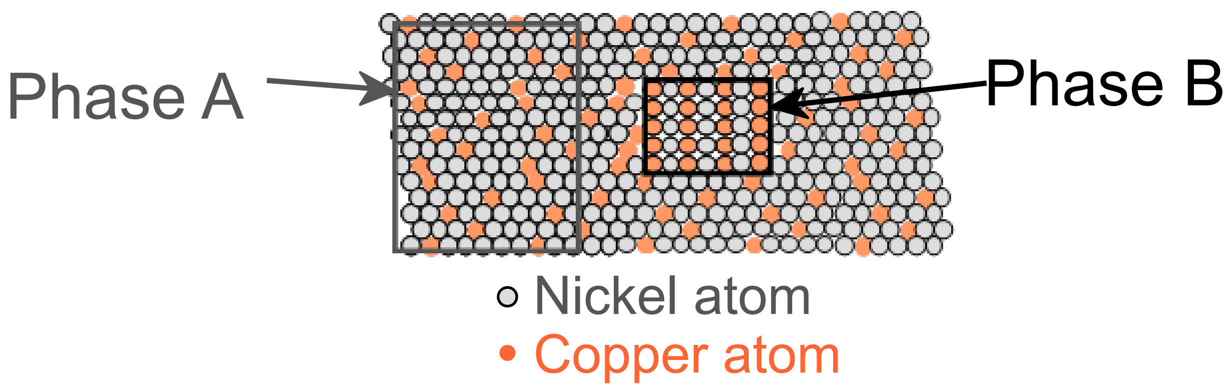
Chapter 11: Phase Diagrams

ISSUES TO ADDRESS...

- When we combine two elements...
  what is the resulting equilibrium state?
- In particular, if we specify...
  -- the composition (e.g., wt% Cu - wt% Ni), and
  -- the temperature (*T*)

  then...
  How many phases form?
  What is the composition of each phase?
  What is the amount of each phase?



Phase Equilibria: Solubility Limit

- Solution – solid, liquid, or gas solutions, single phase
- Mixture – more than one phase

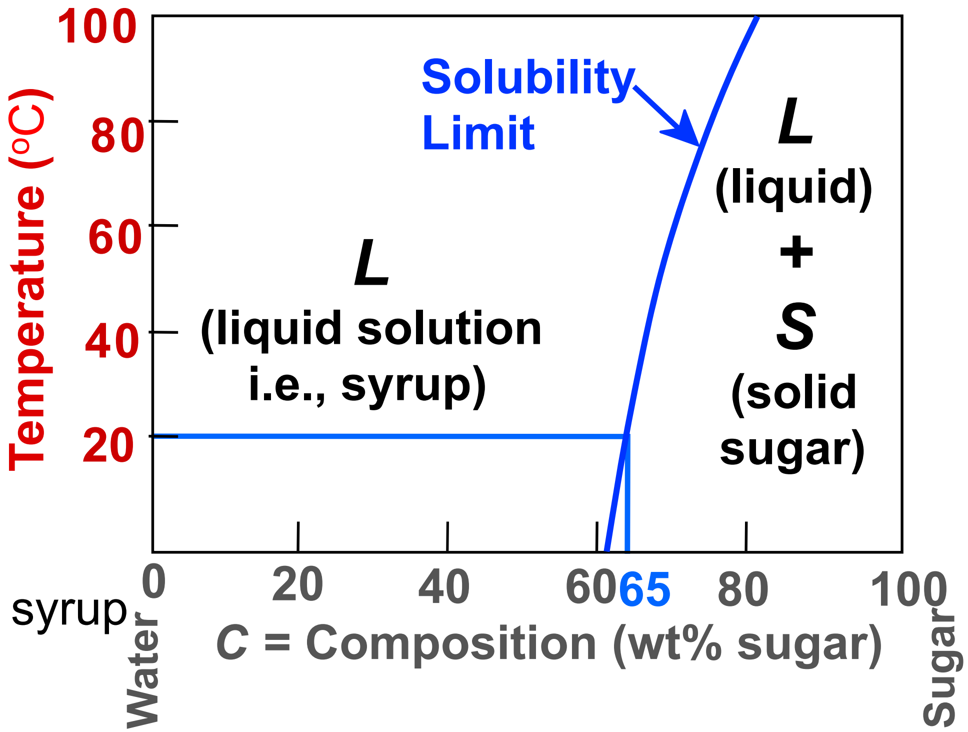
Adapted from Fig. 11.1, *Callister & Rethwisch 9e.*

- Solubility Limit:
  Maximum concentration for which only a single phase solution exists.

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

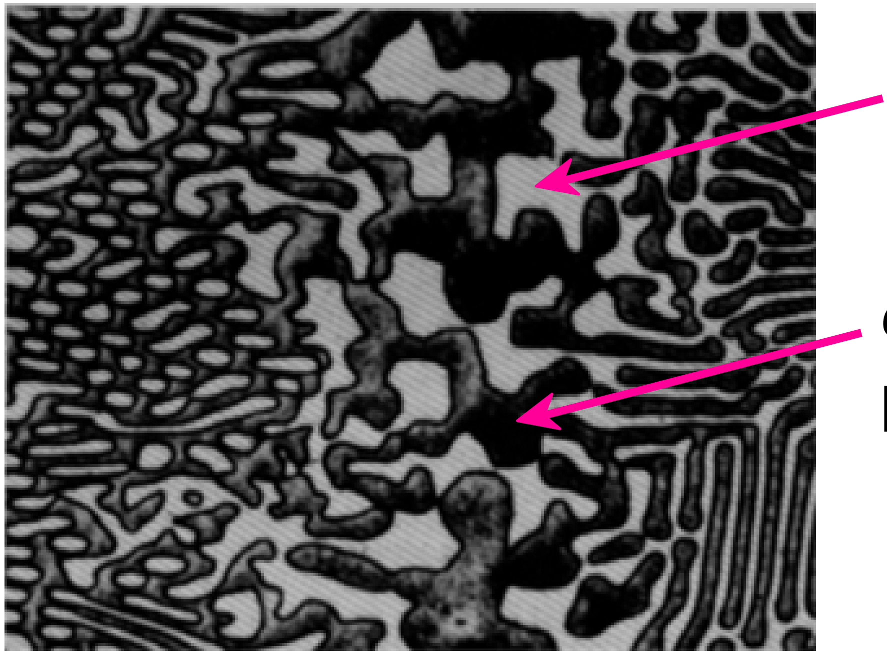
Sugar/Water Phase Diagram



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*.

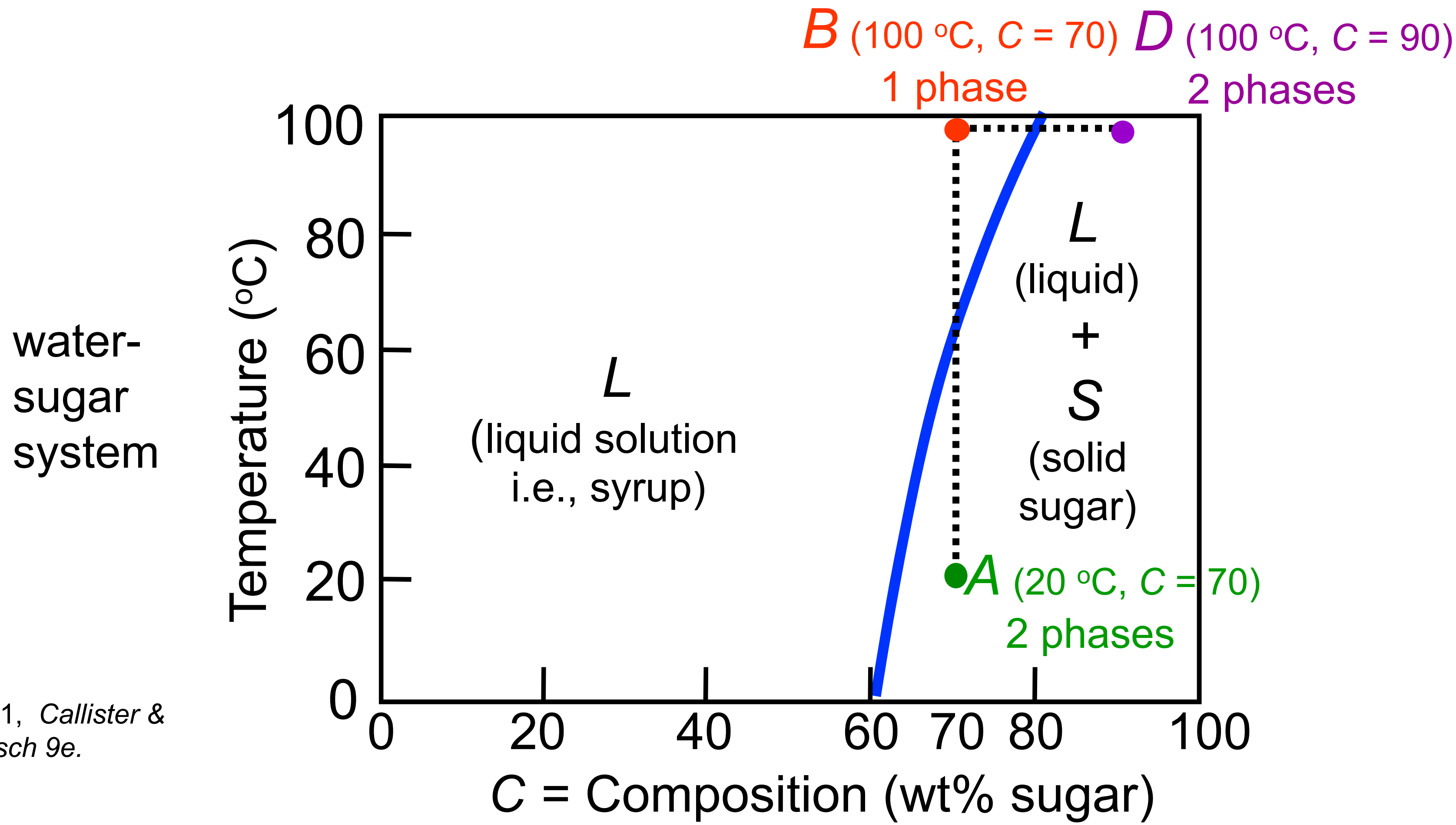


Fig. 11.1, *Callister & Rethwisch 9e.*

Criteria for Solid Solubility

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

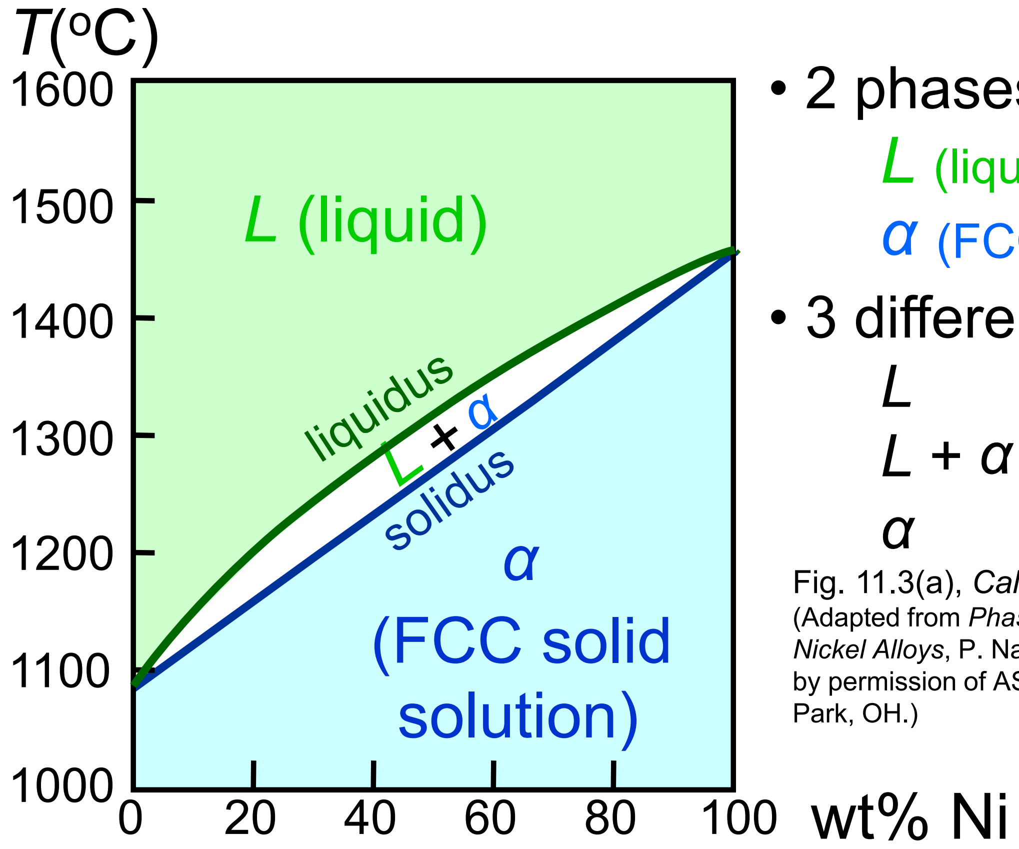
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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

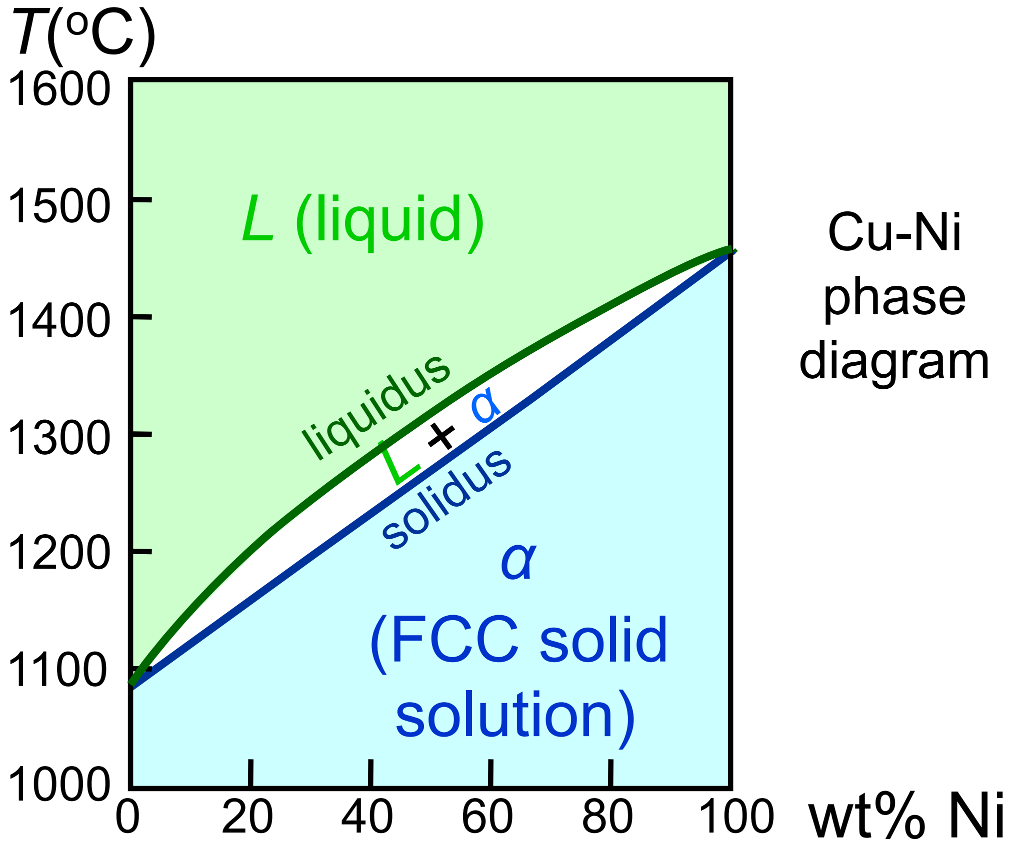


- 2 phases:
  - *L* (liquid)
  - *α* (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + *α*
  - *α*

Fig. 11.3(a), *Callister & Rethwisch 9e.* (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.



