of cooling:
  **Equilibrium** structure

- **Fast rate** of cooling:
  **Cored** structure



# Nonequilibrium Cooling in a Cu-Ni Binary

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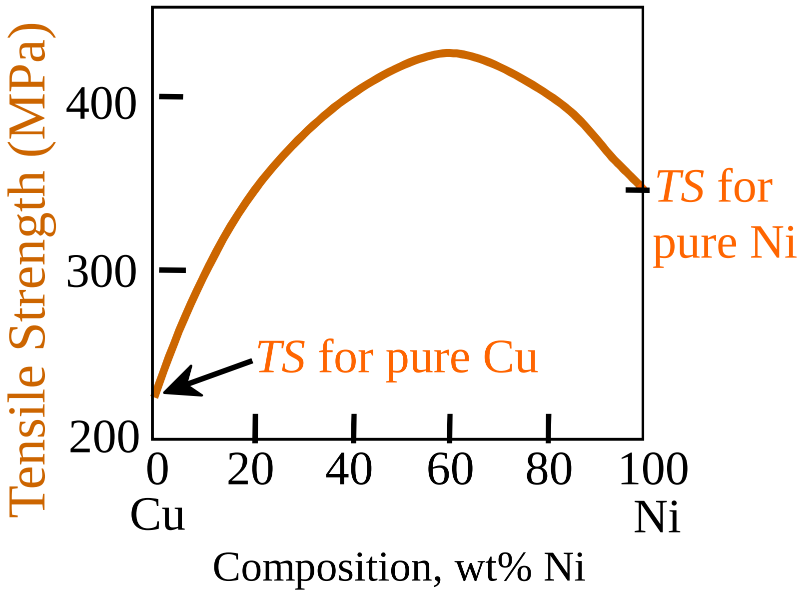
# Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

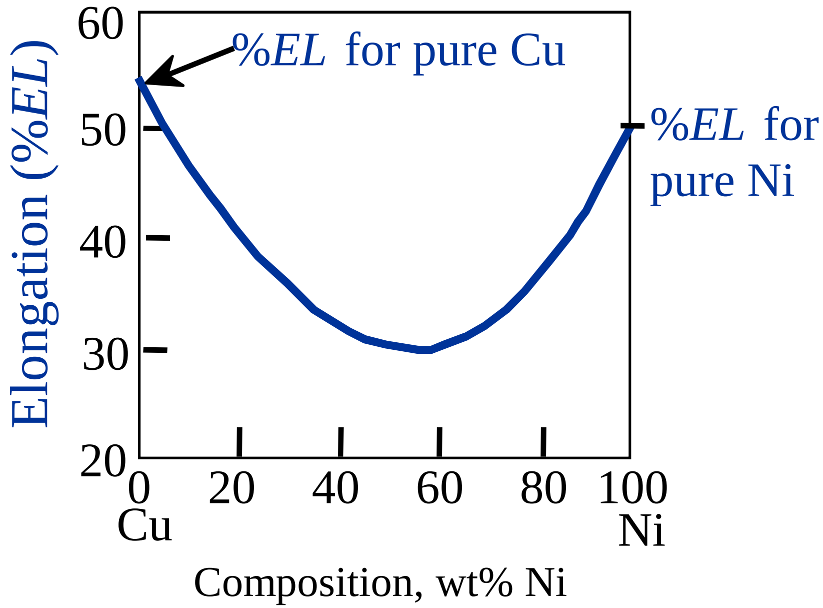
--Tensile strength (*TS*)




Adapted from Fig. 9.6(a), *Callister 7e.*

--Peak as a function of $C_o$

--Ductility (%*EL*,%*AR*)




Adapted from Fig. 9.6(b), *Callister 7e.*

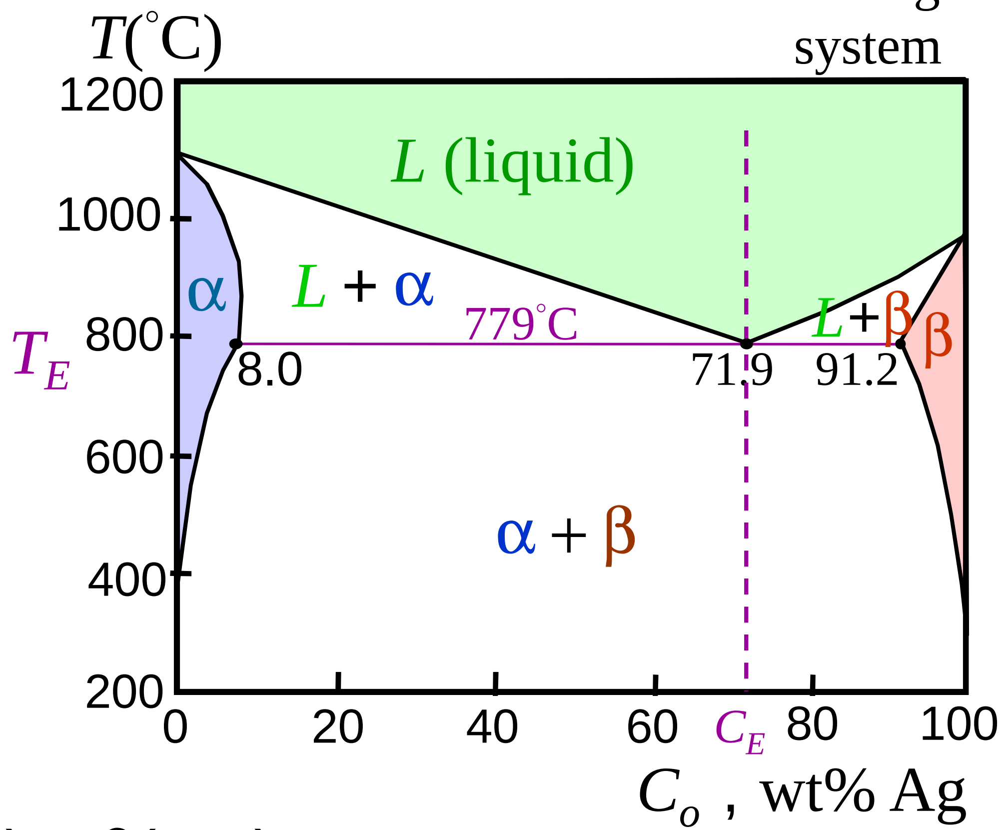
--Min. as a function of $C_o$

# Binary-Eutectic Systems (Cu-Ag)

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 $T_E$
- $C_E$ : Min. melting $T_E$ composition



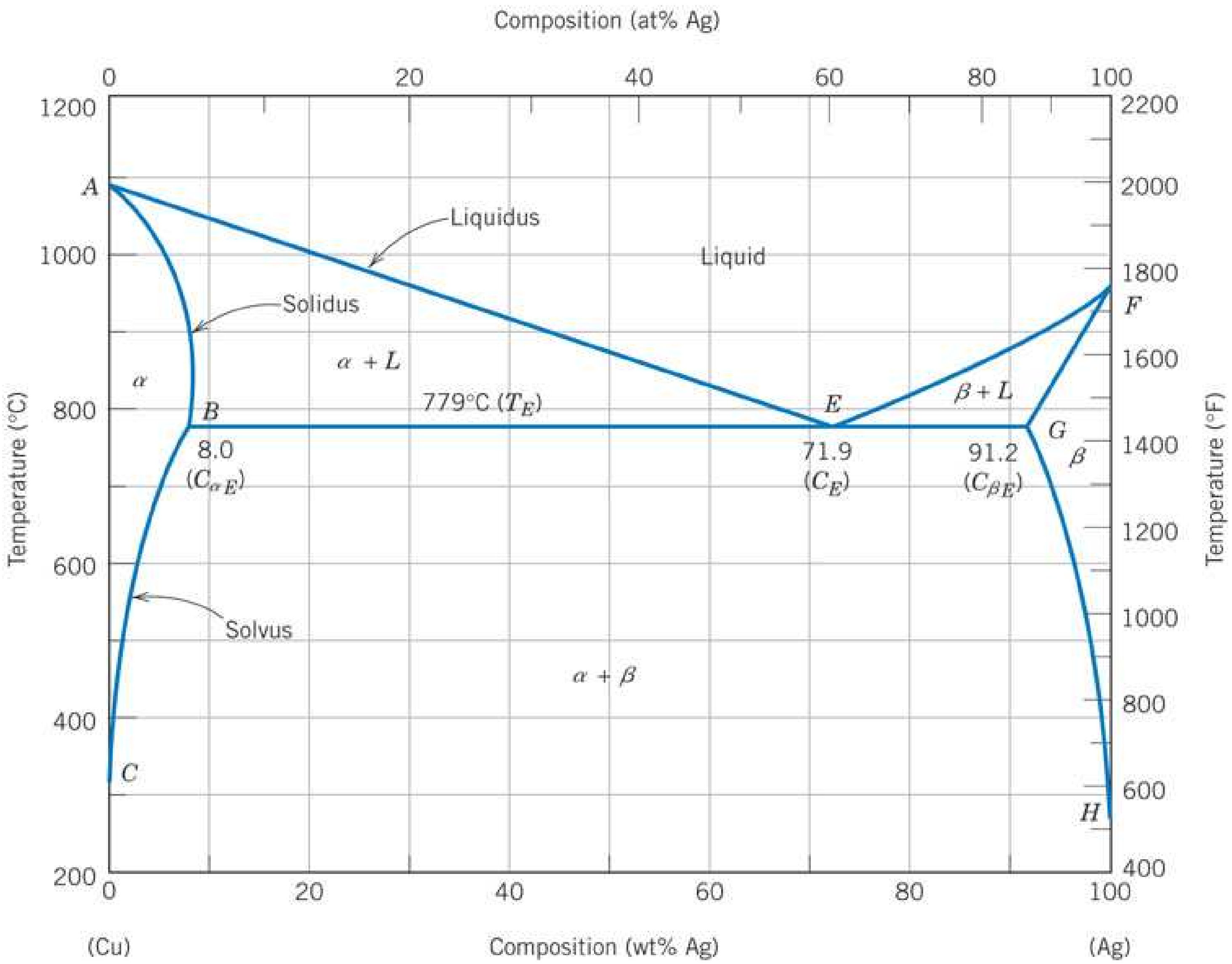

Adapted from Fig. 9.7, *Callister 7e.*

- **Eutectic transition**

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

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

# Binary-Eutectic Systems: Cu-Ag



# EX: Pb-Sn Eutectic System (1)

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

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

  --compositions of phases:

