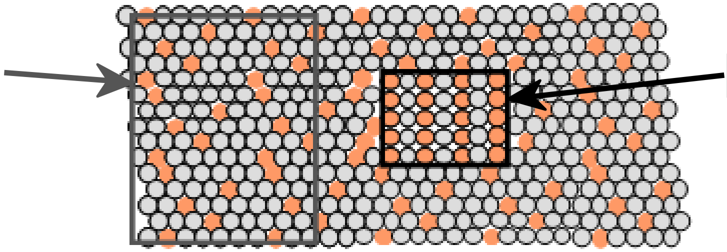
Chapter 11: Phase Diagrams

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?



○ Nickel atom
● Copper atom

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.

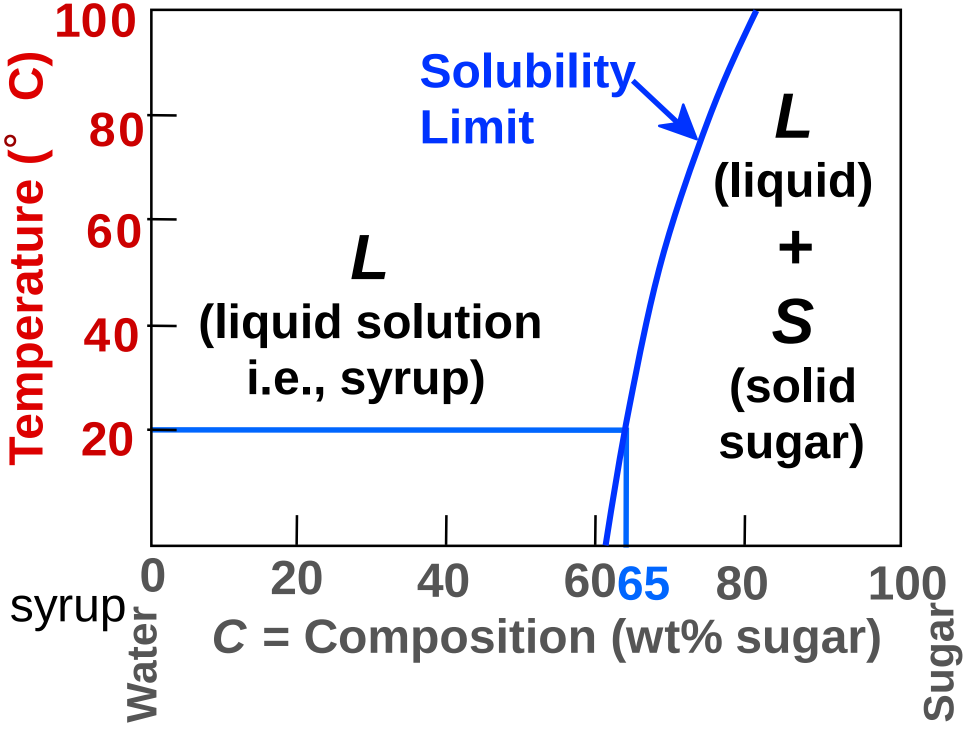
Question: What is the solubility limit for sugar in water at 20° C?

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

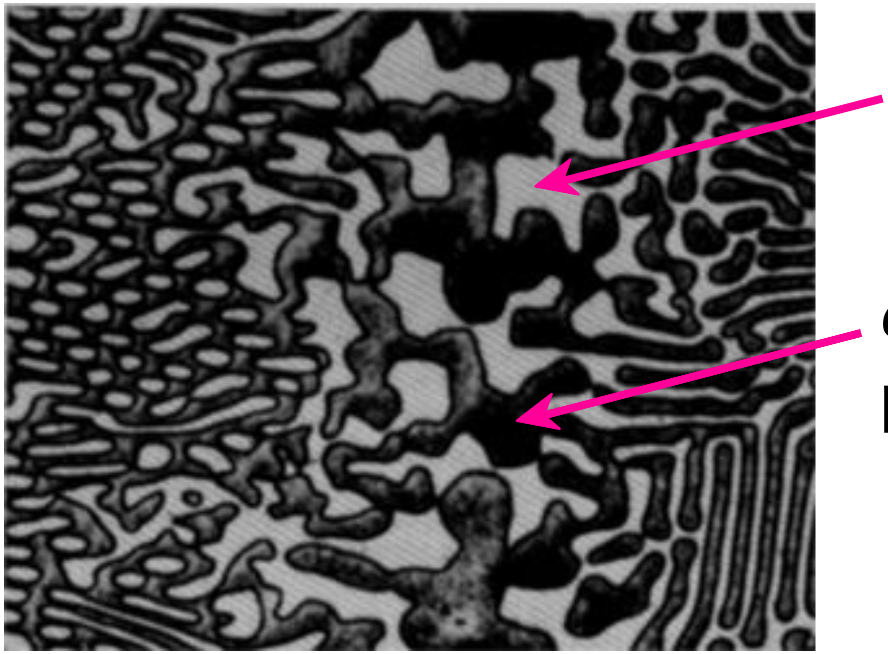
- **Components**:

  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



β (lighter phase)

α (darker phase)

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

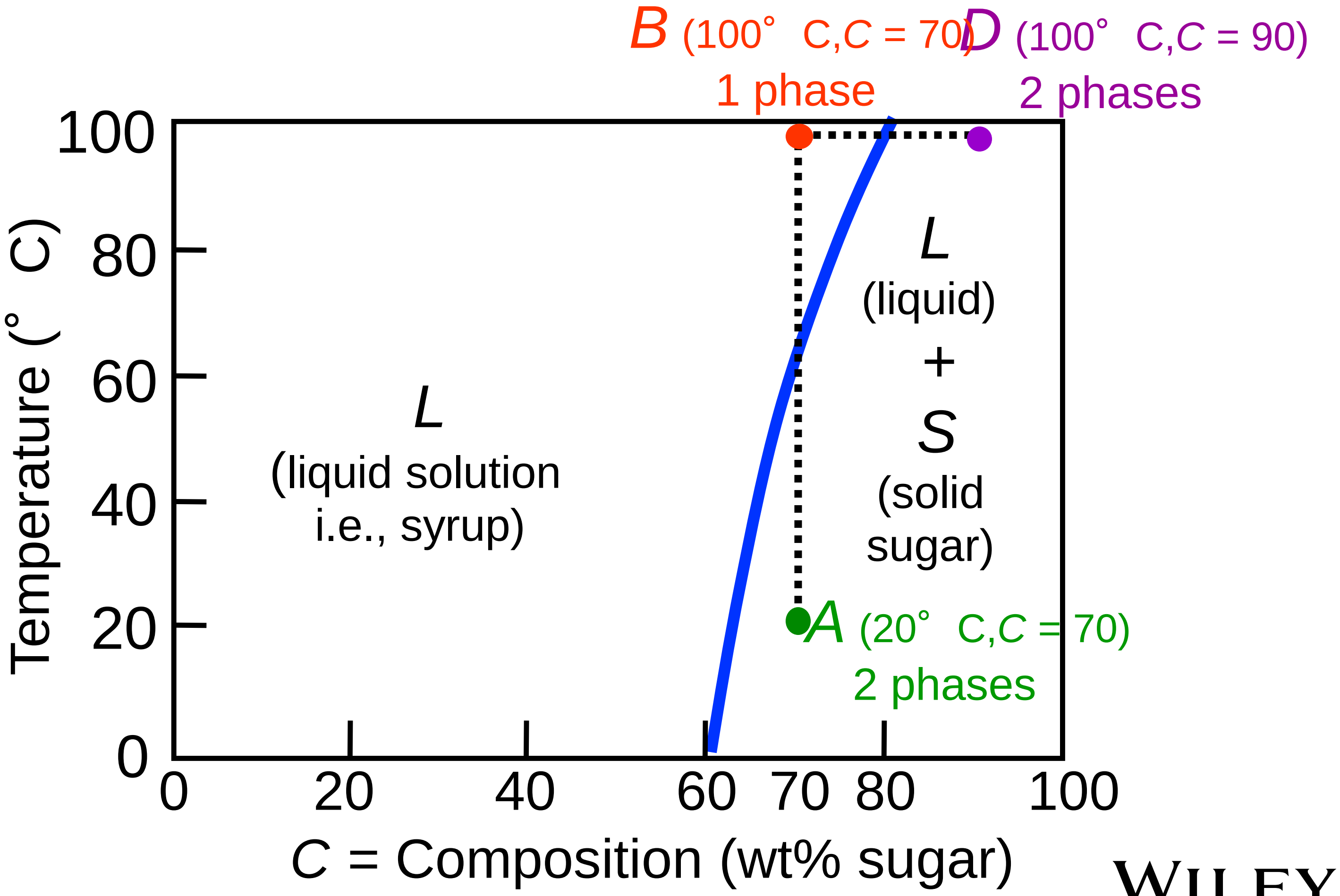


Fig. 11.1, *Callister & Rethwisch 9e.*