Cu-Ni phase diagram

Fig. 11.3(a), *Callister & Rethwisch 9e.*
(Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

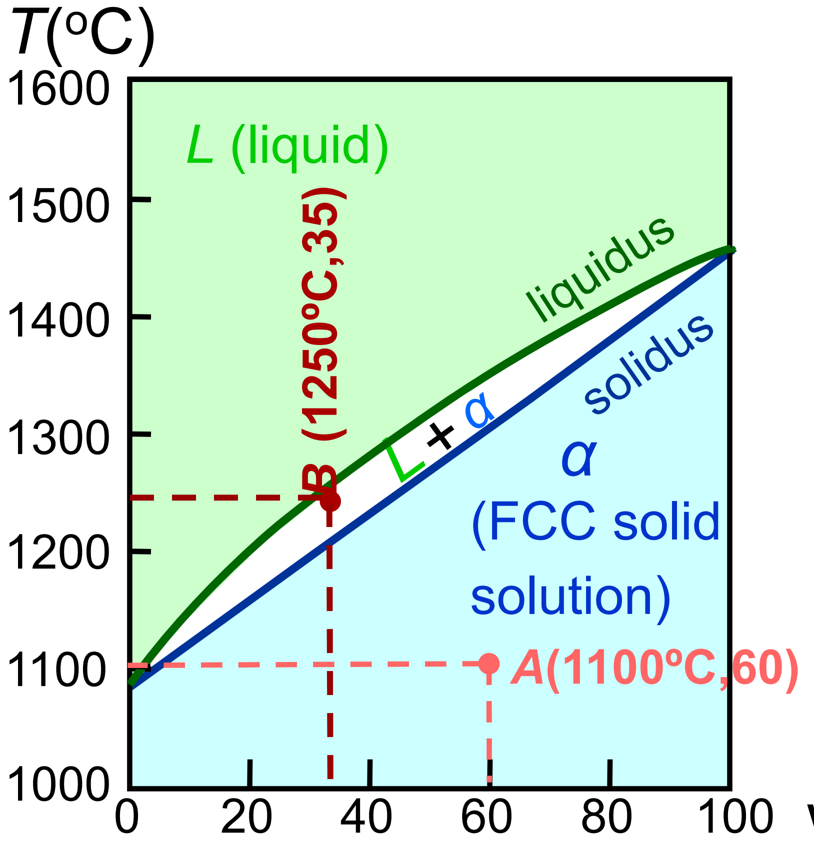
Phase Diagrams:
Determination of phase(s) present

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

- Examples:

  A(1100 ºC, 60 wt% Ni):
  1 phase: *α*

  B(1250 ºC, 35 wt% Ni):
  2 phases: *L* + *α*



Cu-Ni phase diagram

Fig. 11.3(a), *Callister & Rethwisch 9e.*
(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)

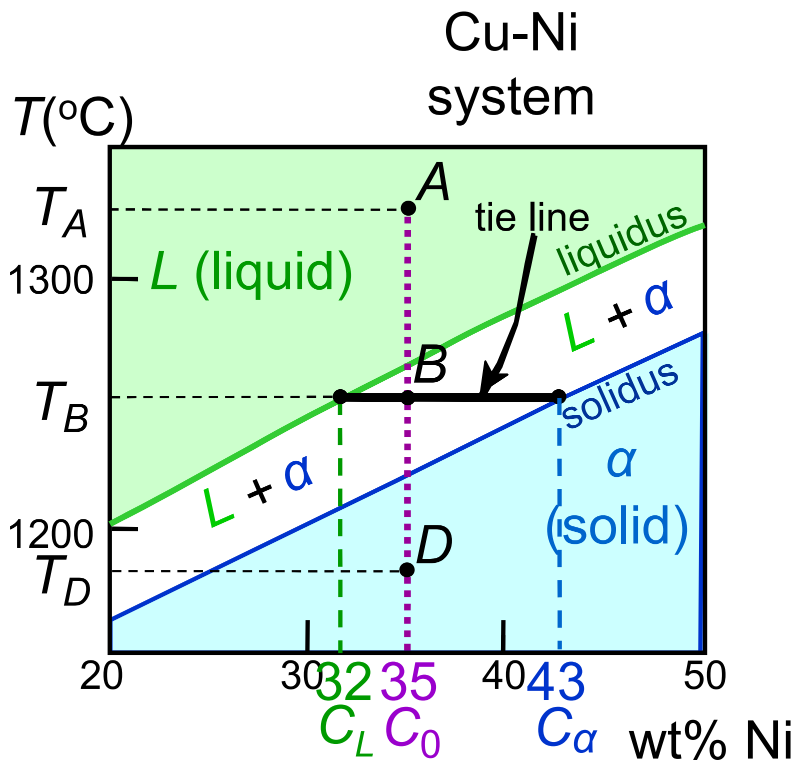


Fig. 11.3(b), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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_α = 0

At T_D : Only Solid (α) present

W_L = 0, W_α = 1.00

At T_B : Both α and L present

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

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

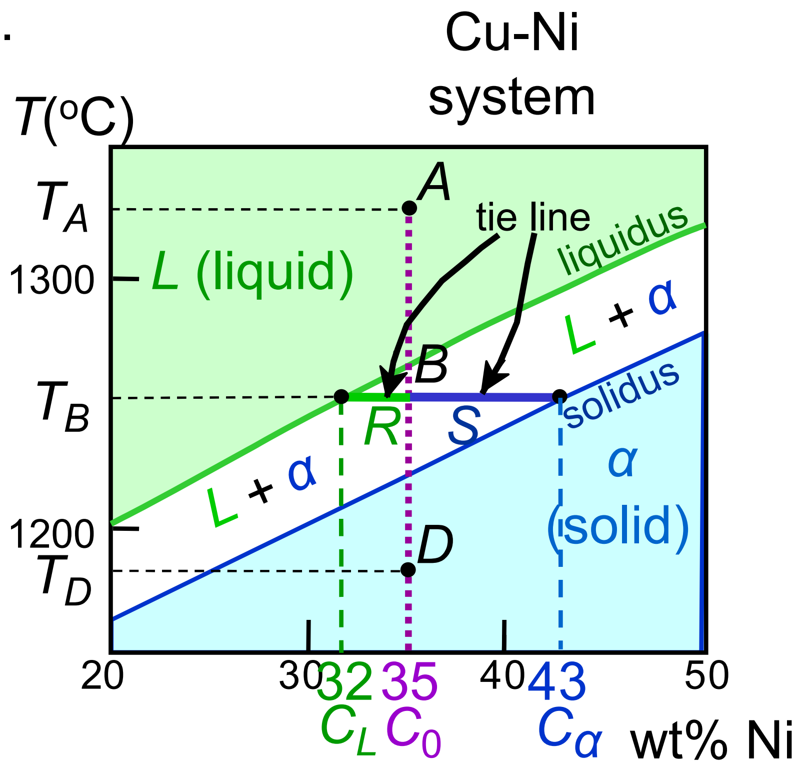
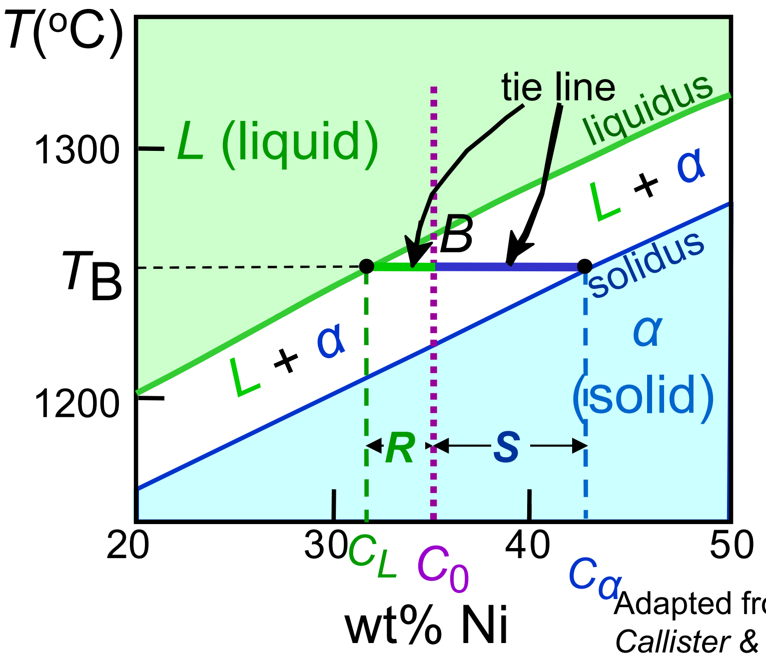


Fig. 11.3(b), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

The Lever Rule

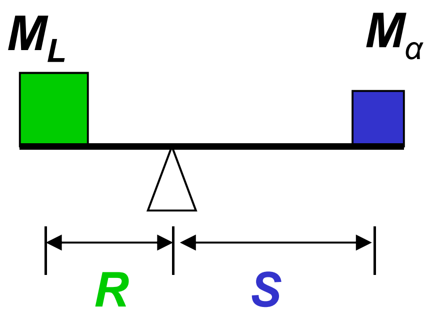
- Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm



Adapted from Fig. 11.3(b), *Callister & Rethwisch 9e.*

What fraction of each phase?

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



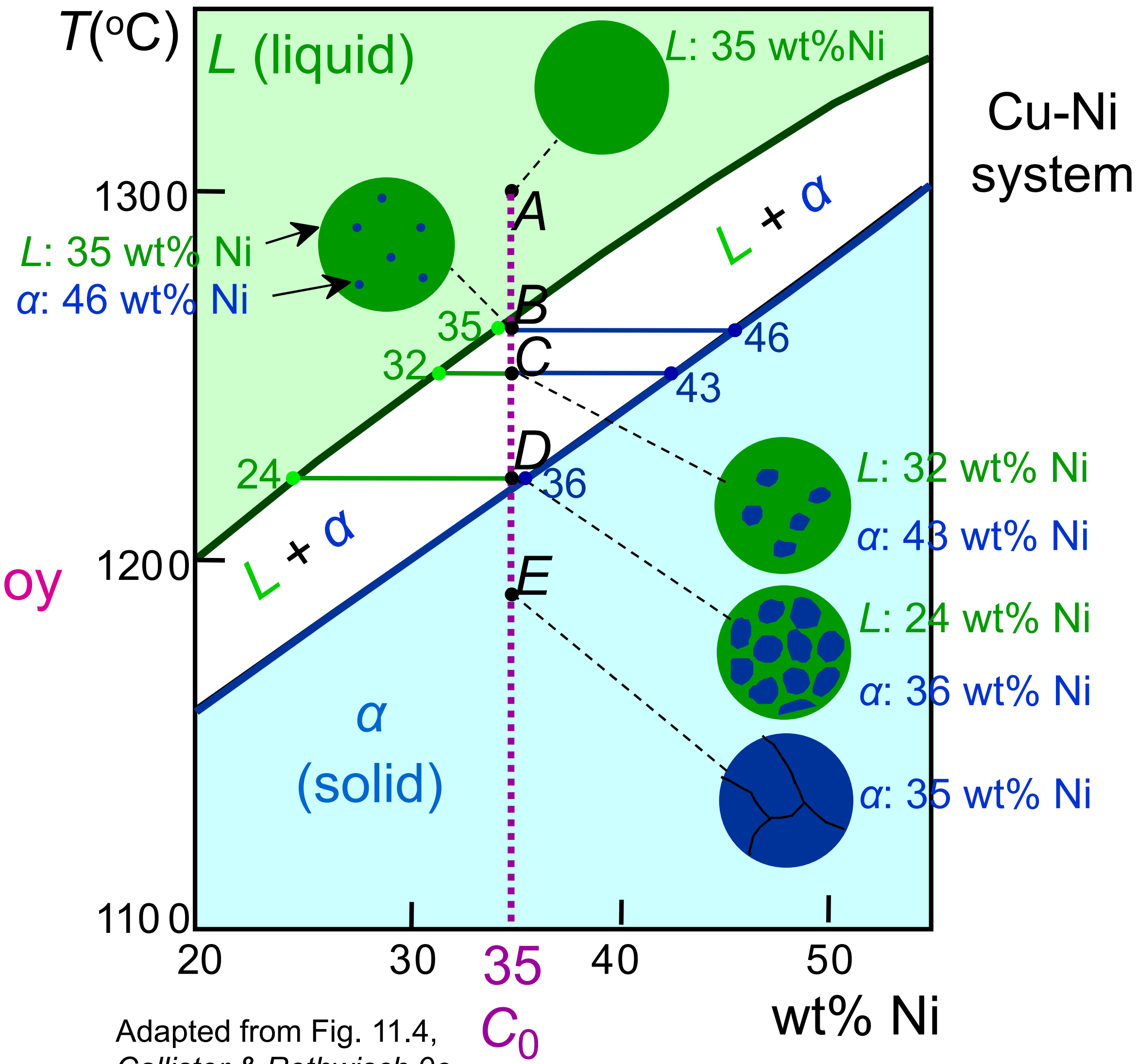
$$M_\alpha \times S = M_L \times R$$

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

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

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

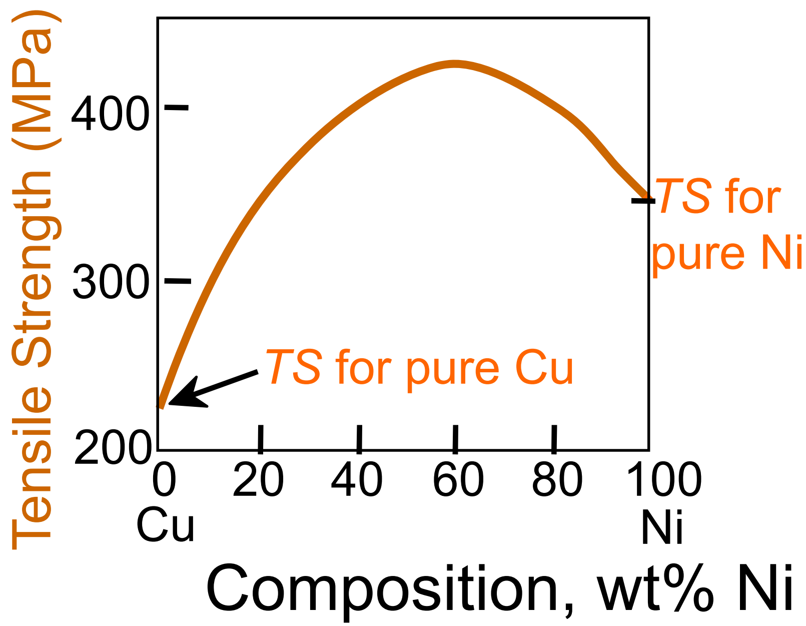


Adapted from Fig. 11.4, *Callister & Rethwisch 9e.*

Mechanical Properties: Cu-Ni System

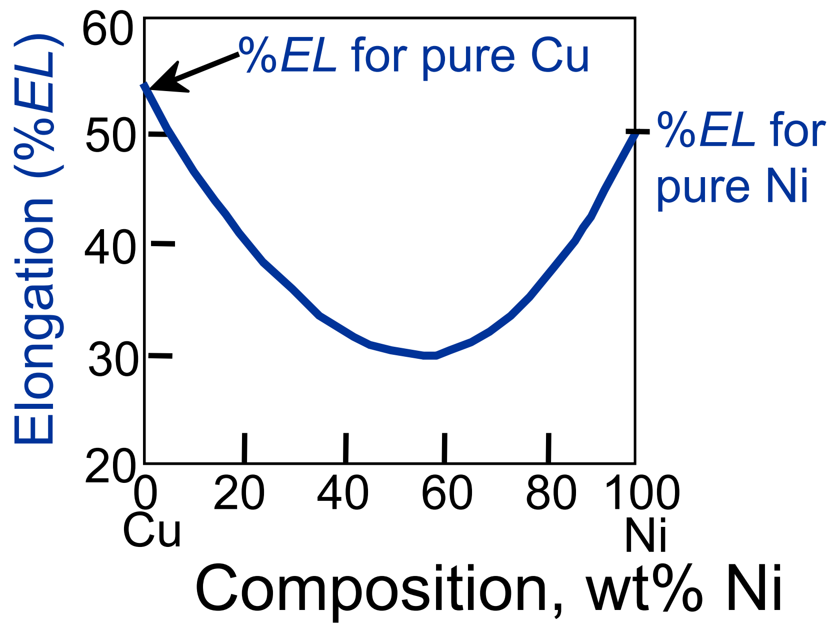
- Effect of solid solution strengthening on:

-- Tensile strength (*TS*)



Adapted from Fig. 11.5(a), *Callister & Rethwisch 9e.*

-- Ductility (%*EL*)



Adapted from Fig. 11.5(b), *Callister & Rethwisch 9e.*

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

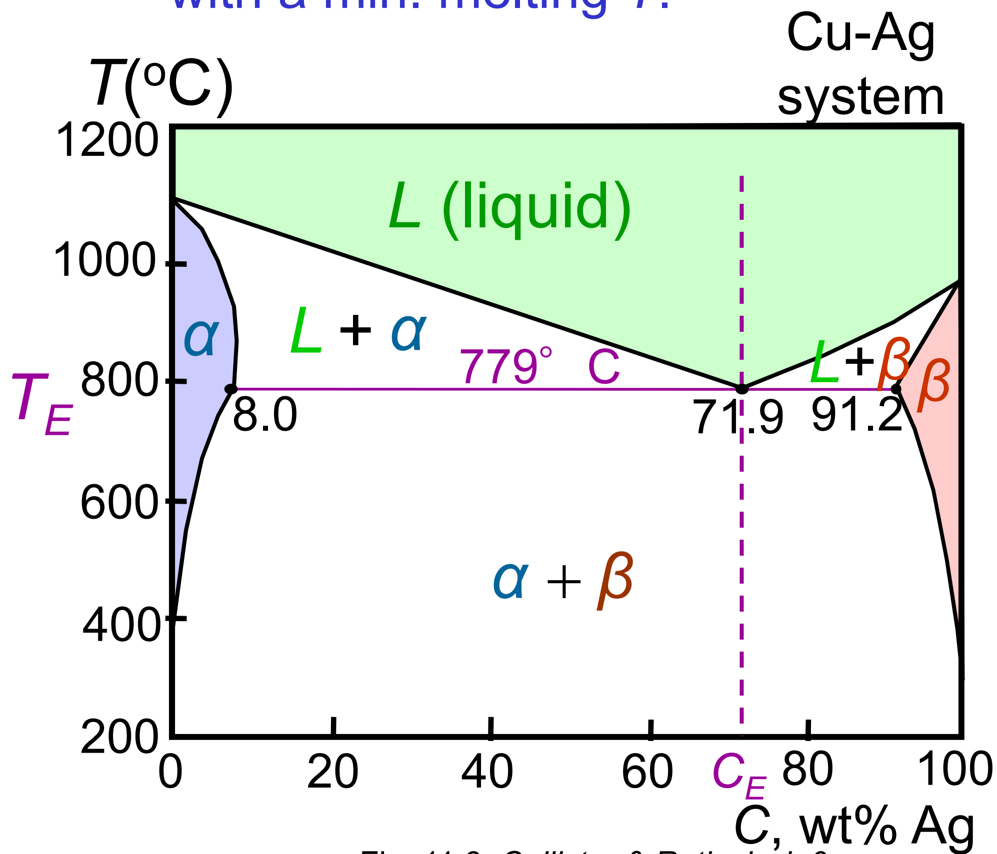


Fig. 11.6, *Callister & Rethwisch 9e* [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.].

- **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: $\alpha + \beta$

  -- the phase compositions

  Answer: C_α = 11 wt% Sn
  C_β = 99 wt% Sn

  -- the relative amount of each phase

  Answer:

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

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

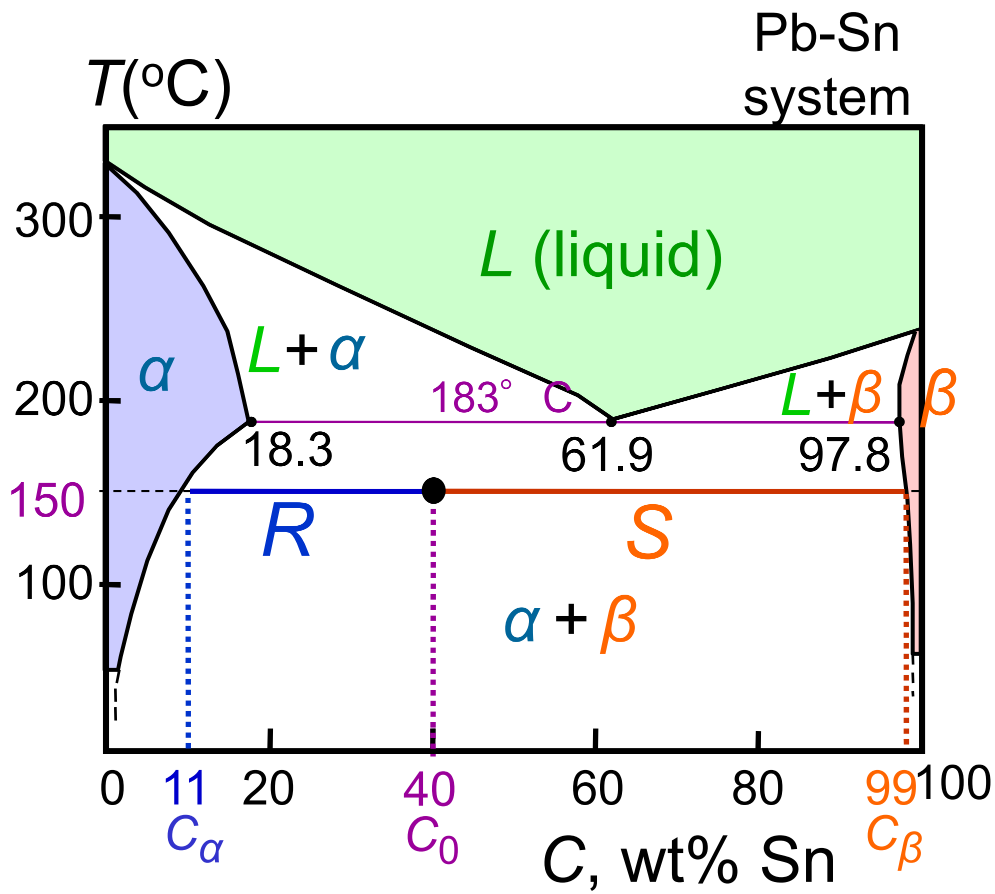


Fig. 11.7, *Callister & Rethwisch 9e.*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

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_α = 17 wt% Sn
  C_L = 46 wt% Sn

  -- the relative amount of each phase

  Answer:

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

$$= \frac{6}{29} = 0.21$$

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

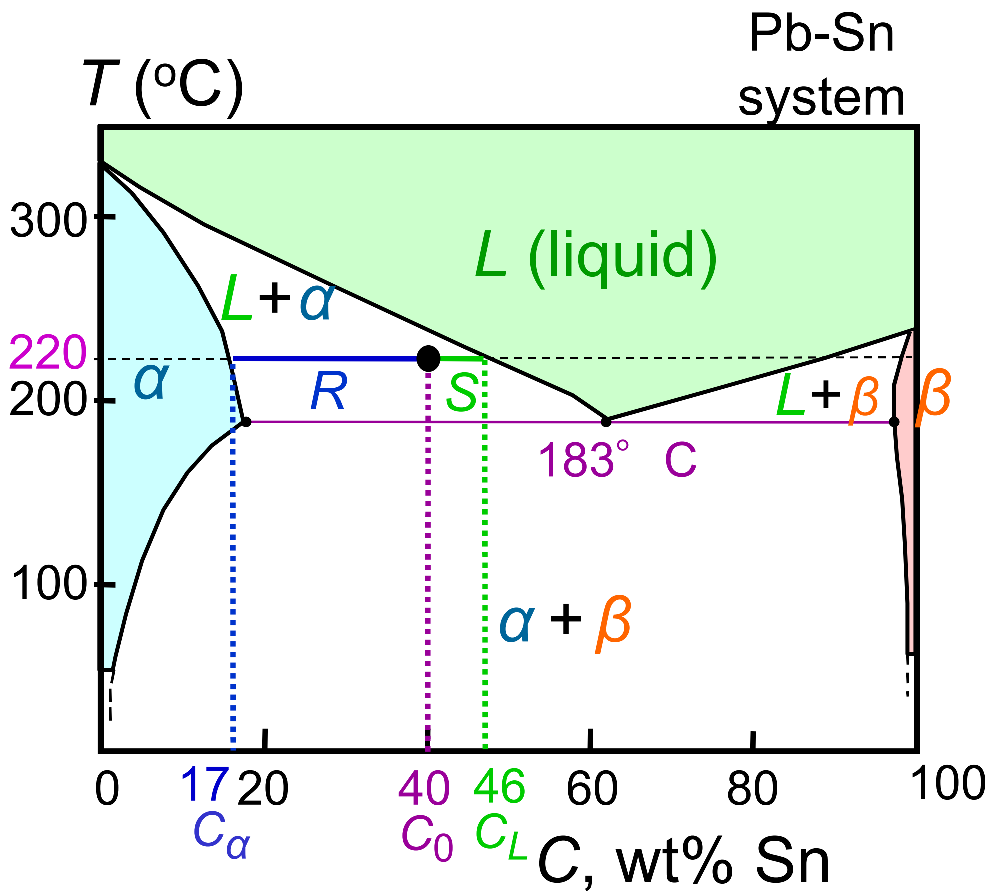


Fig. 11.7, *Callister & Rethwisch 9e.*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

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

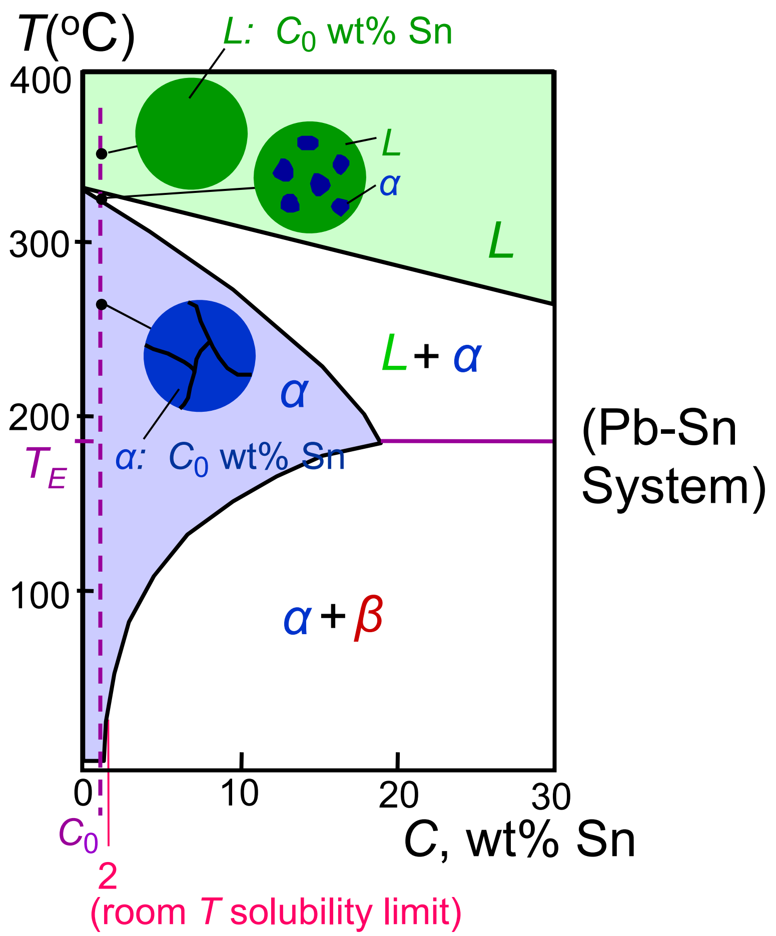


Fig. 11.10, *Callister & Rethwisch 9e.*

Microstructural Developments in Eutectic Systems II

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

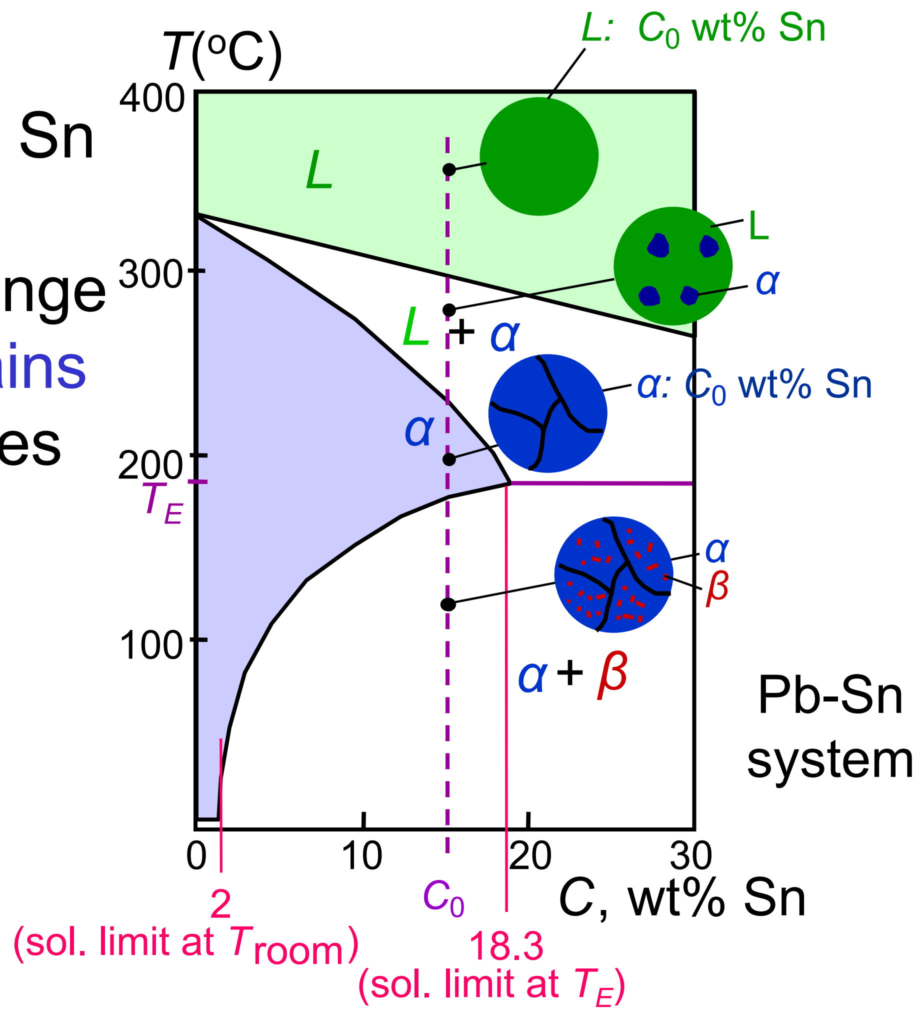


Fig. 11.11, *Callister & Rethwisch 9e.*

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.