  $C_O$ = 40 wt% Sn

  $C_\alpha$ = 11 wt% Sn

  $C_\beta$ = 99 wt% Sn

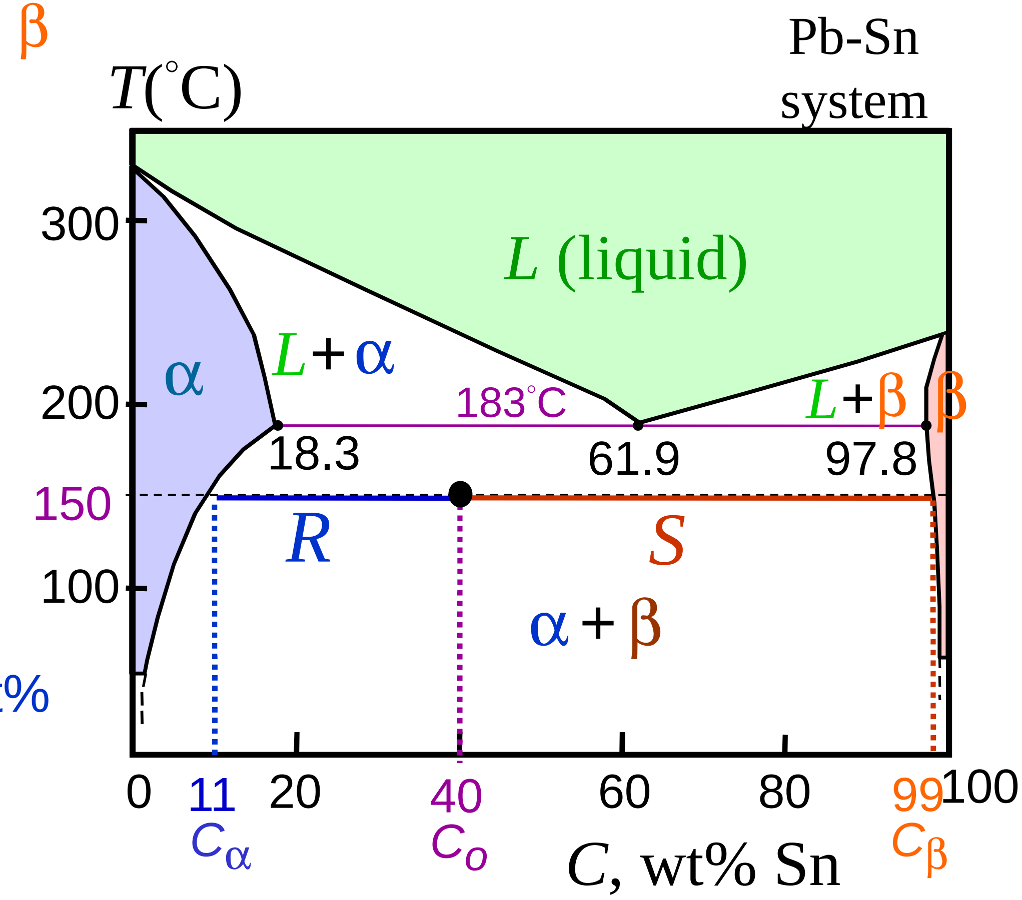
  --the relative amount of each phase:

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_O}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%}$$

$$W_\beta = \frac{R}{R+S} = \frac{C_O - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%}$$




Adapted from Fig. 9.8, *Callister 7e.*

# EX: Pb-Sn Eutectic System (2)

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find...
  - --the phases present: $\alpha + L$
  - --compositions of phases:

    $C_O$ = 40 wt% Sn

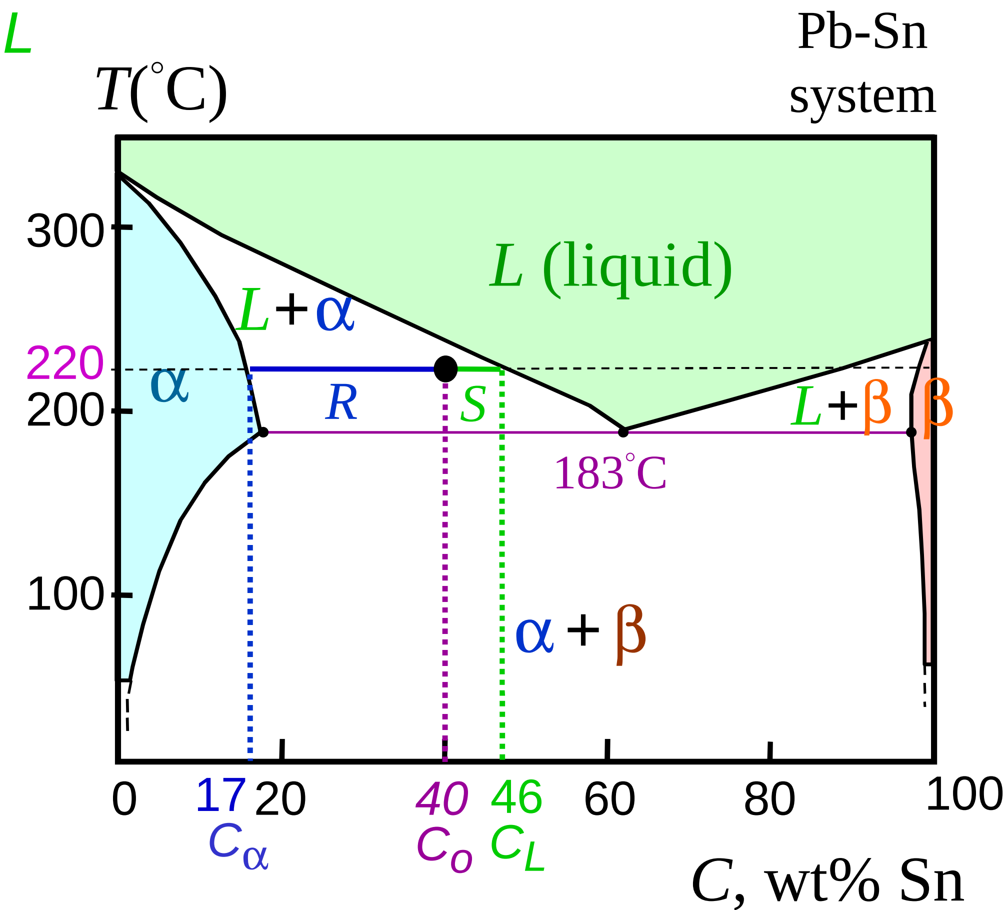
    $C_\alpha$ = 17 wt% Sn

    $C_L$ = 46 wt% Sn

  - --the relative amount of each phase:

$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$




Adapted from Fig. 9.8, *Callister 7e.*

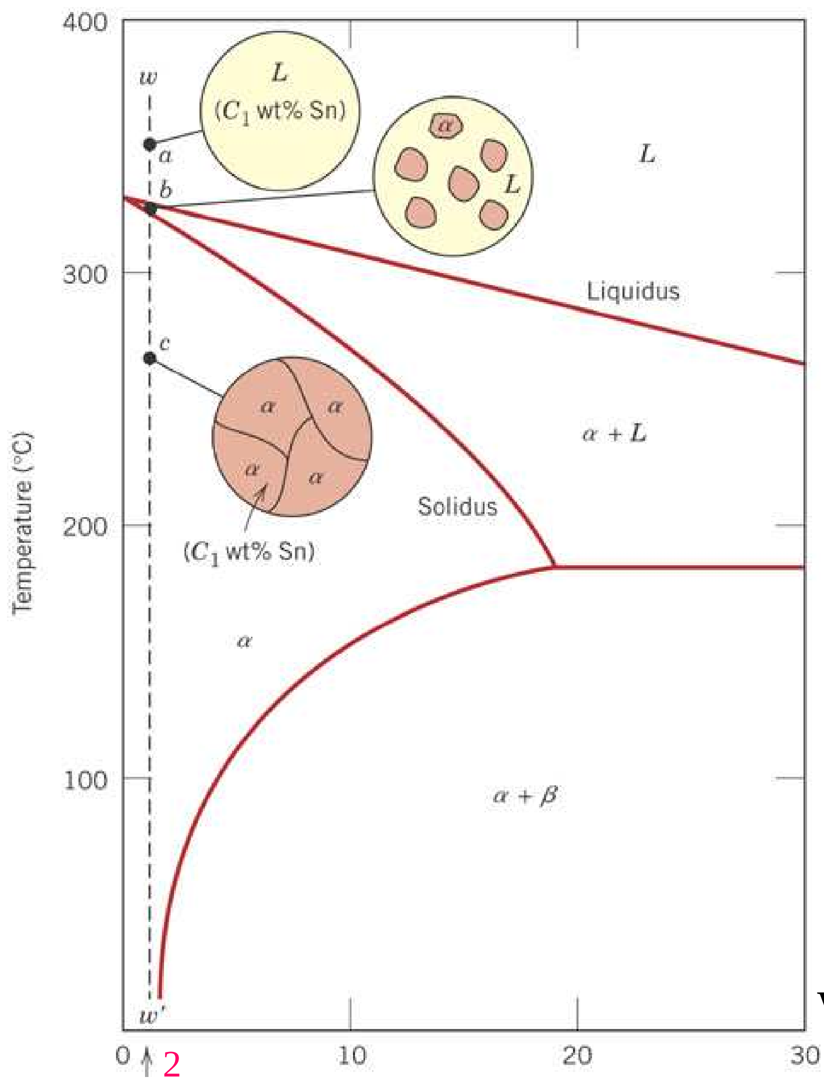
# Microstructures in Eutectic Systems: I

- $C_o$ < 2 wt% Sn
- Result:

--at extreme ends

--polycrystal of α grains

i.e., **only one solid phase**.