Criteria for Solid Solubility

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

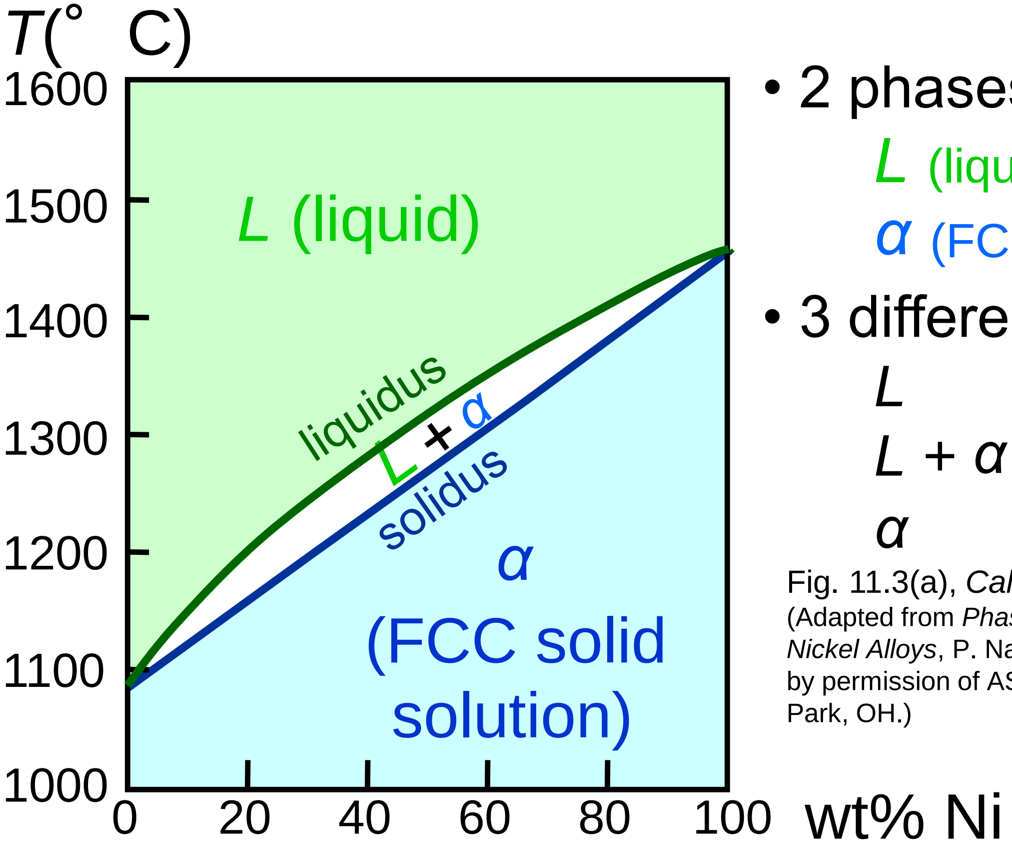
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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