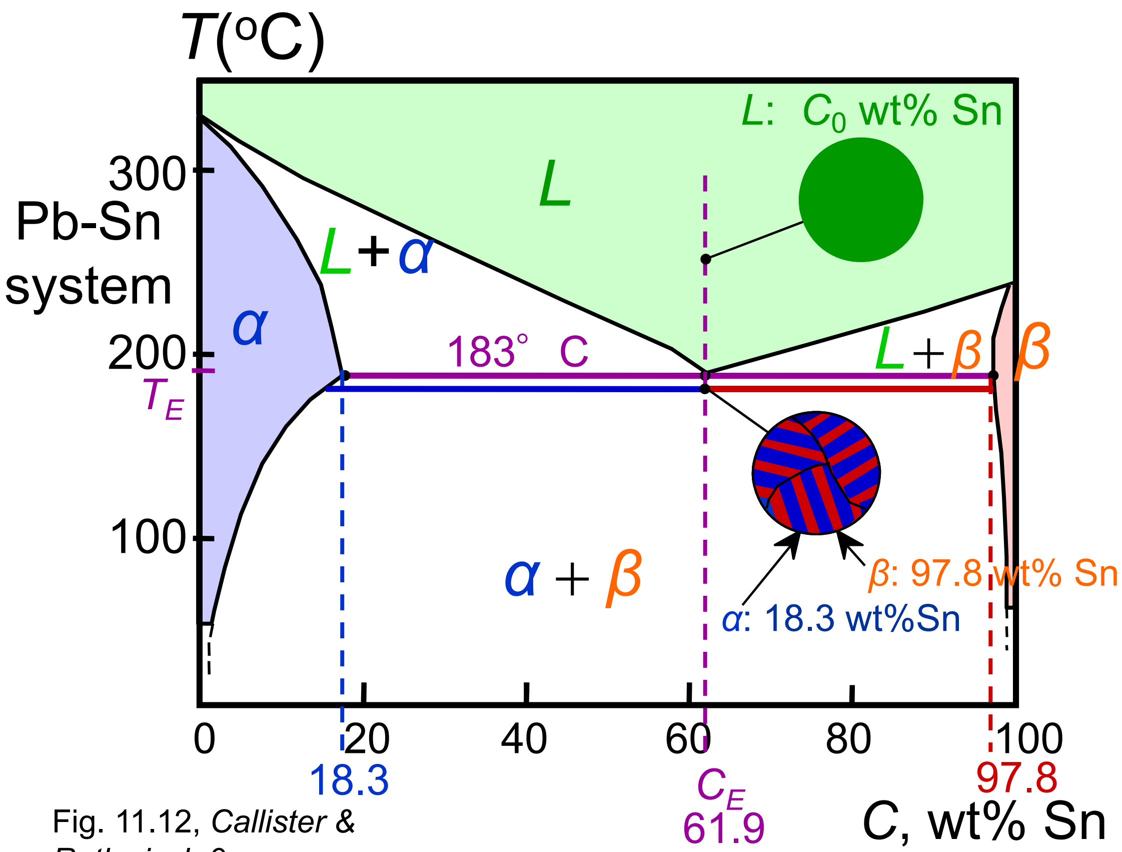


Fig. 11.12, *Callister & Rethwisch 9e.*

Micrograph of Pb-Sn eutectic microstructure

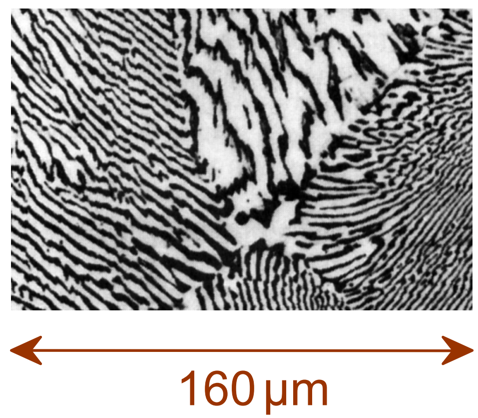
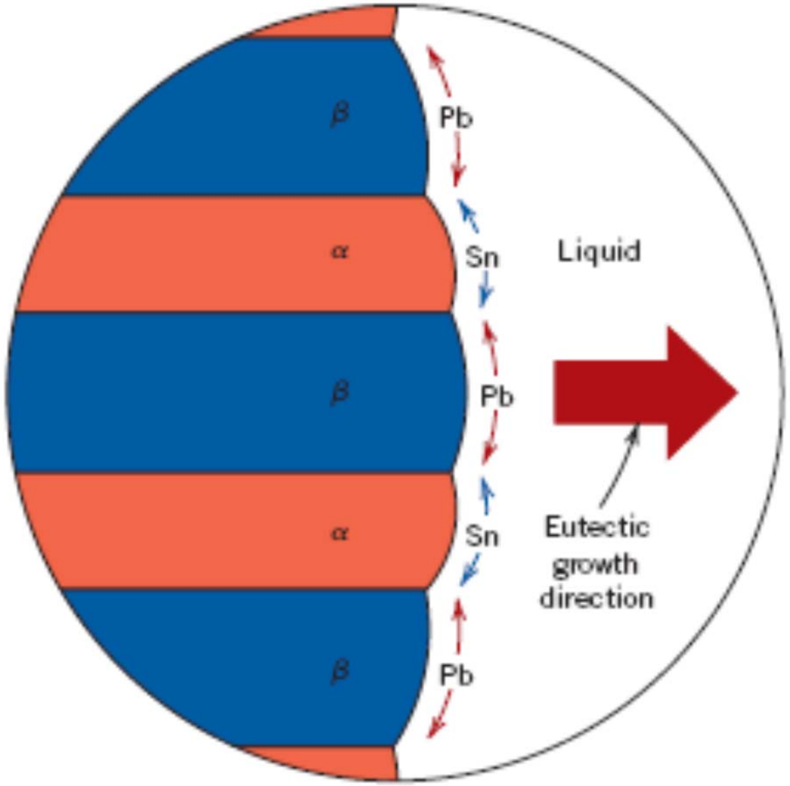
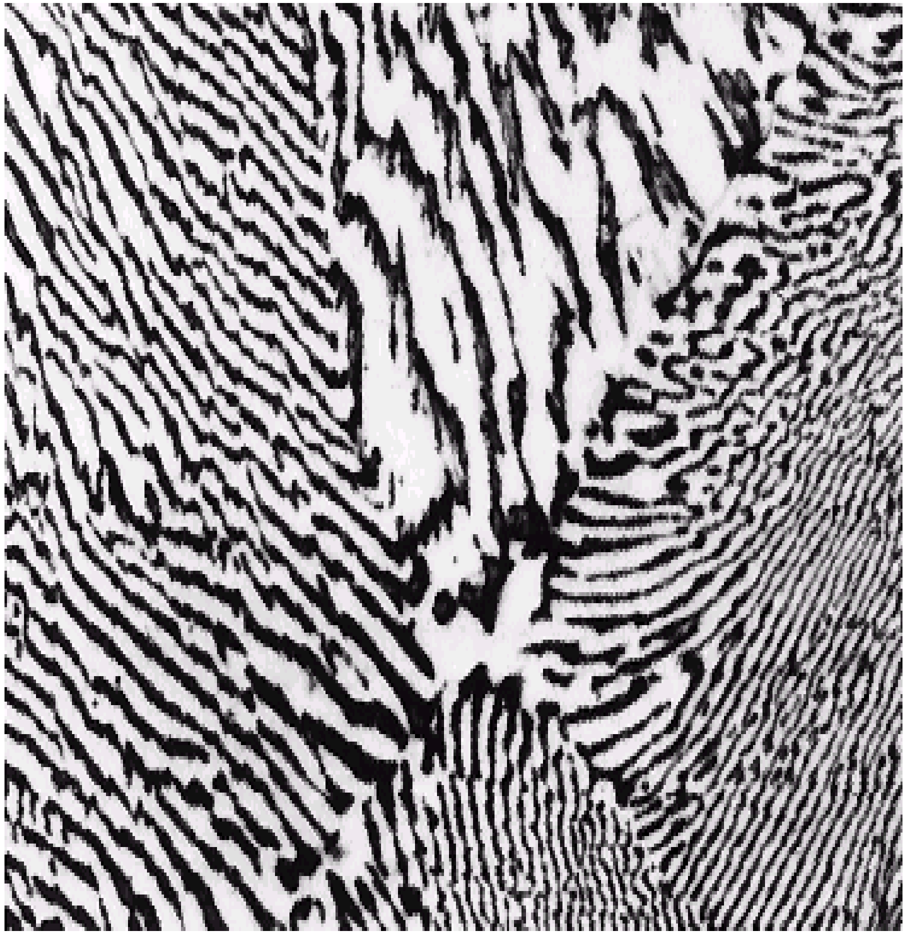


Fig. 11.13, *Callister & Rethwisch 9e.*
(From *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

Lamellar Eutectic Structure





Figs. 11.13 & 11.14, *Callister & Rethwisch 9e.*
(Fig. 11.13 from *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

Microstructural Developments in Eutectic Systems IV

- For alloys for which 18.3 wt% Sn < C_0 < 61.9 wt% Sn
- Result: α phase particles and a eutectic microconstituent

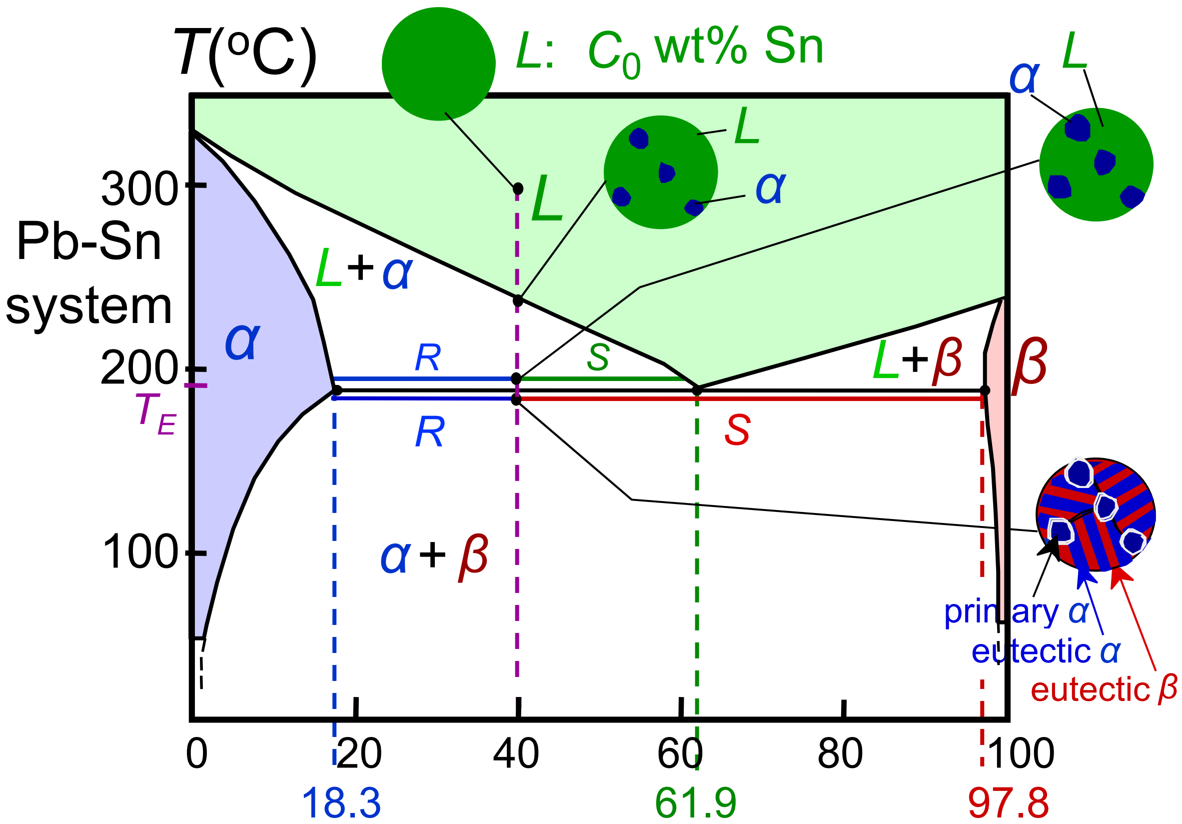


Fig. 11.15, *Callister & Rethwisch 9e.*

- Just above T_E:

C_α = 18.3 wt% Sn

C_L = 61.9 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.50$$

$W_L = (1 - W_\alpha) = 0.50$

- Just below T_E:

C_α = 18.3 wt% Sn

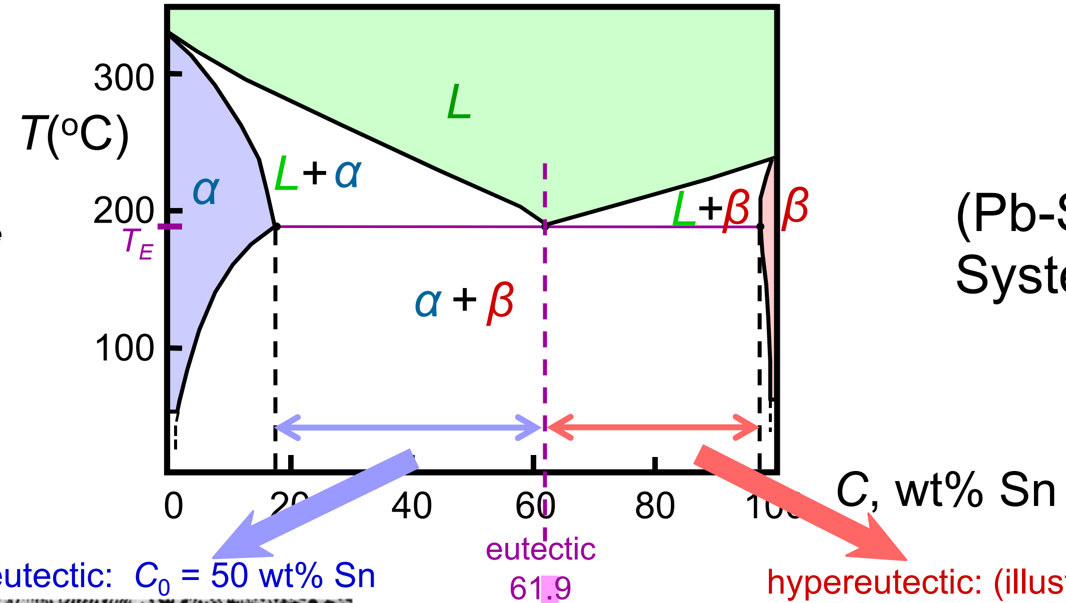
C_β = 97.8 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.73$$

W_β = 0.27

Hypoeutectic & Hypereutectic

Fig. 11.7, *Callister & Rethwisch 9e.* [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.]



(Pb-Sn System)

(Figs. 11.13 and 11.16 from *Metals Handbook*, 9th ed., Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