(Pb-Sn System)

wt% Sn

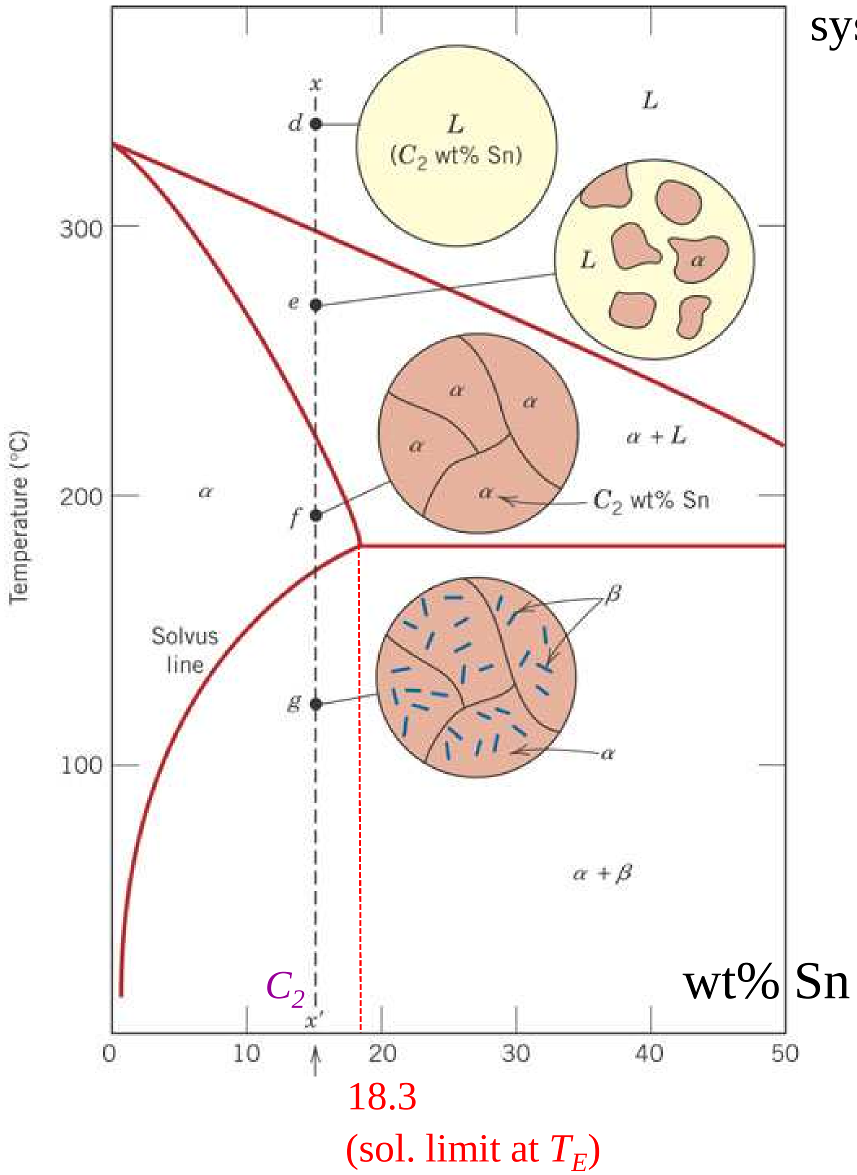
$C_o$ (room $T$ solubility limit)

Adapted from Fig. 9.11, *Callister 7e.*

# Microstructures in Eutectic Systems: II

- 2 wt% Sn < $C_2$ < 18.3 wt% Sn
- Result:
  - Initially liquid + α
  - then α alone
  - finally two phases
    - α polycrystal
    - fine β-phase inclusions

Pb-Sn system

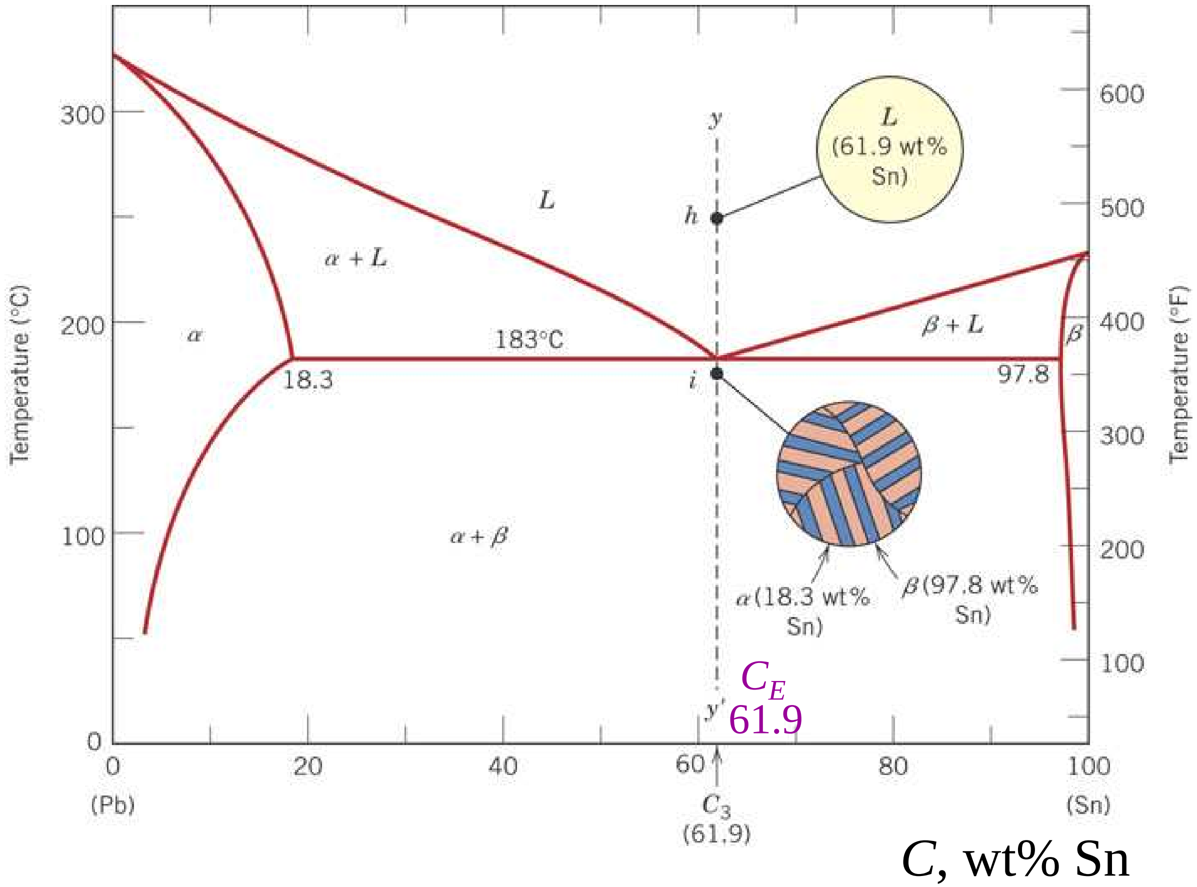



Adapted from Fig. 9.12, *Callister 7e.*

# Microstructures in Eutectic Systems: III

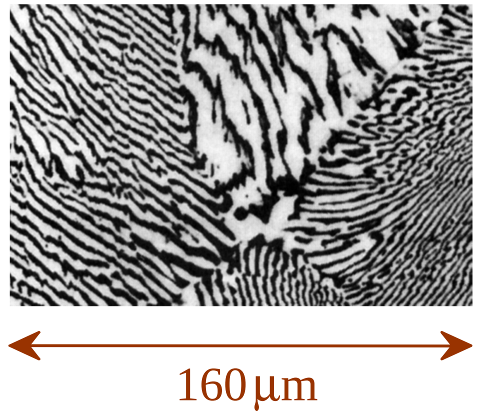
$$L(61.9\text{ wt\% Sn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(18.3\text{ wt\% Sn}) + \beta(97.8\text{ wt\% Sn})$$

- Result: Eutectic microstructure (lamellar structure)
  --alternating layers (lamellae) of α and β crystals.




Adapted from Fig. 9.13, *Callister 7e.*

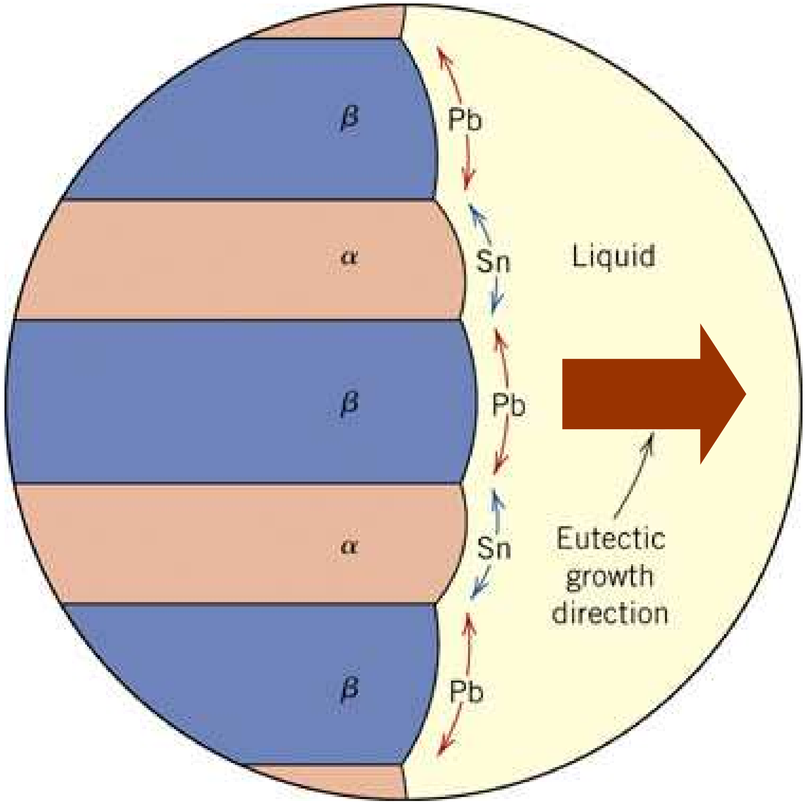
Micrograph of Pb-Sn eutectic microstructure