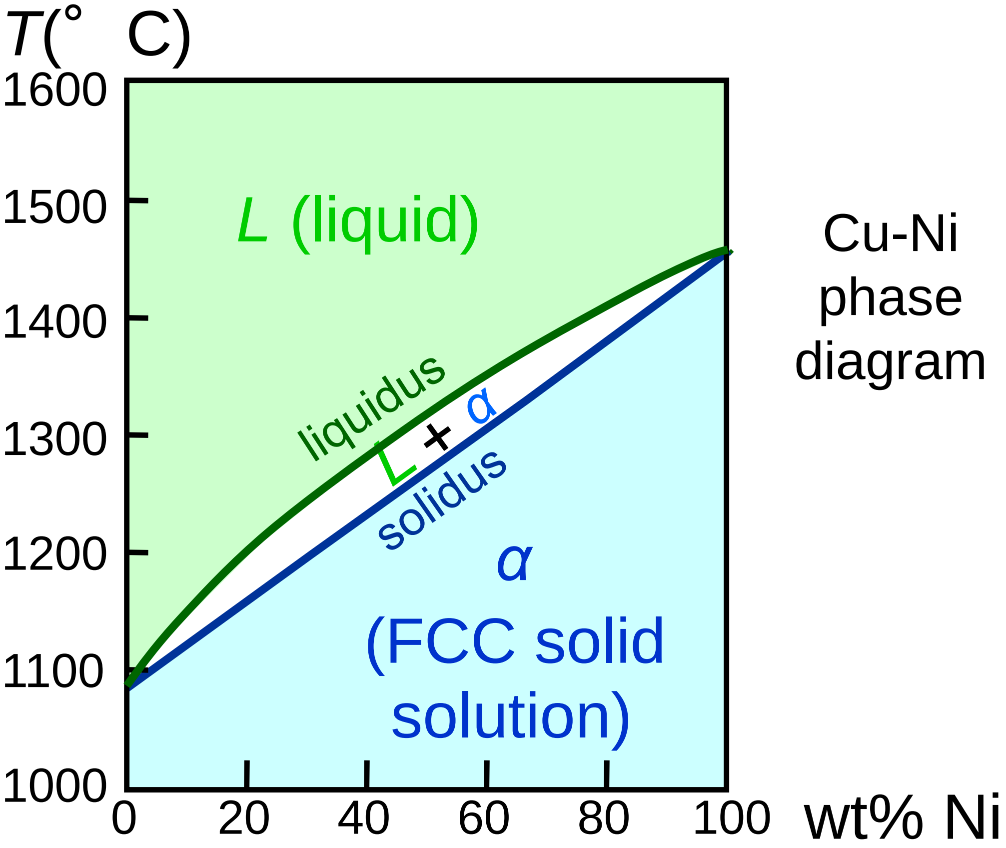


- 2 phases:
  - *L* (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + α
  - α

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.)

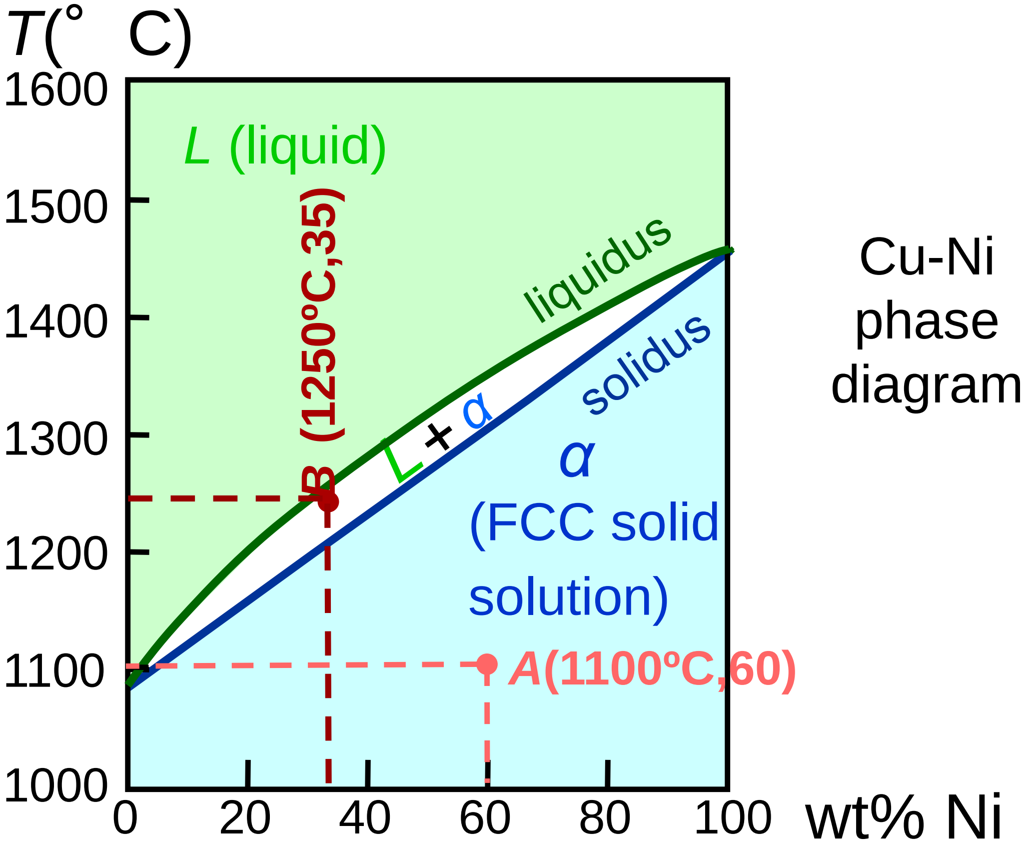
Phase Diagrams:
Determination of phase(s) present