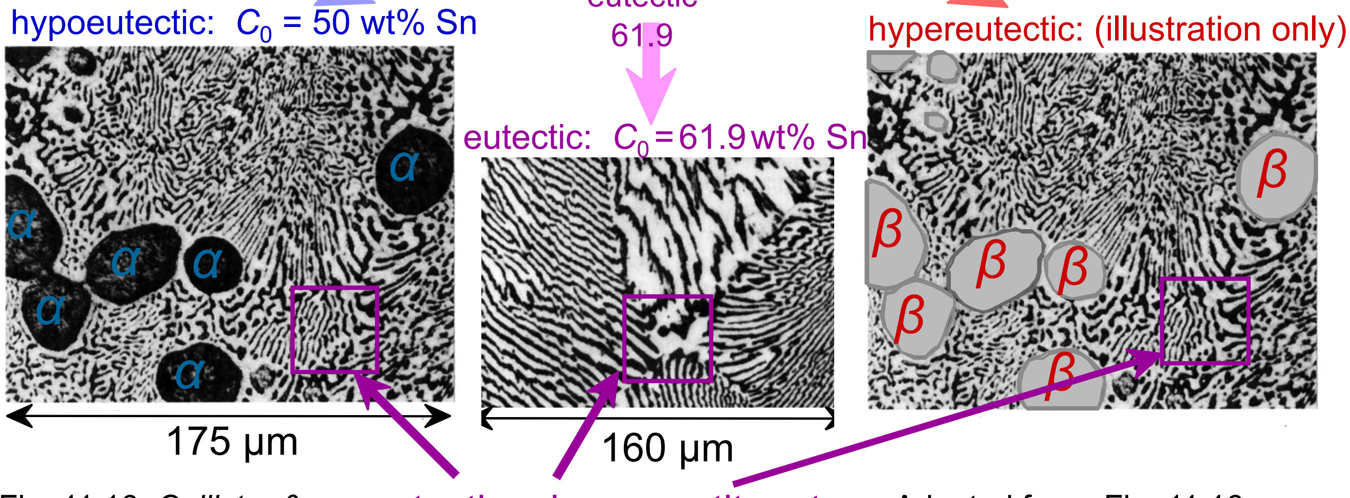
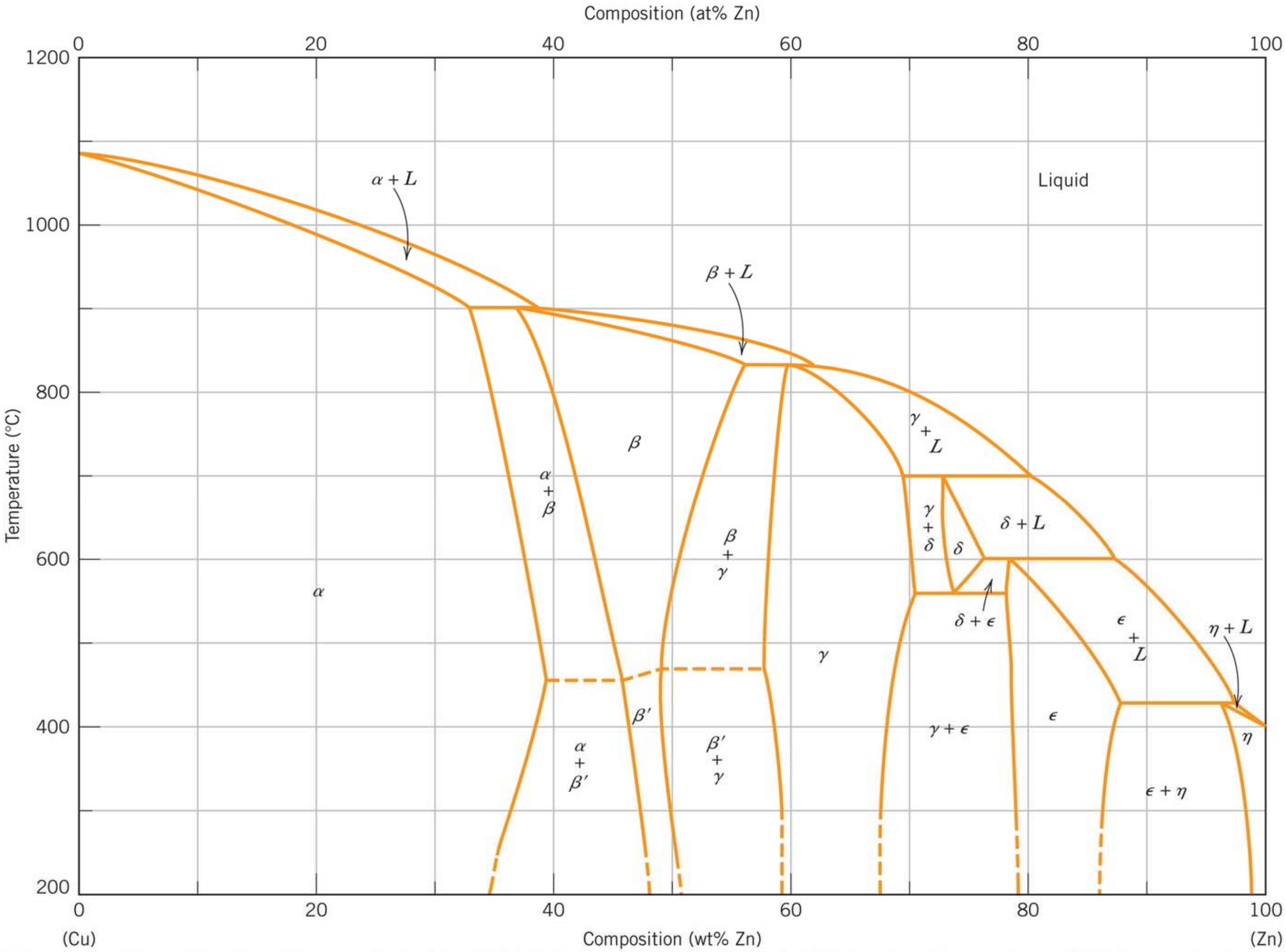


Fig. 11.16, *Callister & Rethwisch 9e.*

Fig. 11.13, *Callister & Rethwisch 9e.*

Adapted from Fig. 11.16, *Callister & Rethwisch 9e.* (Illustration only)

Intermediate Phases (Intermediate Solid Solutions)



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Intermetallic Compounds

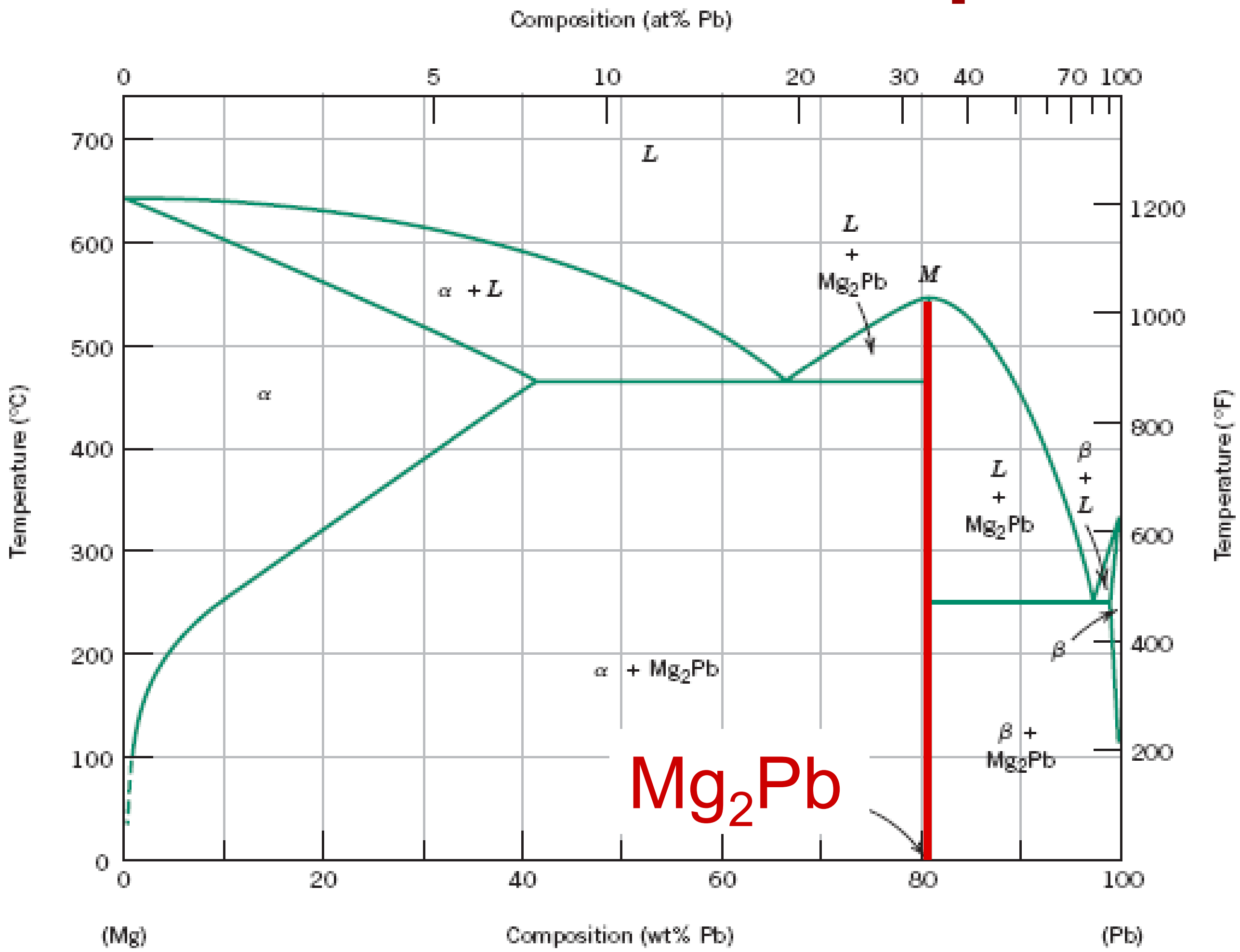
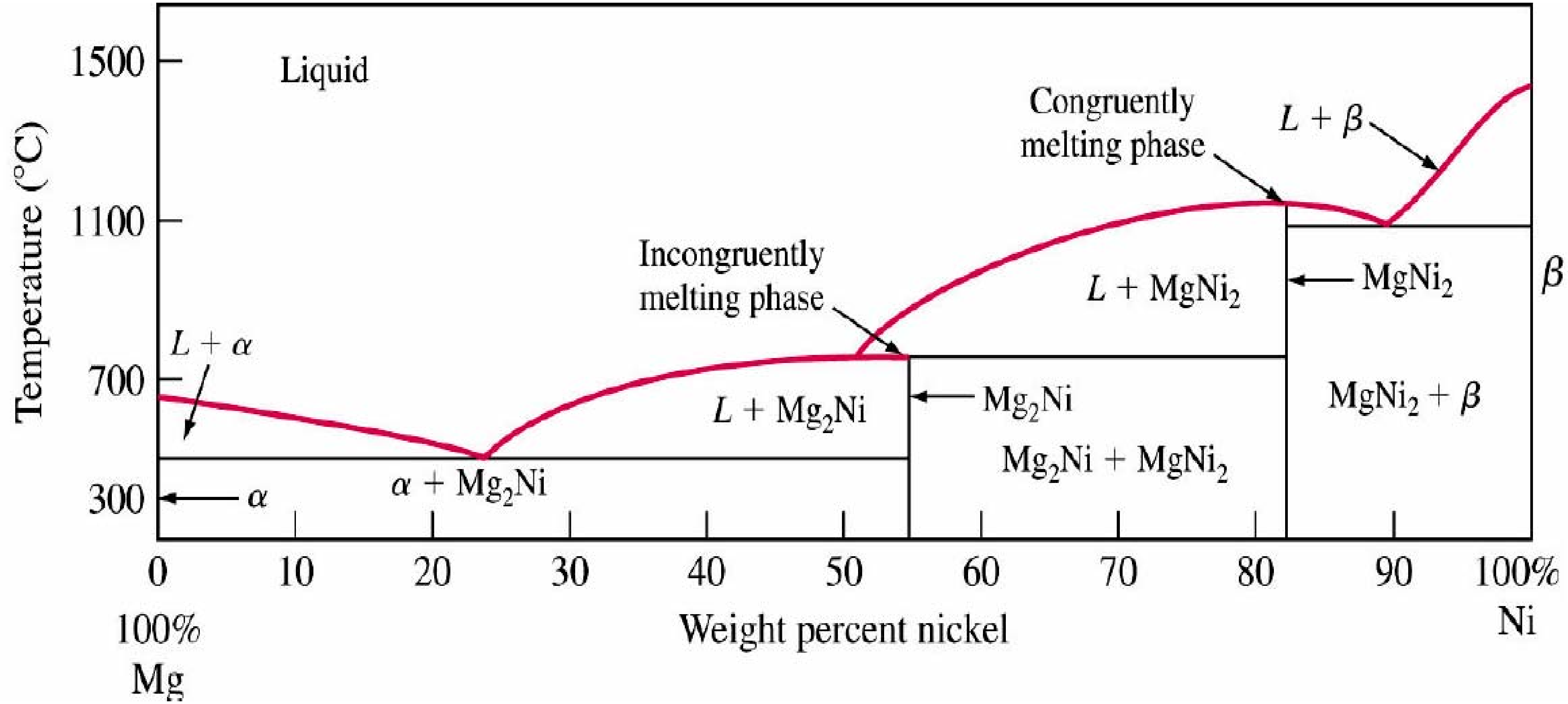


Fig. 11.19, *Callister & Rethwisch 9e.*
[Adapted from *Phase Diagrams of Binary Magnesium Alloys*, A. A. Nayeb-Hashemi and J. B. Clark (Editors), 1988. Reprinted by permission of ASM International, Materials Park, OH.]

Note: intermetallic compound exists as a line on the diagram - not an area - because of stoichiometry (i.e. composition of a compound is a fixed value).

Congruent melting vs. Incongruent melting



Eutectic, Eutectoid, & Peritectic

- Eutectic - liquid transforms to two solid phases

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

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

$$S_2 \rightleftharpoons S_1 + S_3$$

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

intermetallic compound - cementite

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

$$S_1 + L \rightleftharpoons S_2$$

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

Peritectoid & Monotectic

- Peritectoid – one solid and another solid react to produce a new solid

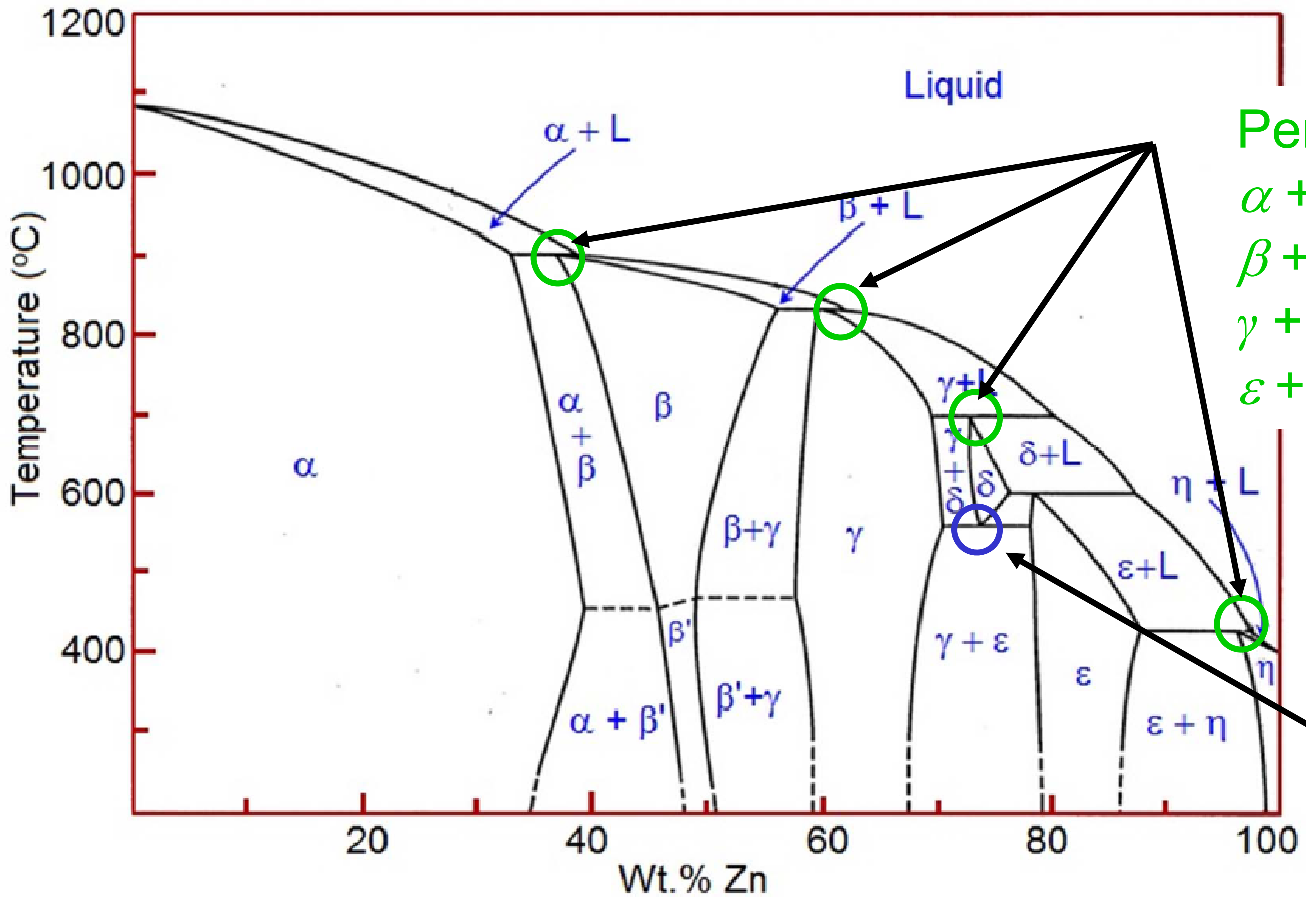
  $\alpha + \beta \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \gamma$ (For Co-Cr, 976 ^{o}C, 37.6 wt% Cr)

- Monotectic – liquid 1 decomposes to liquid 2 and a solid

  $L_1 \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} L_2 + \alpha$ (For Cu-Pb, 955 ^{o}C, 36 wt% Pb)