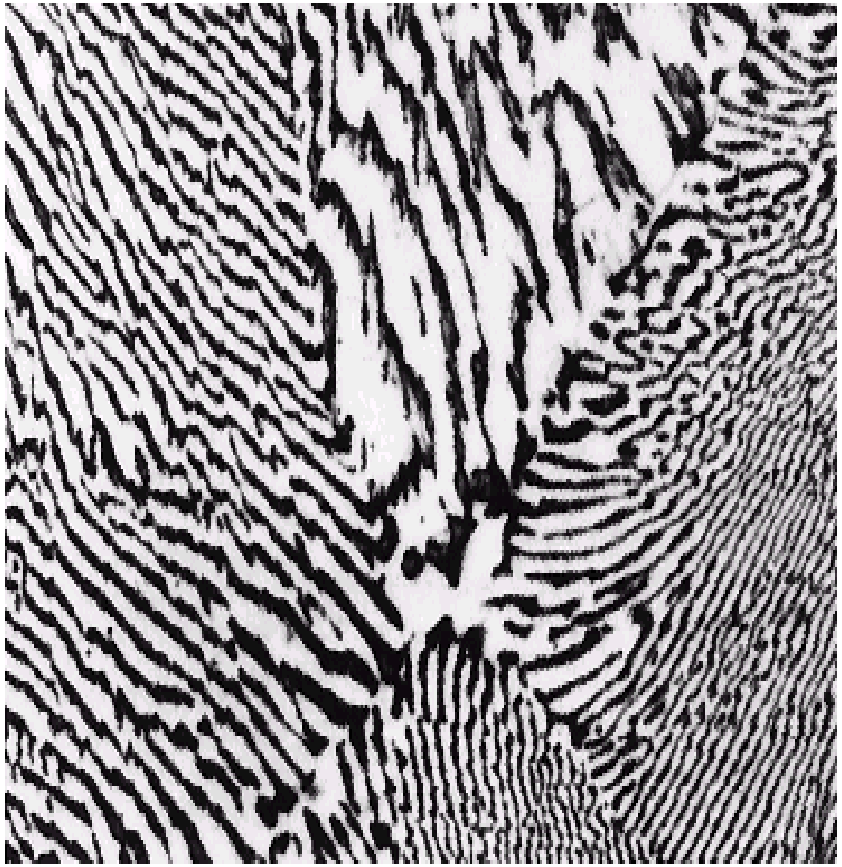

Adapted from Fig. 9.14, *Callister 7e.*

# Lamellar Eutectic Structure

$$L(61.9\ \text{wt\% Sn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(18.3\ \text{wt\% Sn}) + \beta(97.8\ \text{wt\% Sn})$$

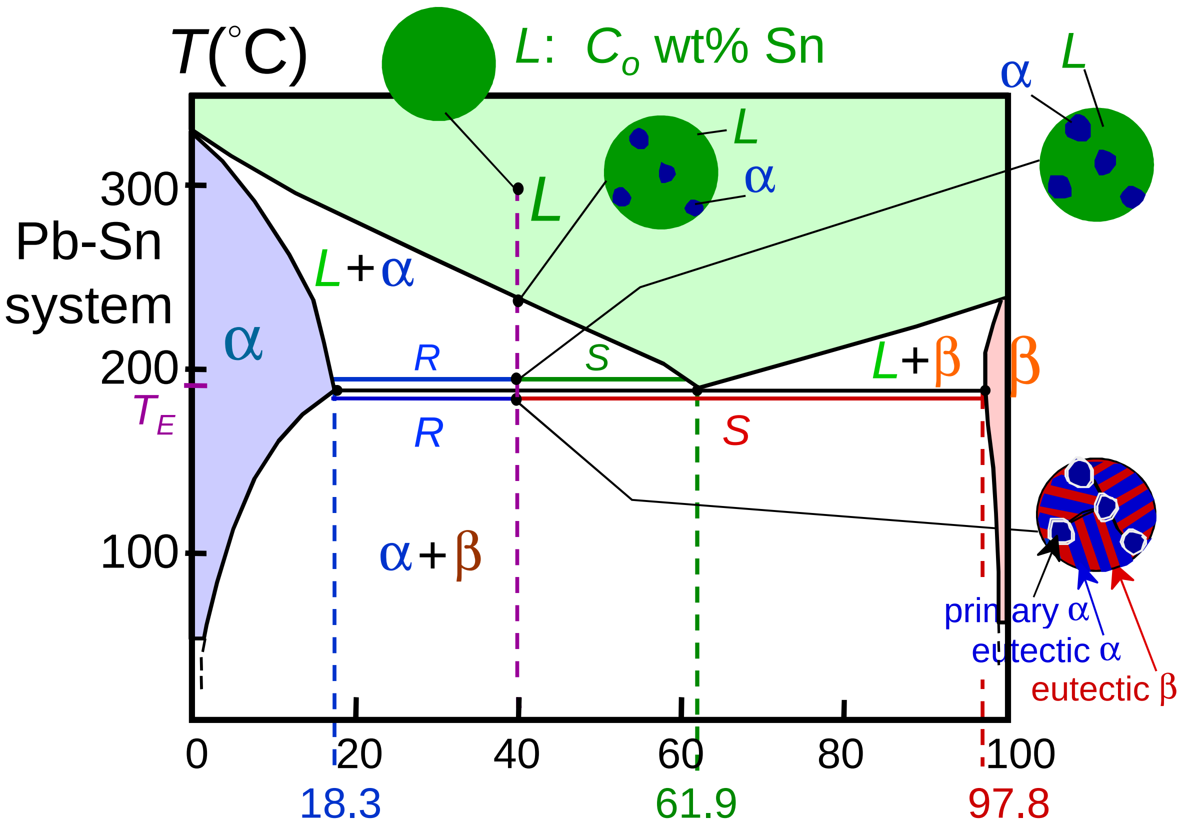



Adapted from Figs. 9.14 & 9.15, *Callister 7e.*



# Microstructures in Eutectic Systems: IV

- $18.3$ wt% Sn < $C_o$ < $61.9$ wt% Sn
- Result: α crystals and a eutectic microstructure




Adapted from Fig. 9.16, *Callister 7e.*

- Just above $T_E$ :

$C_\alpha = 18.3$ wt% Sn

$C_L = 61.9$ wt% Sn

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

$$W_L = (1 - W_\alpha) = 50 \text{ wt\%}$$

- Just below $T_E$ :

$C_\alpha = 18.3$ wt% Sn

$C_\beta = 97.8$ wt% Sn

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

$W_\beta = 27$ wt%

# Eutectic, Eutectoid, & Peritectic

- Eutectic - liquid transforms to two solid phases

$$L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + \beta \qquad \text{(For Pb-Sn, 183°C, 61.9 wt\% Sn)}$$

- Eutectoid – one solid phase transforms to two other solid phases

intermetallic compound
- cementite

$$S_2 \rightleftharpoons S_1 + S_3$$

$$\gamma \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + Fe_3C \qquad \text{(For Fe-C, 727°C, 0.76 wt\% C)}$$

- Peritectic - liquid and one solid phase transform to a second solid phase

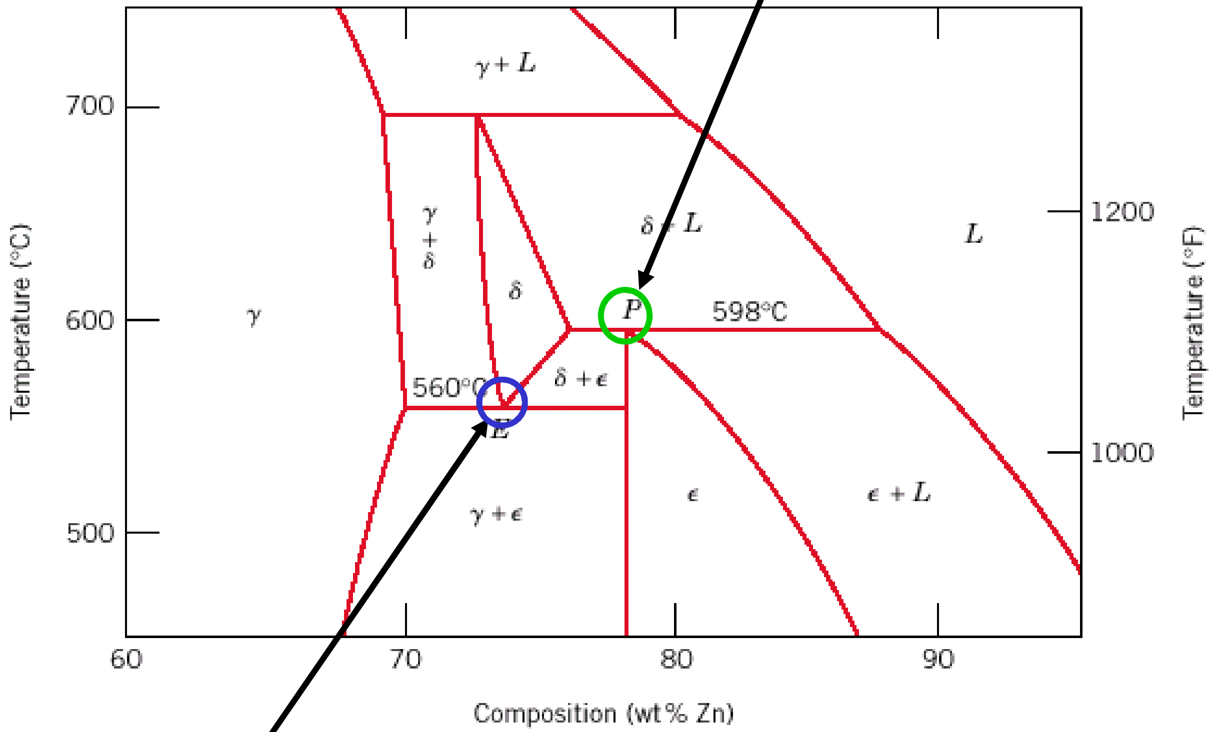
$$S_1 + L \rightleftharpoons S_2$$

$$\delta + L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \gamma \qquad \text{(For Fe-C, 1493°C, 0.16 wt\% C)}$$