Eutectoid & Peritectic

Cu-Zn Phase diagram



Peritectic transformations

$\alpha + L \longleftrightarrow \beta$

$\beta + L \longleftrightarrow \gamma$

$\gamma + L \longleftrightarrow \delta$

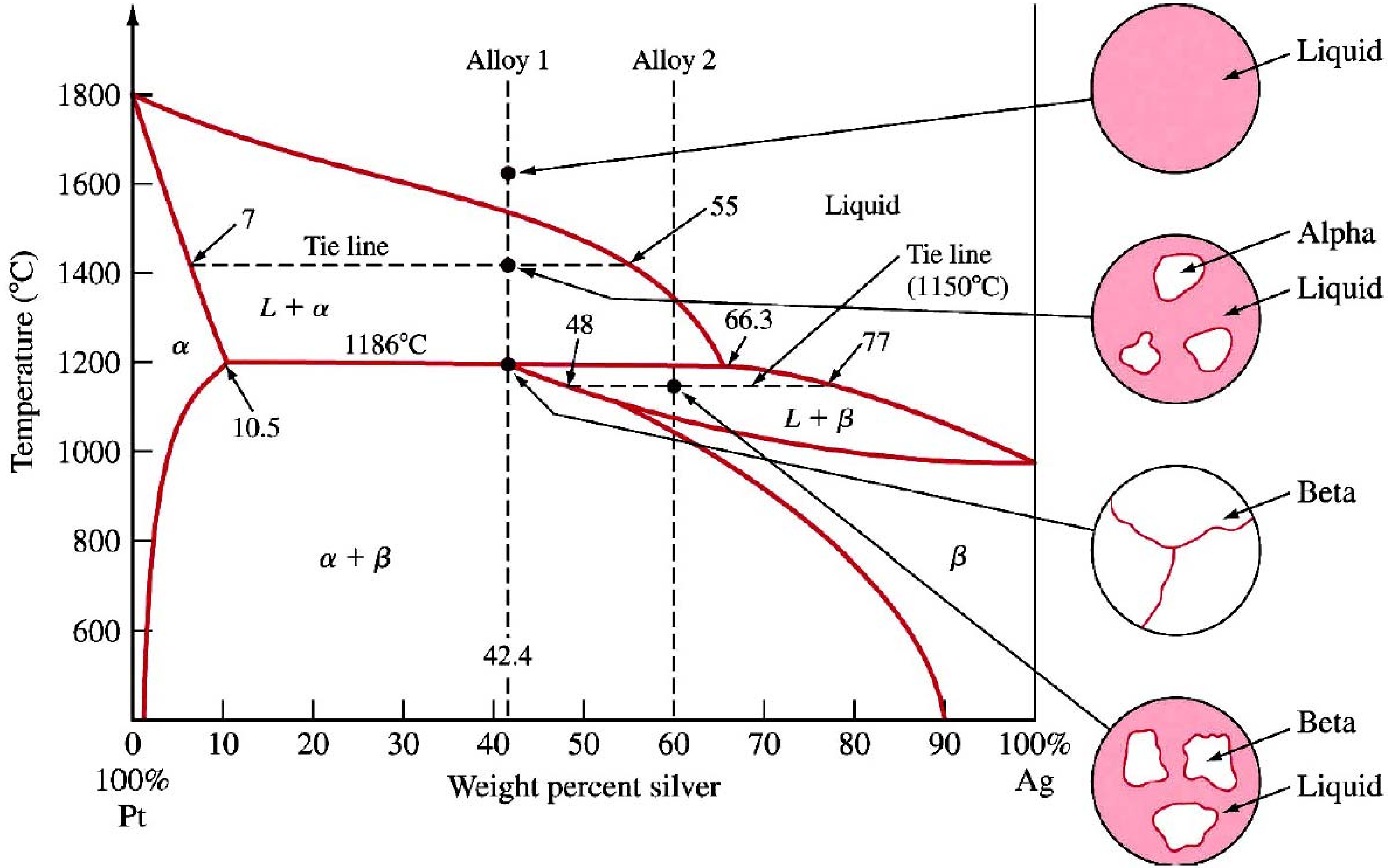
$\varepsilon + L \longleftrightarrow \eta$

Eutectoid transformat

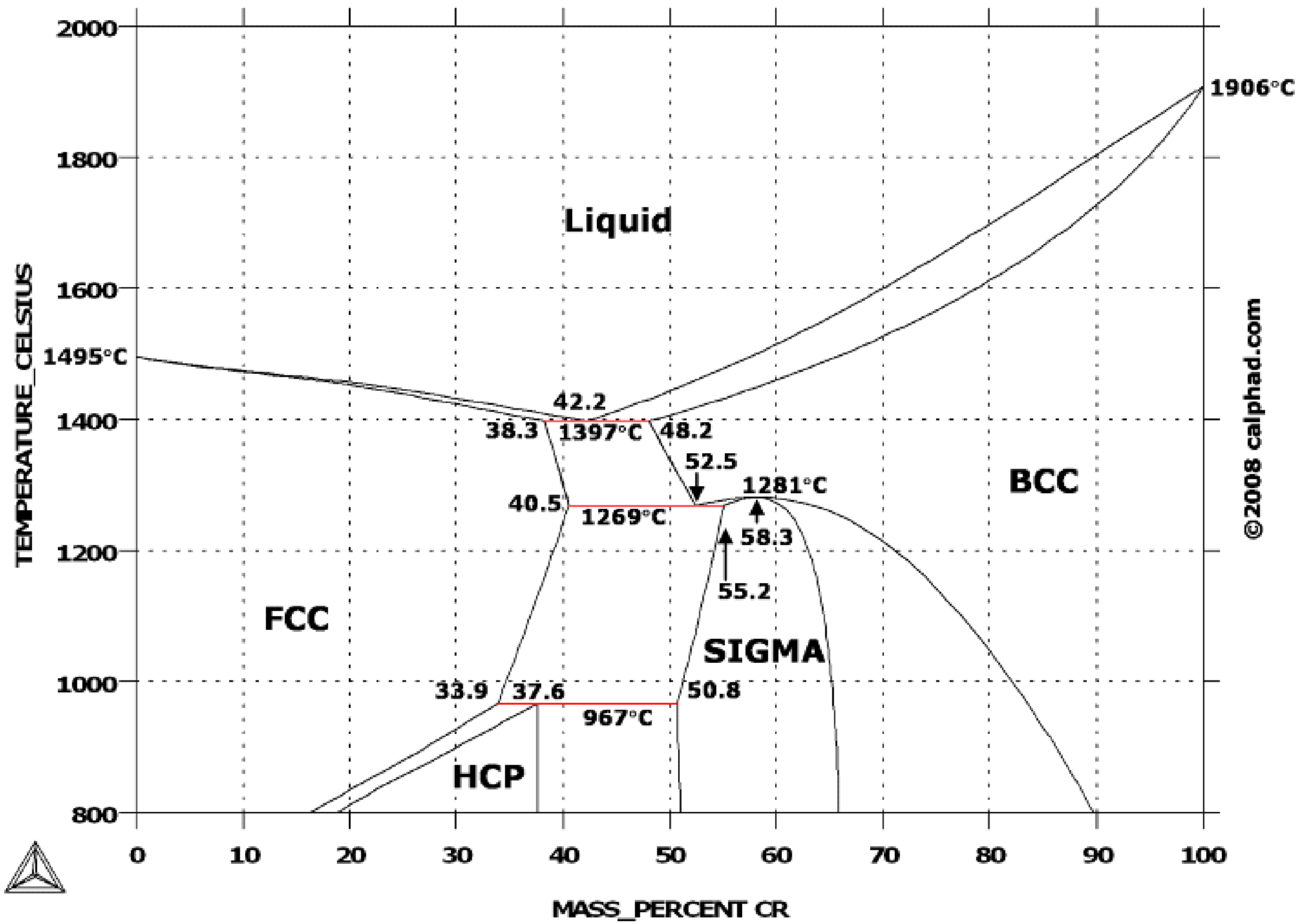
$\delta \longleftrightarrow \gamma + e$

Cu-Zn phase diagram. α and η are terminal phases and β, γ, δ and ε are intermediate phases.

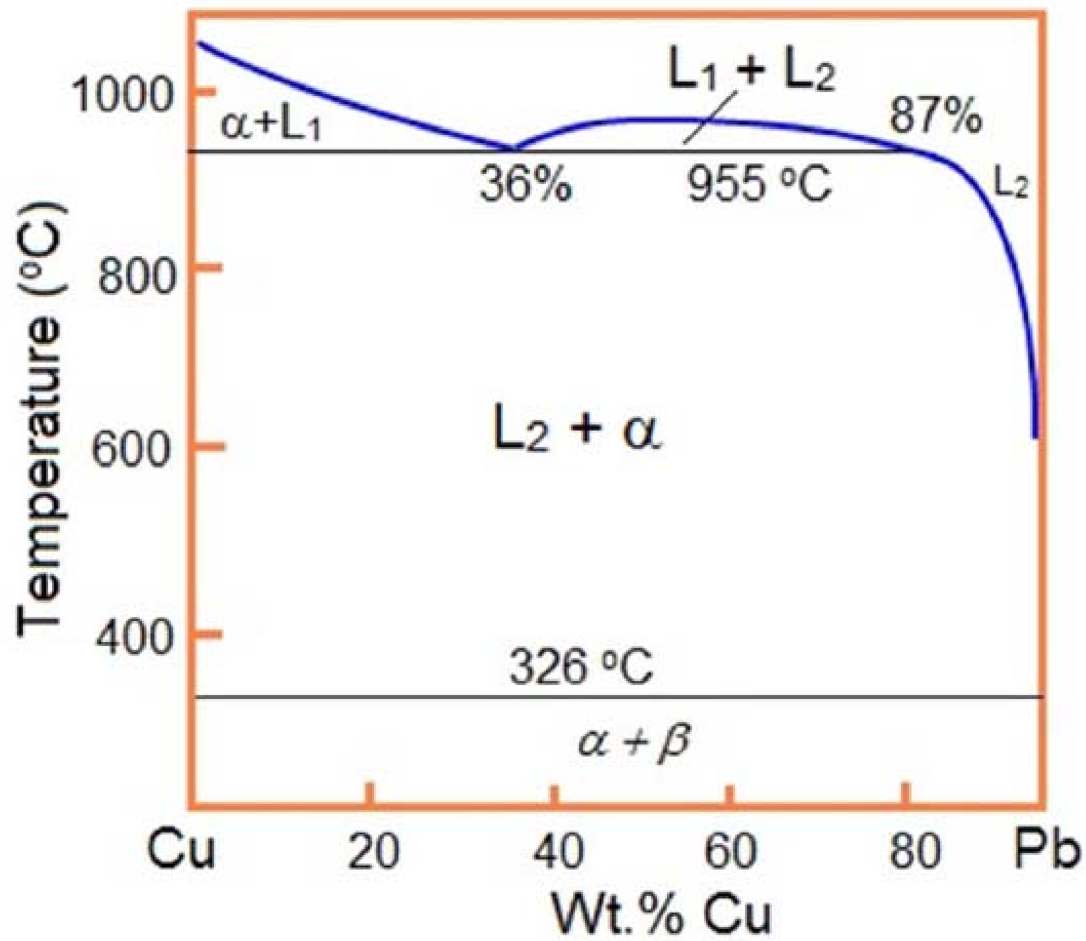
Peritectic reaction



Peritectoid



Monotectic



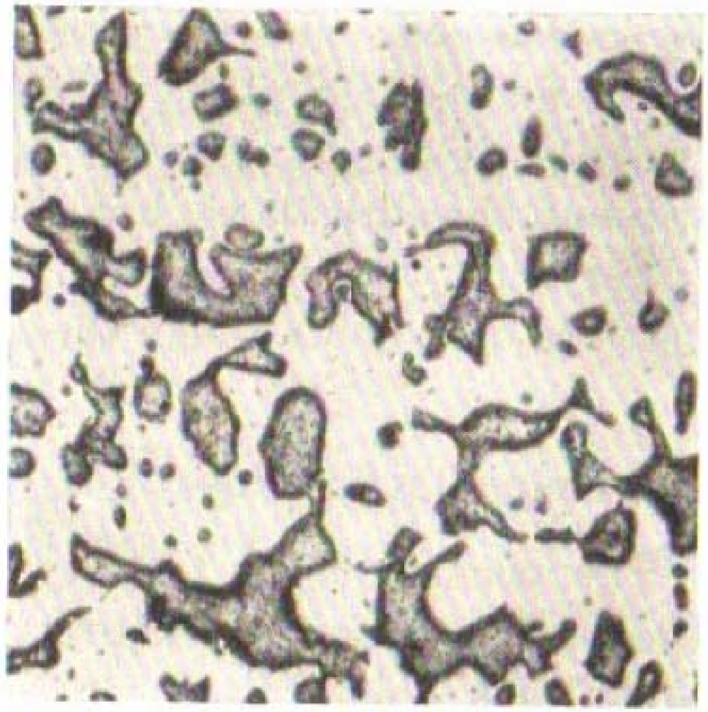


FIG. 6-4. Microstructure of cast monotectic alloy Cu + 36% Pb. Light areas are the Cu-rich matrix of the monotectic constituent; dark areas are the Pb-rich portion, which existed as L_{II} at the monotectic temperature. Magnification 100.

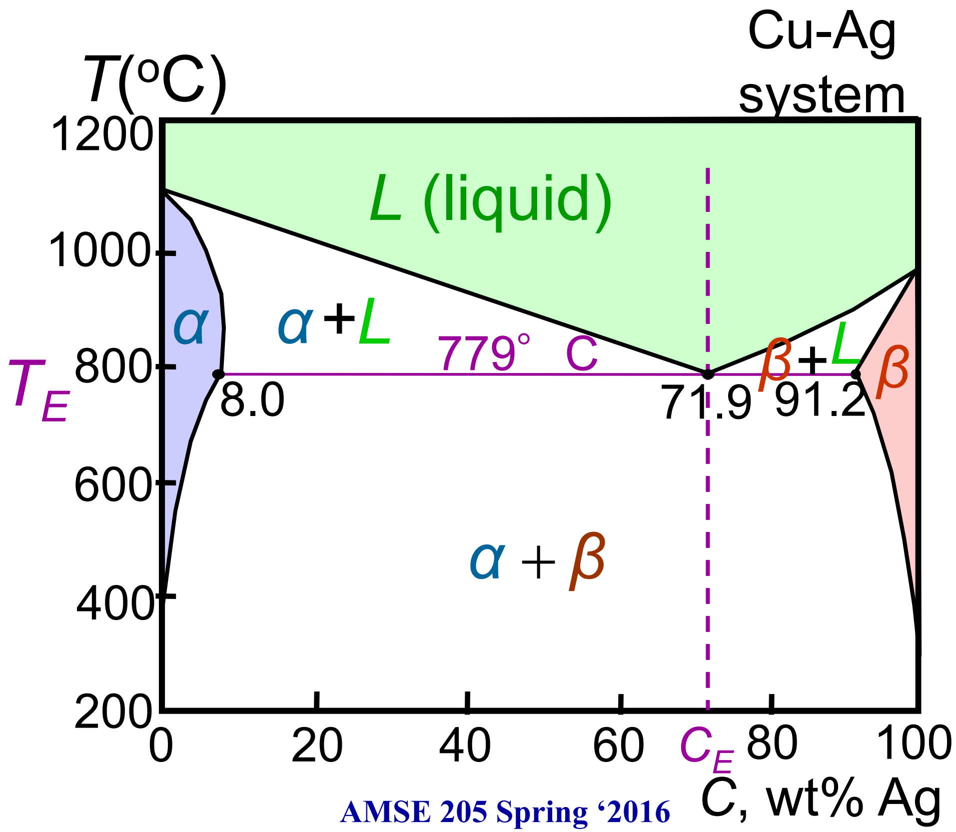
Gibbs Phase Rule

- **P+F = C+2**

  P: # of phase; F: # of degree of freedom; C: # of components

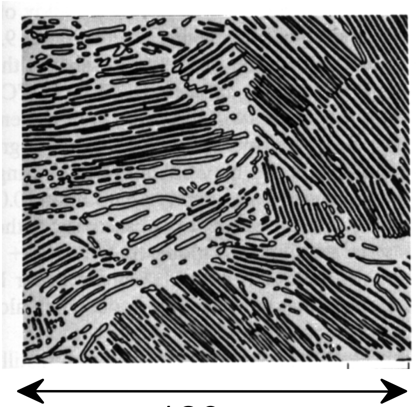
  when Pressure is fixed at 1 atm

- **P+F = C+1→ F = 3 – P for binary system**



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 α and Fe_3C phases

Fig. 11.26, *Callister & Rethwisch 9e.*
(From *Metals Handbook*, Vol. 9, 9th ed., *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

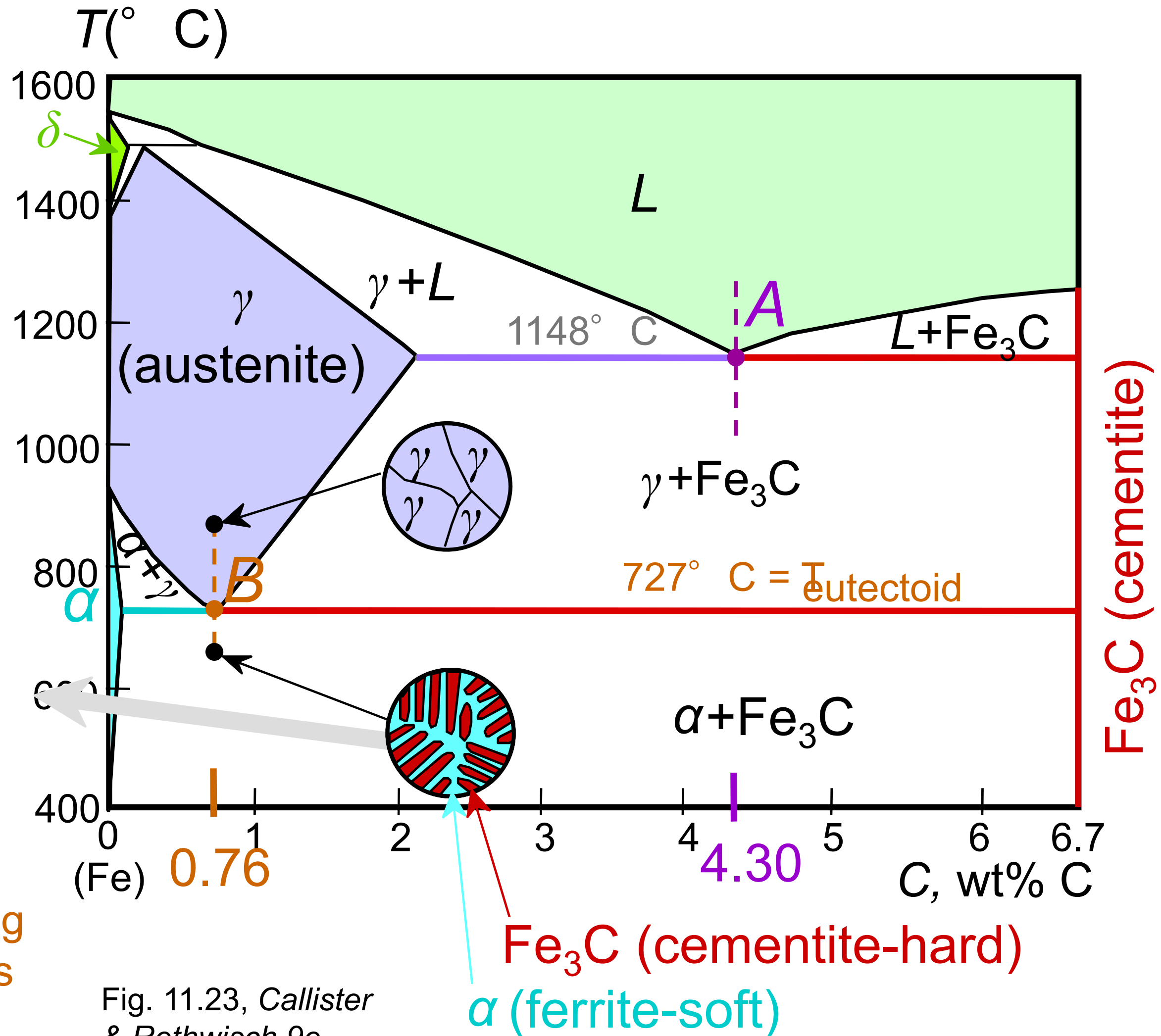
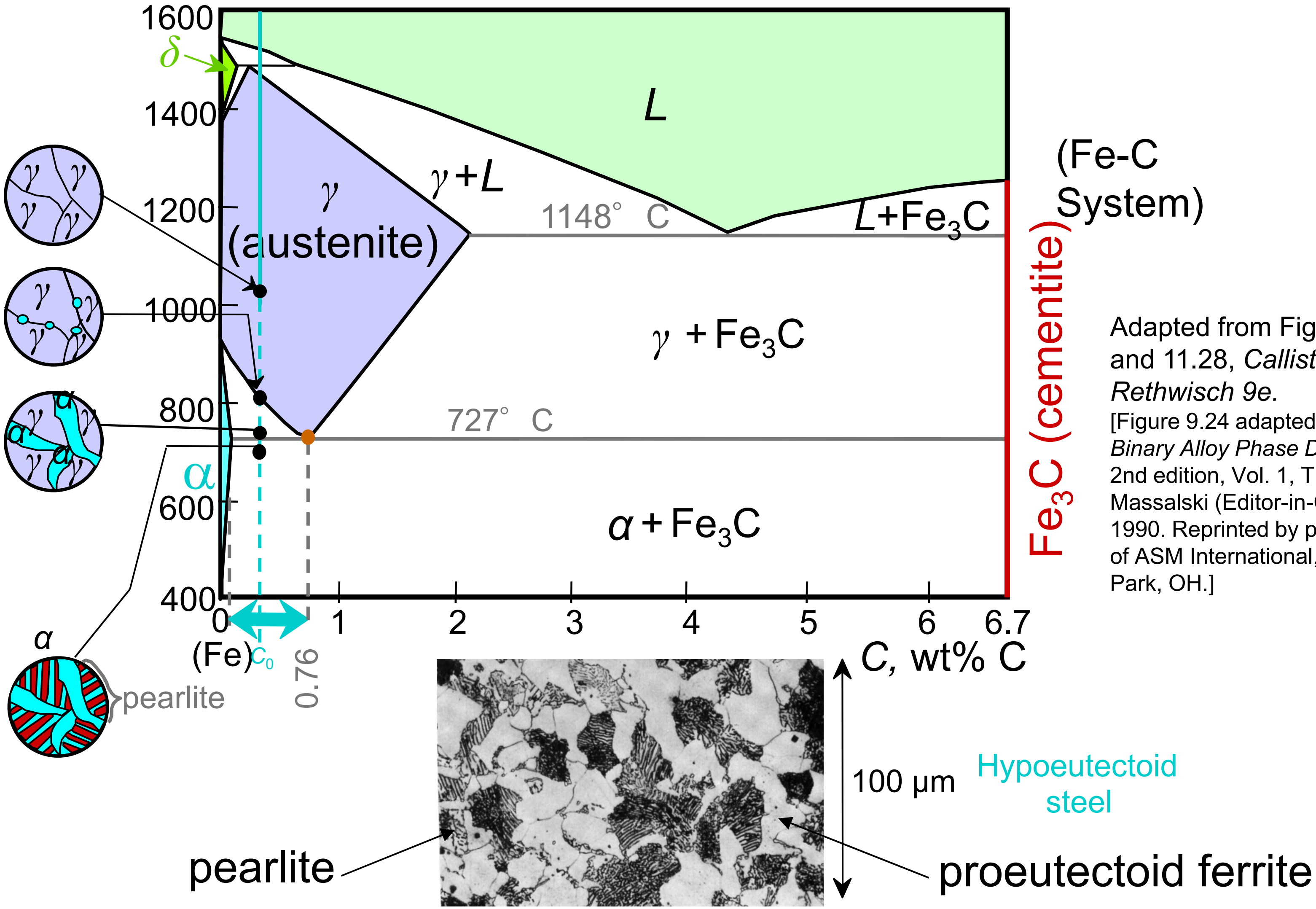


Fig. 11.23, *Callister & Rethwisch 9e.*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

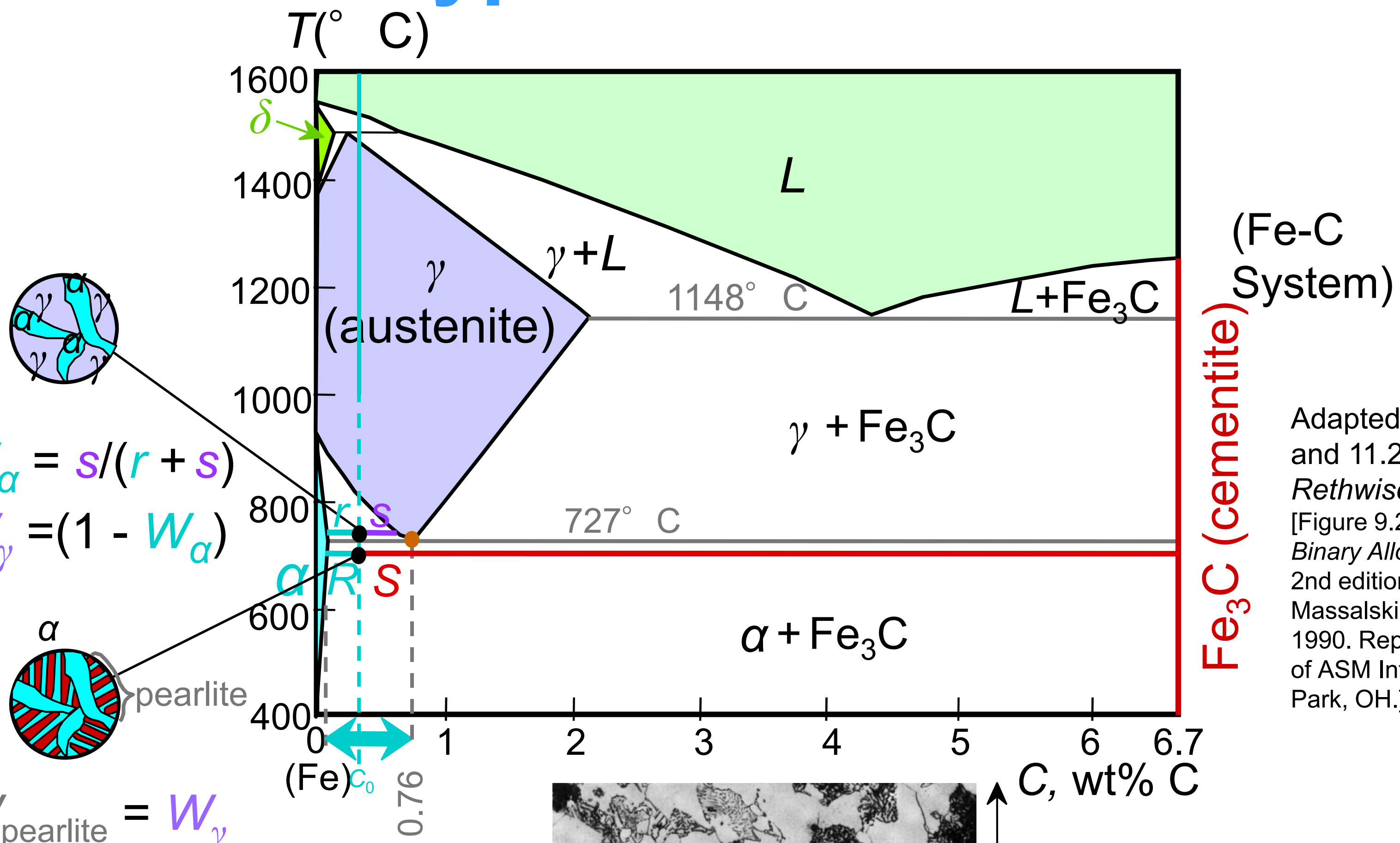
Hypoeutectoid Steel



Adapted from Figs. 11.23 and 11.28, *Callister & Rethwisch 9e.* [Figure 9.24 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.]

Adapted from Fig. 11.29, *Callister & Rethwisch 9e.*
(Photomicrograph courtesy of Republic Steel Corporation.)

Hypoeutectoid Steel



$W_{\alpha} = s/(r+s)$

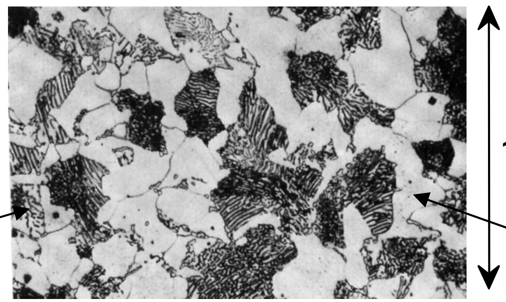
$W_{\gamma} = (1 - W_{\alpha})$

$W_{pearlite} = W_{\gamma}$

$W_{\alpha'} = S/(R+S)$

$W_{Fe_3C} = (1 - W_{\alpha'})$

Adapted from Figs. 11.23 and 11.28, *Callister & Rethwisch 9e.*
[Figure 9.24 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.]



pearlite

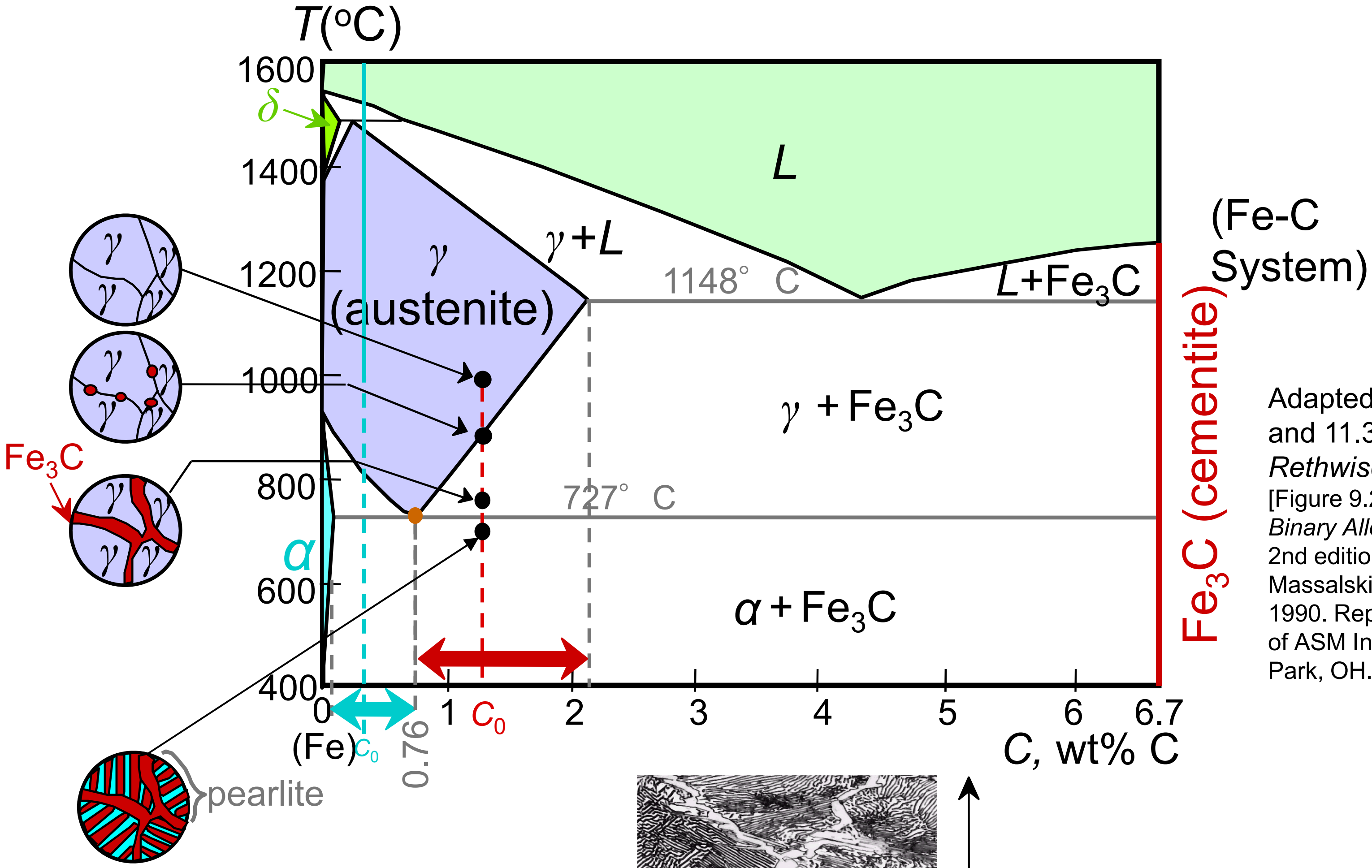
100 μm

Hypoeutectoid steel

proeutectoid ferrite

Adapted from Fig. 11.29, *Callister & Rethwisch 9e.*
(Photomicrograph courtesy of Republic Steel Corporation.)