# Eutectoid & Peritectic

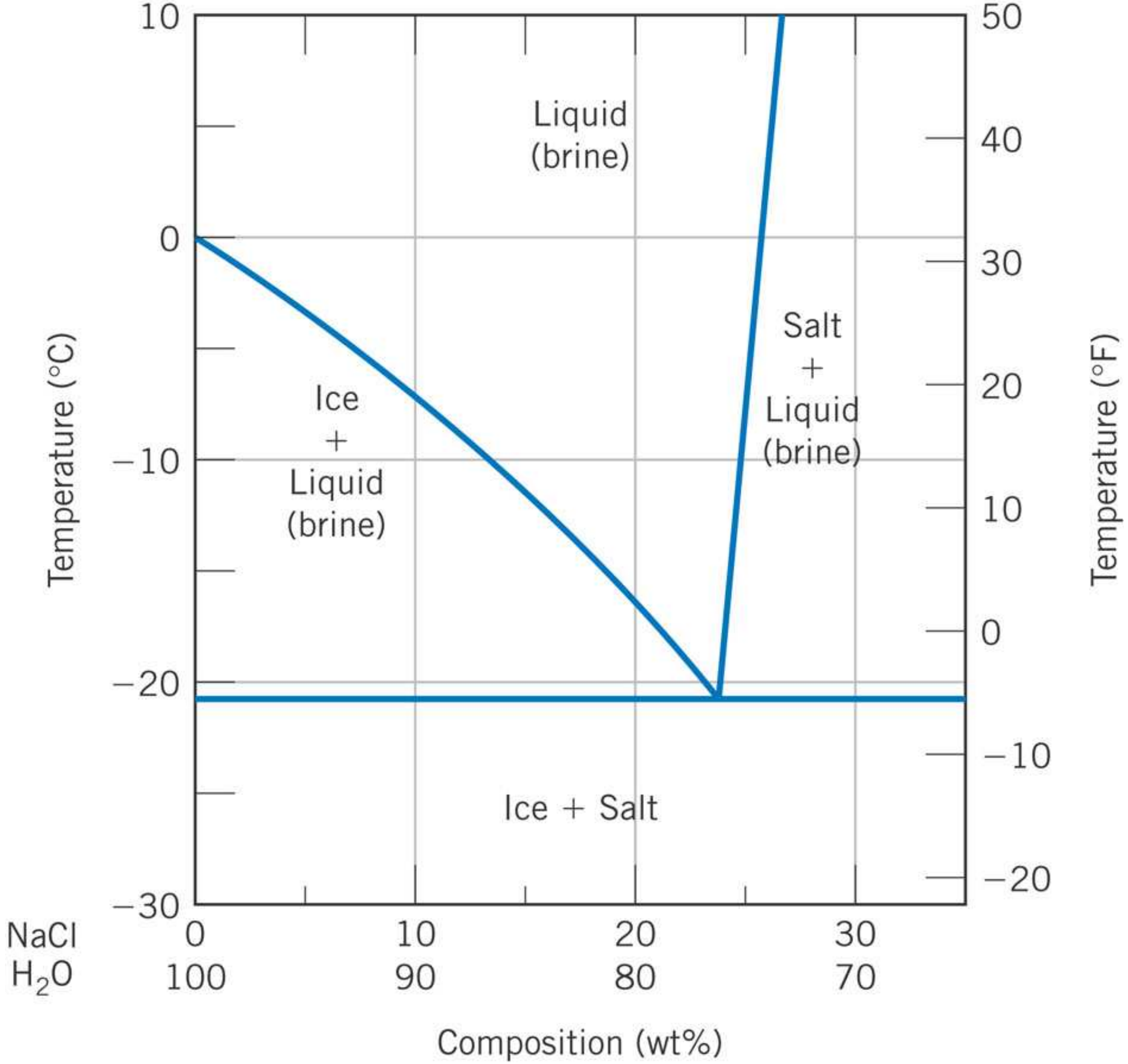
Peritectic transition $\gamma + L \rightleftharpoons \delta$

## Cu-Zn Phase diagram




Adapted from
Fig. 9.21, *Callister 7e.*

Eutectoid transition $\delta \rightleftharpoons \gamma + \varepsilon$

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# Iron-Carbon (Fe-C) Phase Diagram

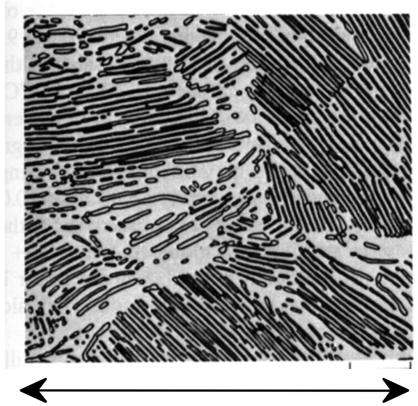
- 2 important points

  -Eutectic ($A$):

  $L \Rightarrow \gamma + Fe_3C$

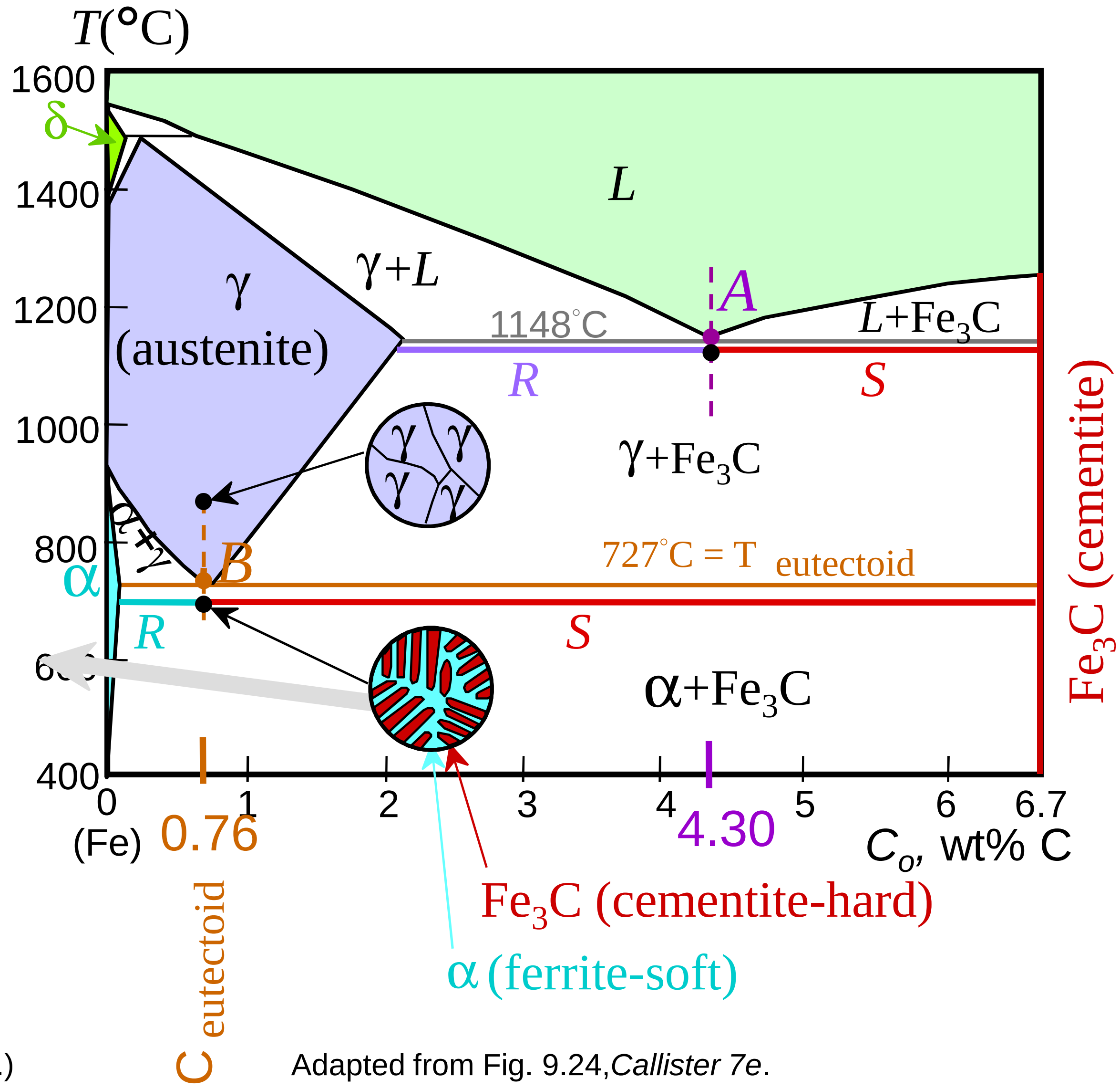
  -Eutectoid ($B$):

  $\gamma \Rightarrow \alpha + Fe_3C$



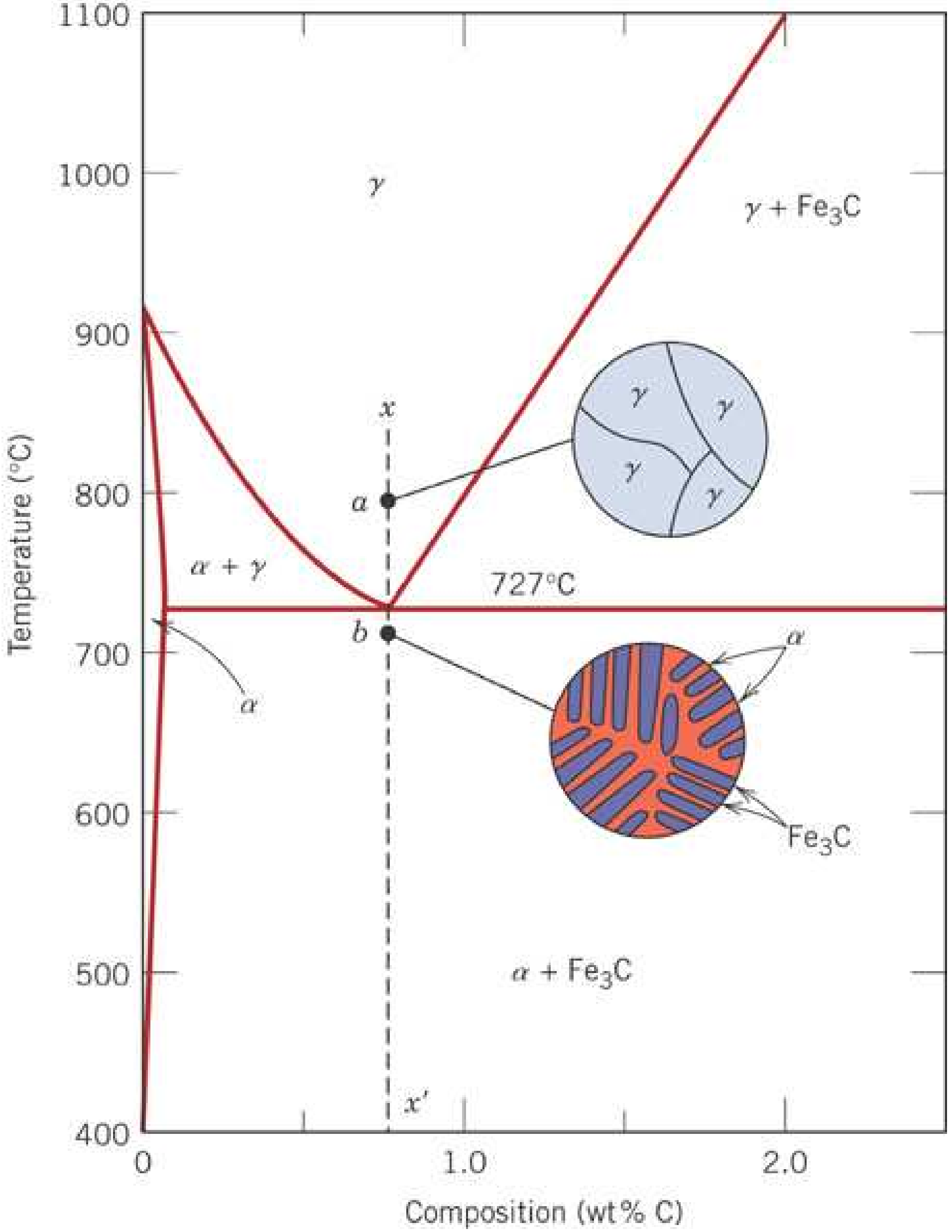

Result: Pearlite = alternating layers of $\alpha$ and $Fe_3C$ phases

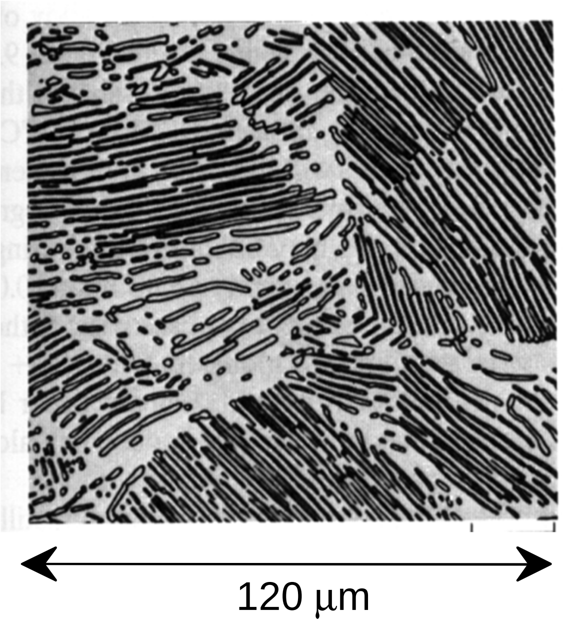
(Adapted from Fig. 9.27, *Callister 7e*.)




Adapted from Fig. 9.24, *Callister 7e*.

# Microstructures in Fe-C Systems: I

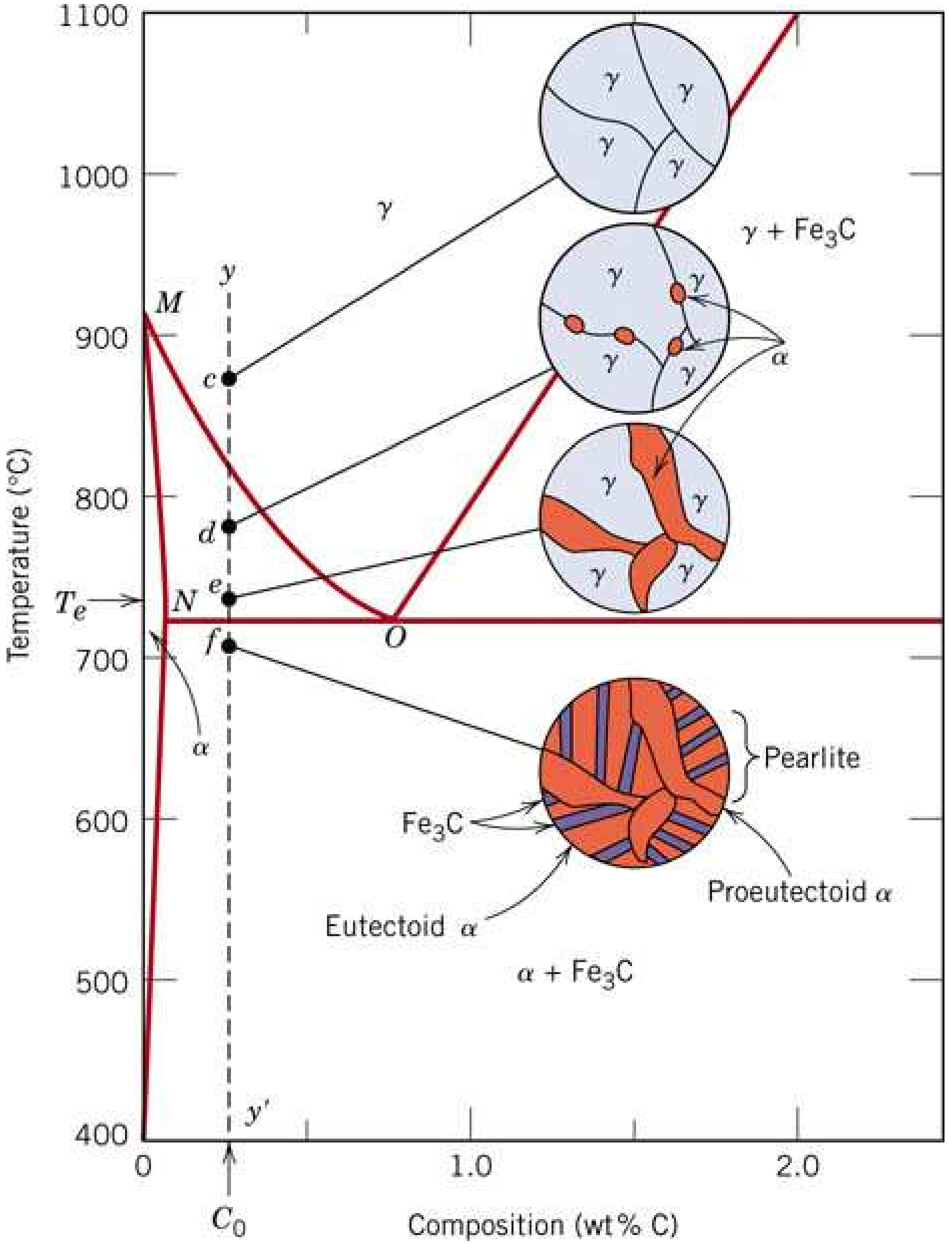


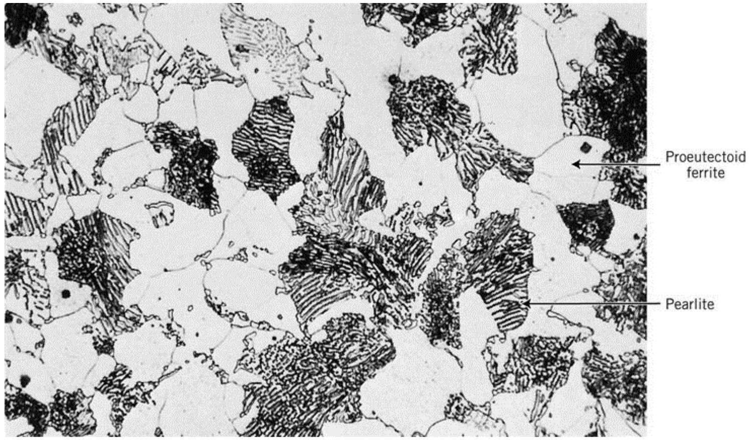

Result: Pearlite = alternating layers of α and $Fe_3C$ phases

(Adapted from Fig. 9.27, *Callister 7e*.)