Hypereutectoid Steel



Adapted from Figs. 11.23 and 11.31, *Callister & Rethwisch 9e.*
[Figure 9.24 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.]

Adapted from Fig. 11.32, *Callister & Rethwisch 9e*.
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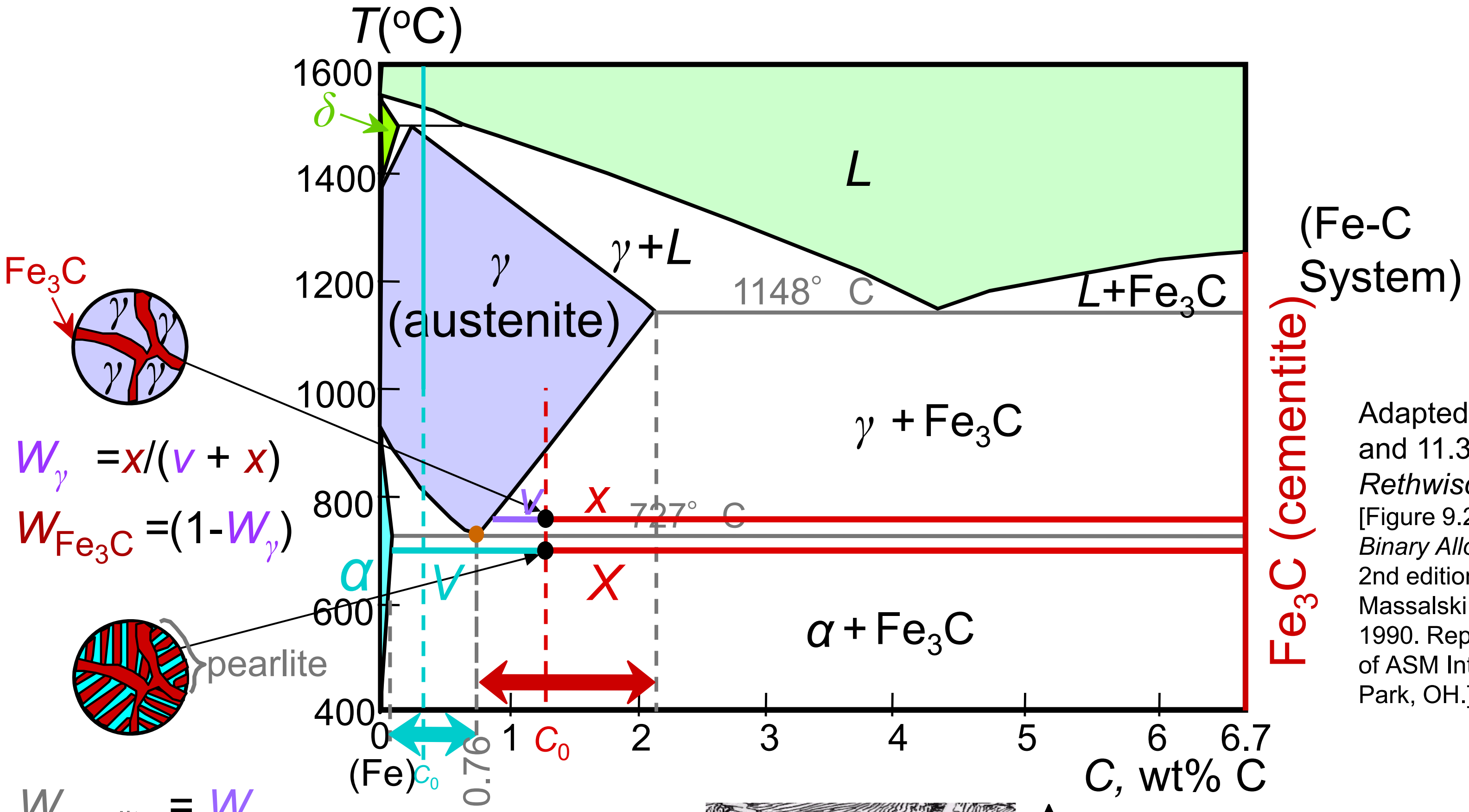
Hypereutectoid Steel



$W_{\gamma} = x/(v + x)$

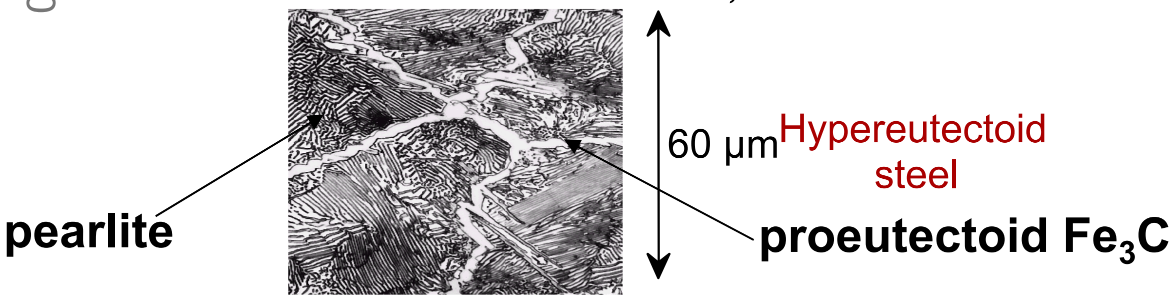
$W_{Fe_3C} = (1 - W_{\gamma})$

$W_{pearlite} = W_{\gamma}$

$W_{\alpha} = X/(V + X)$

$W_{Fe_3C'} = (1 - W_{\alpha})$

Adapted from Figs. 11.23 and 11.31, *Callister & Rethwisch 9e.*
[Figure 9.24 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.]



Adapted from Fig. 11.32, *Callister & Rethwisch 9e.*
(Copyright 1971 by United States Steel Corporation.)

Example Problem

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

a) The compositions of Fe_3C and ferrite (α).

b) The amount of cementite (in grams) that forms in 100 g of steel.

c) The amounts of pearlite and proeutectoid ferrite (α) in the 100 g.

Solution to Example Problem

a) Using the *RS* tie line just below the eutectoid

C_α = 0.022 wt% C
C_{Fe_3C} = 6.70 wt% C

b) Using the lever rule with the tie line shown

$$W_{Fe_3C} = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha}$$

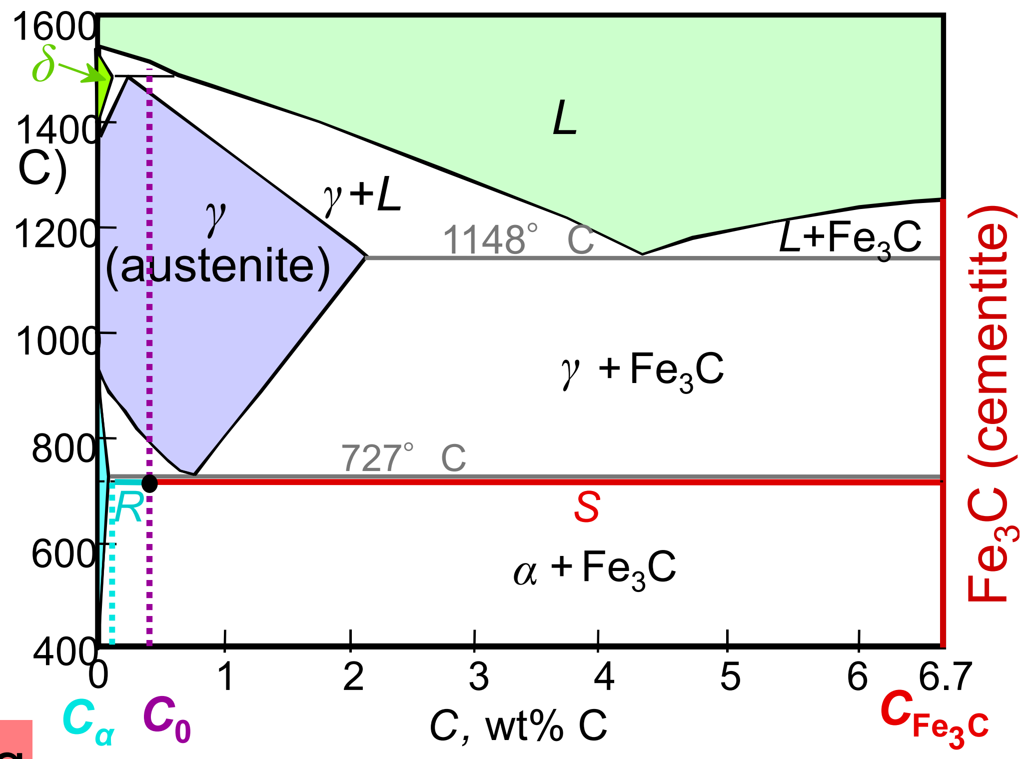
$$= \frac{0.40 - 0.022}{6.70 - 0.022} = 0.057$$

Amount of Fe_3C in 100 g

= (100 g)W_{Fe_3C}

= (100 g)(0.057) = **5.7 g**

Fig. 11.23, *Callister & Rethwisch 9e.*
[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.]



Solution to Example Problem (cont.)

c) Using the *VX* tie line just above the eutectoid and realizing that

$C_0 = 0.40$ wt% C
$C_\alpha = 0.022$ wt% C
$C_{pearlite} = C_\gamma = 0.76$ wt% C

$$W_{pearlite} = \frac{V}{V+X} = \frac{C_0 - C_\alpha}{C_\gamma - C_\alpha}$$

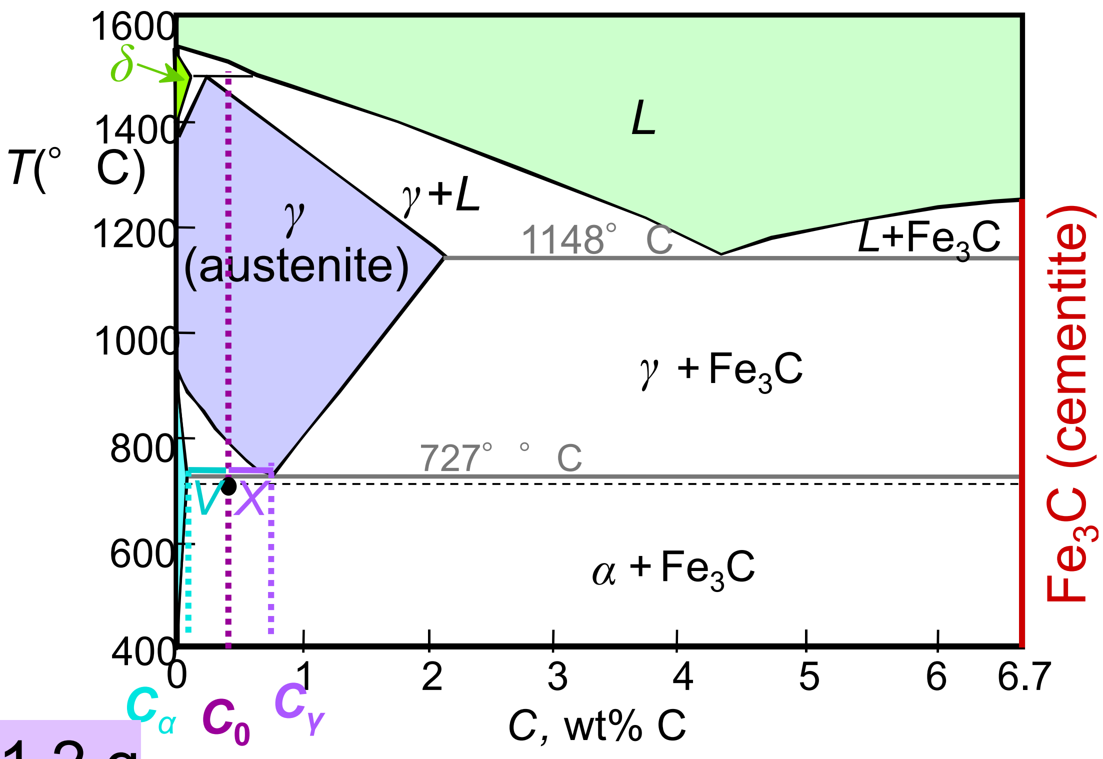
$$= \frac{0.40 - 0.022}{0.76 - 0.022} = 0.512$$

Amount of pearlite in 100 g

$= (100\text{ g})W_{pearlite}$

$= (100\text{ g})(0.512) = 51.2\text{ g}$

Fig. 11.23, *Callister & Rethwisch 9e.* [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.]



Alloying with Other Elements

- $T_{eutectoid}$ changes:

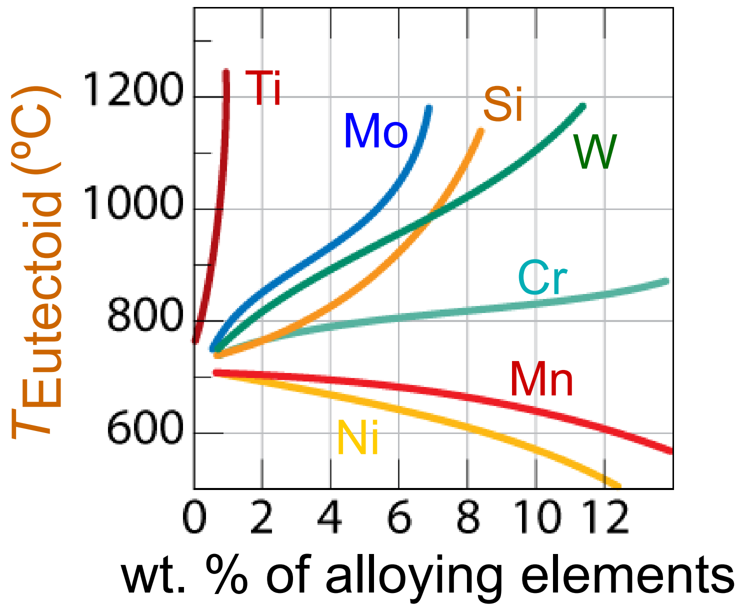


Fig. 11.33, *Callister & Rethwisch 9e.*
(From Edgar C. Bain, *Functions of the Alloying Elements in Steel,* 1939. Reproduced by permission of ASM International, Materials Park, OH.)

- $C_{eutectoid}$ changes:

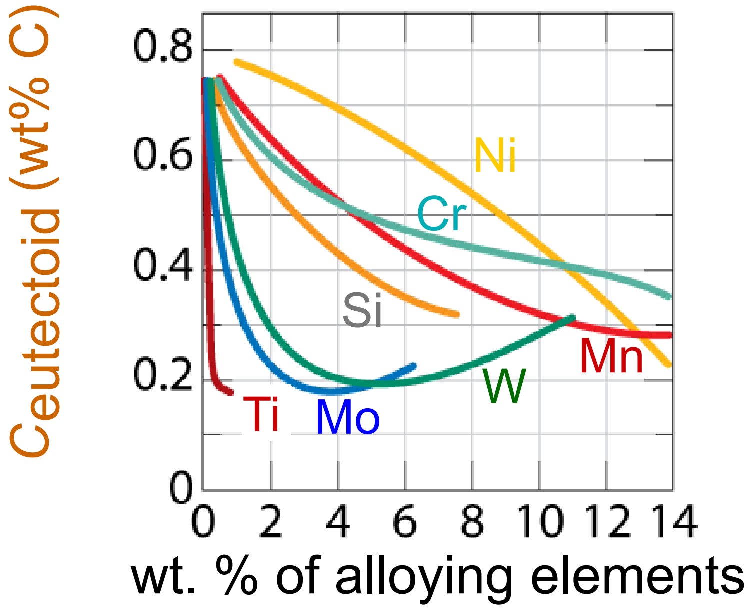


Fig. 11.34, *Callister & Rethwisch 9e.*
(From Edgar C. Bain, *Functions of the Alloying Elements in Steel,* 1939. Reproduced by permission of ASM International, Materials Park, OH.)

Summary

- Phase diagrams are useful tools to determine:
  - -- the number and types of phases present,
  - -- the composition of each phase,
  - -- and the weight fraction of each phase

  given the temperature and composition of the system.
- The microstructure of an alloy depends on
  - -- its composition, and
  - -- whether or not cooling rate allows for maintenance of equilibrium.
- Important phase diagram phase transformations include eutectic, eutectoid, and peritectic.