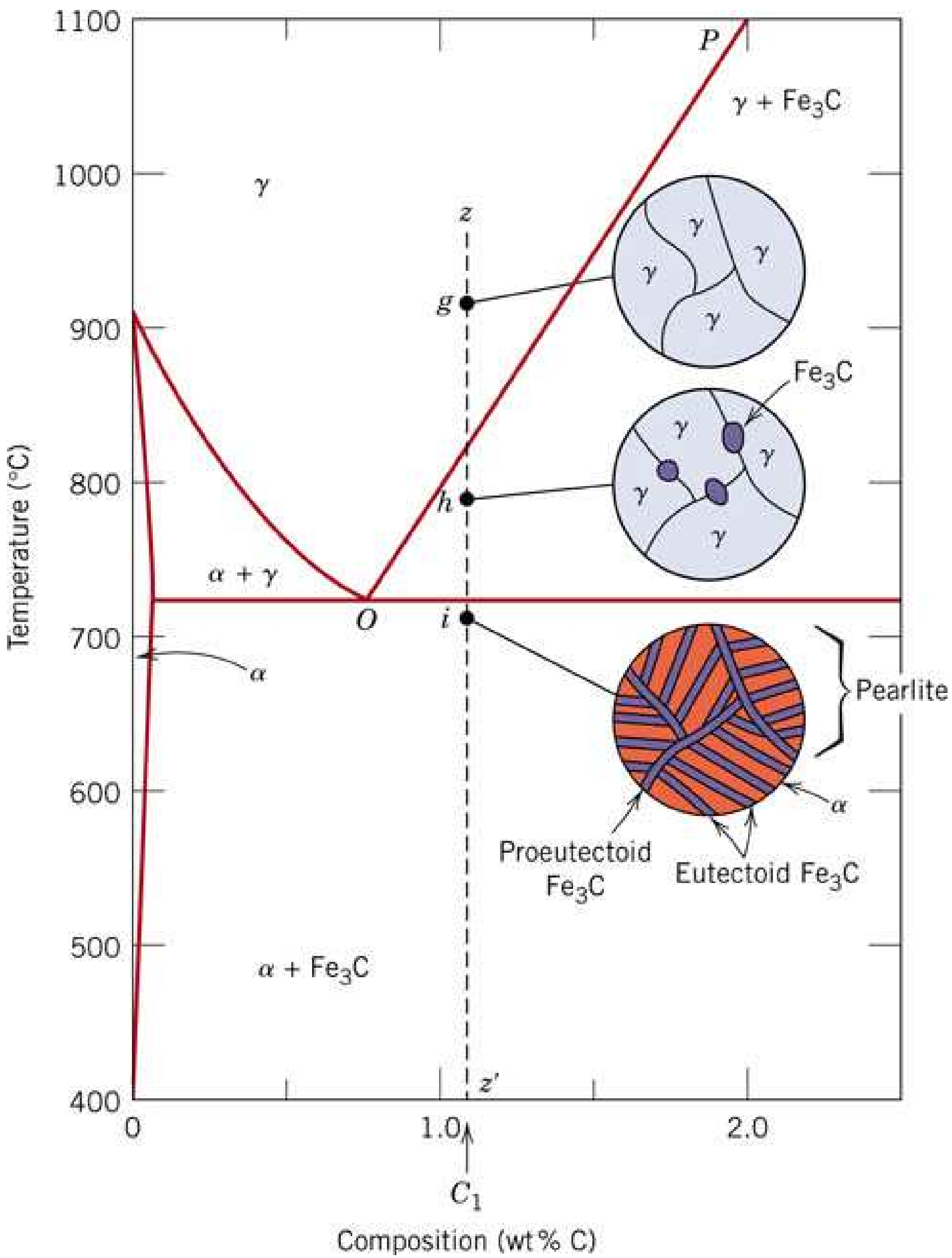
# Microstructures in Fe-C Systems: II



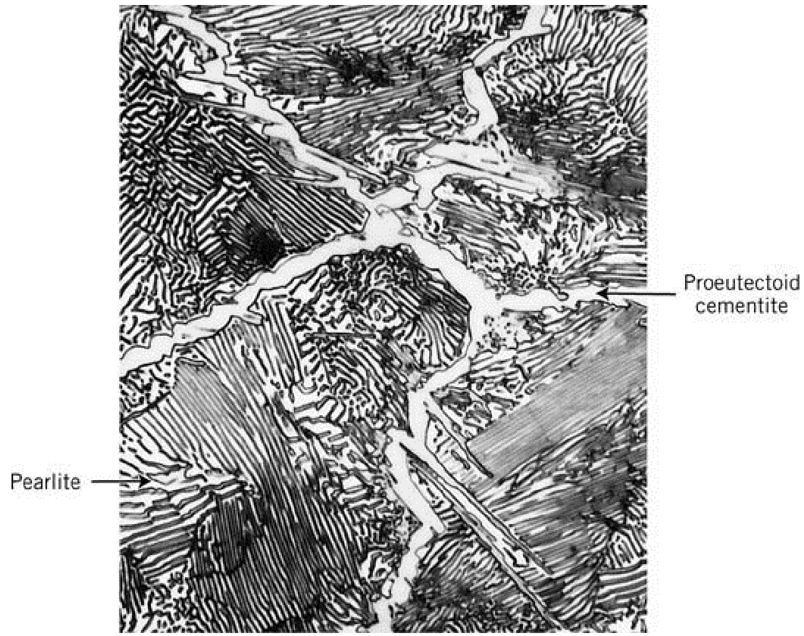

## Hypoeutectoid Steel

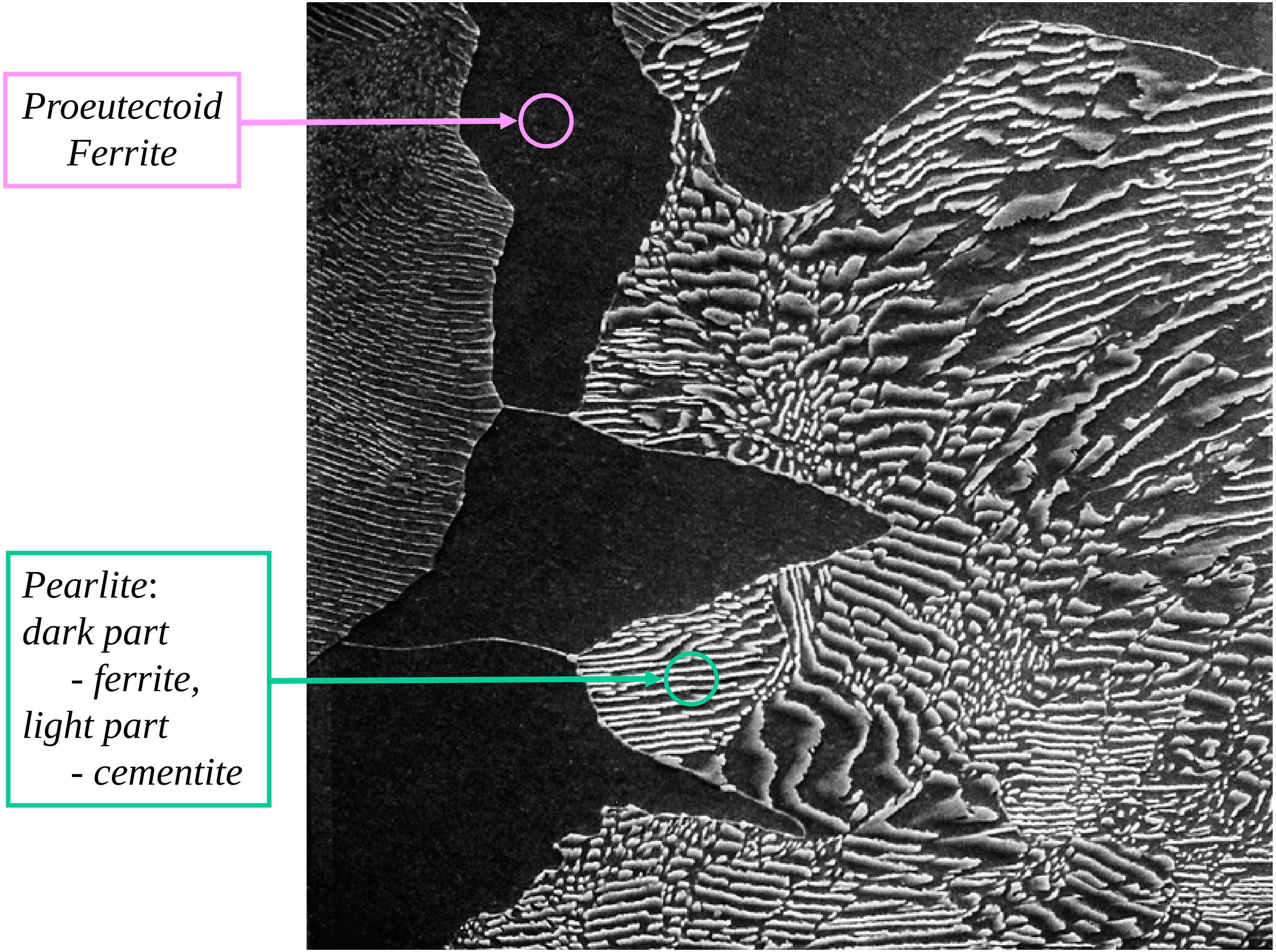


# Microstructures in Fe-C Systems: II




## Hypereutectoid Steel






Microstructure of a plain carbon steel (*0.44 wt% C*)

# Example: Phase Equilibria

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following

a) composition of $Fe_3C$ and ferrite ($\alpha$)
b) the amount of carbide (cementite) in grams that forms per 100 g of steel
c) the amount of pearlite and proeutectoid ferrite ($\alpha$)

# Chapter 9 – Phase Equilibria

**Solution:** a) composition of $Fe_3C$ and ferrite ($\alpha$)

b) the amount of **carbide** (**cementite**) in grams that forms per 100 g of steel

$C_o = 0.40$ wt% C

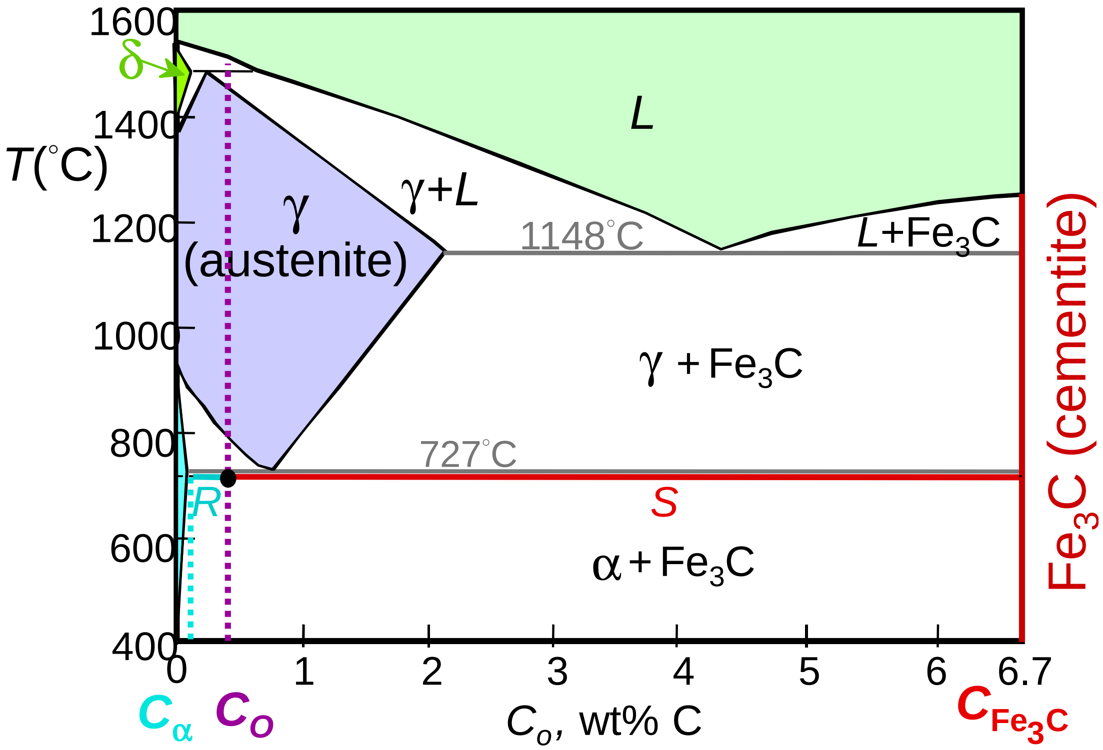
$C_\alpha = 0.022$ wt% C

$C_{Fe_3C} = 6.70$ wt% C

$$\frac{Fe_3C}{Fe_3C + \alpha} = \frac{C_o - C_\alpha}{C_{Fe_3C} - C_\alpha} x100$$

$$= \frac{0.4 - 0.022}{6.7 - 0.022} x\,100 = 5.7\text{g}$$

$$\boxed{\begin{aligned} Fe_3C &= 5.7\text{ g} \\ \alpha &= 94.3\text{ g} \end{aligned}}$$



# Chapter 9 – Phase Equilibria

c. the amount of pearlite and proeutectoid ferrite ($\alpha$)

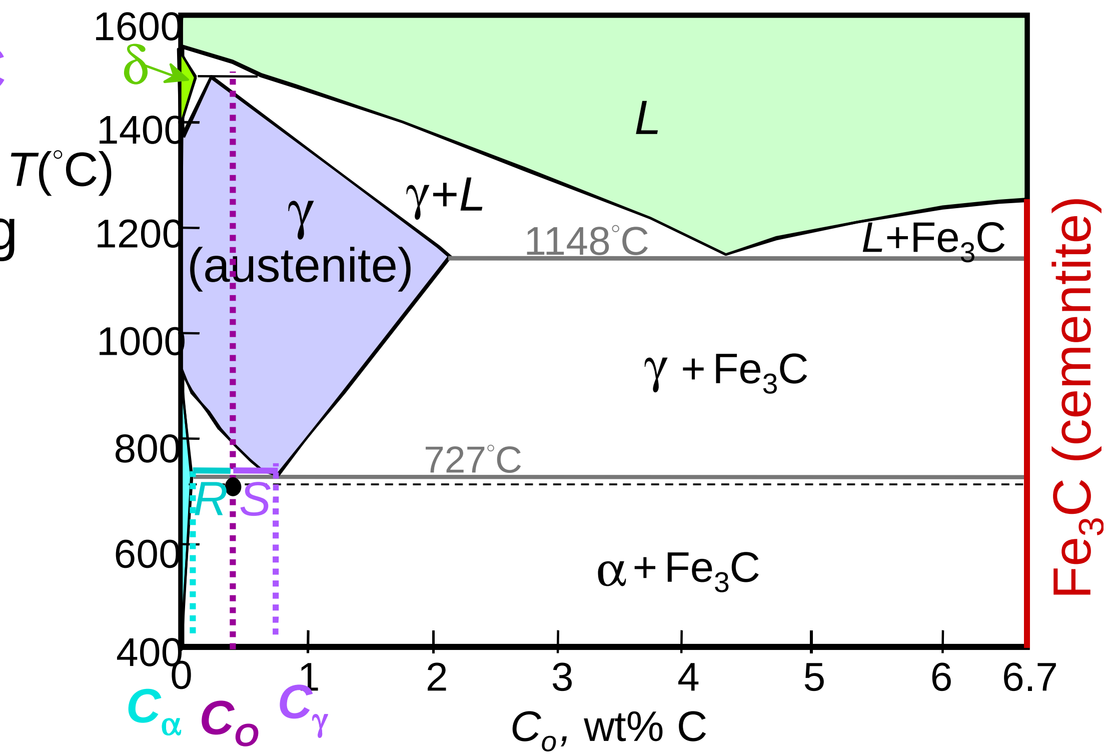
note: amount of pearlite = amount of $\gamma$ just above $T_E$

$C_o$ = 0.40 wt% C

$C_\alpha$ = 0.022 wt% C

$C_{pearlite} = C_\gamma$ = 0.76 wt% C

$$\frac{\gamma}{\gamma+\alpha} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha} \times 100 = 51.2 \text{ g}$$

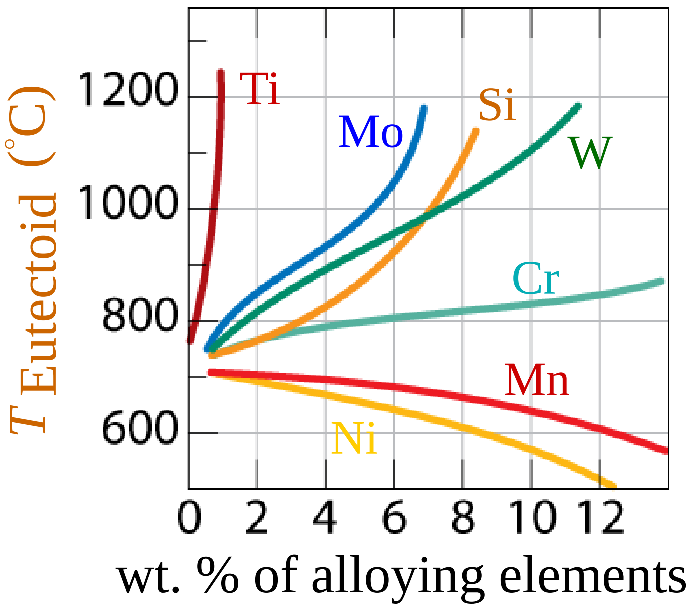



pearlite = 51.2 g

proeutectoid $\alpha$ = 48.8 g

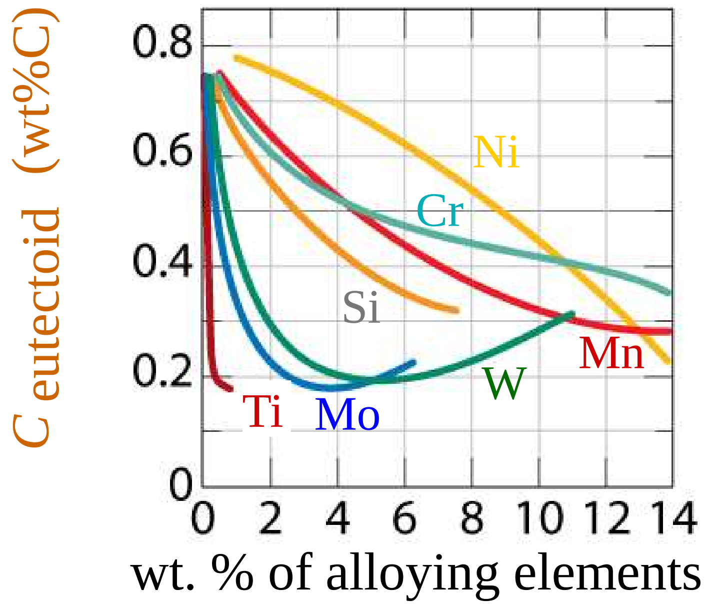
# Alloying Steel with More Elements

- $T_{eutectoid}$ changes:




Adapted from Fig. 9.34,*Callister 7e*. (Fig. 9.34 from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)

- $C_{eutectoid}$ changes:




Adapted from Fig. 9.35,*Callister 7e*. (Fig. 9.35 from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)

# Summary

- Phase diagrams are useful tools to determine:
  --the number and types of phases,
  --the wt% of each phase,
  --and the composition of each phase
  for a given *T* and composition of the system.

- Alloying to produce a solid solution usually
  --increases the tensile strength (*TS*)
  --decreases the ductility.

- Binary eutectics and binary eutectoids allow for a range of microstructures.