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

- Examples:

A(1100°C, 60 wt% Ni):
1 phase: α

B(1250°C, 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

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

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

Cu-Ni system

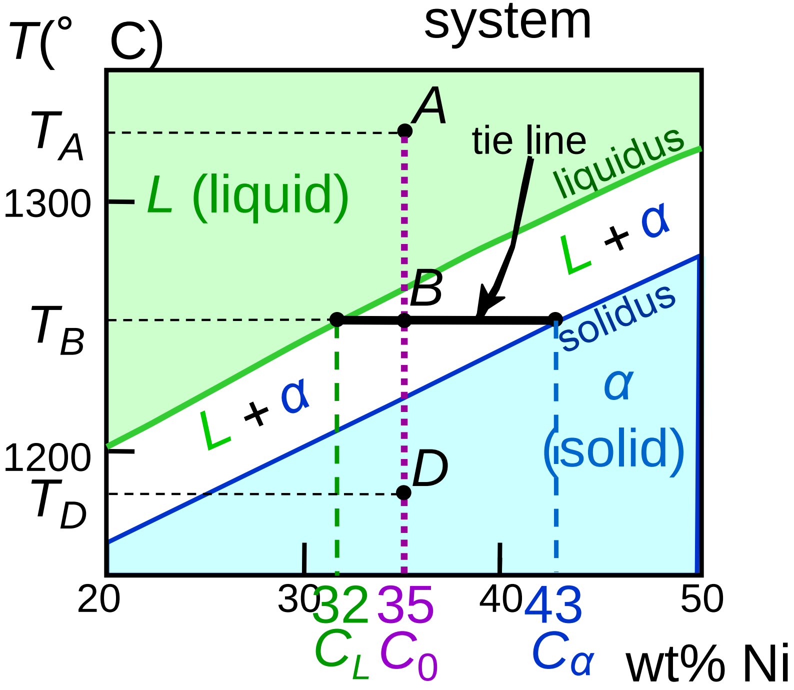


Fig. 11.3(b), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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

$$W_L = 1.00,\ W_\alpha = 0$$

At T_D : Only Solid (α) present

$$W_L = 0,\ W_\alpha = 1.00$$

At T_B : Both α and L present

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

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

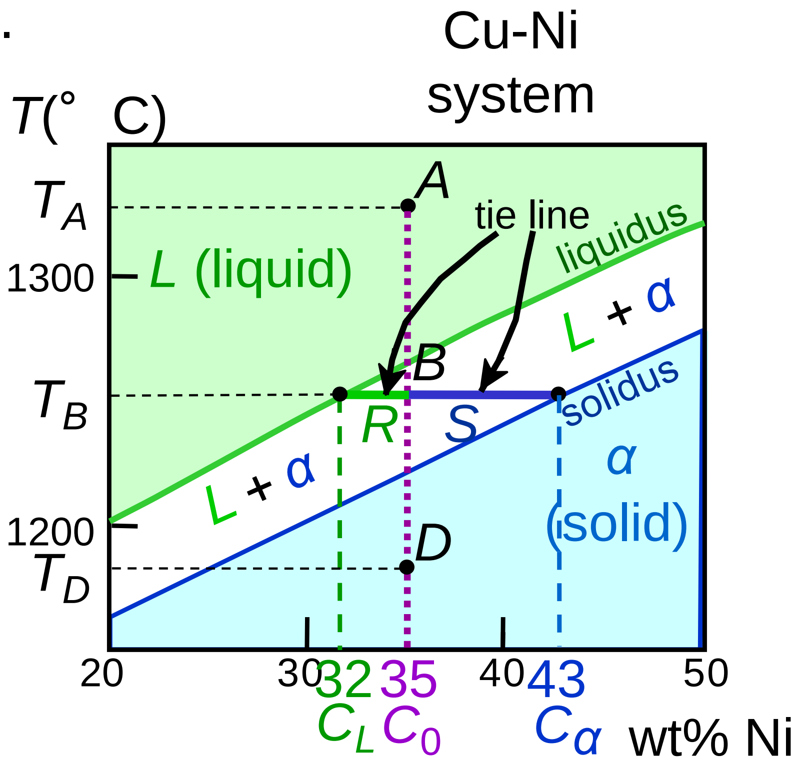
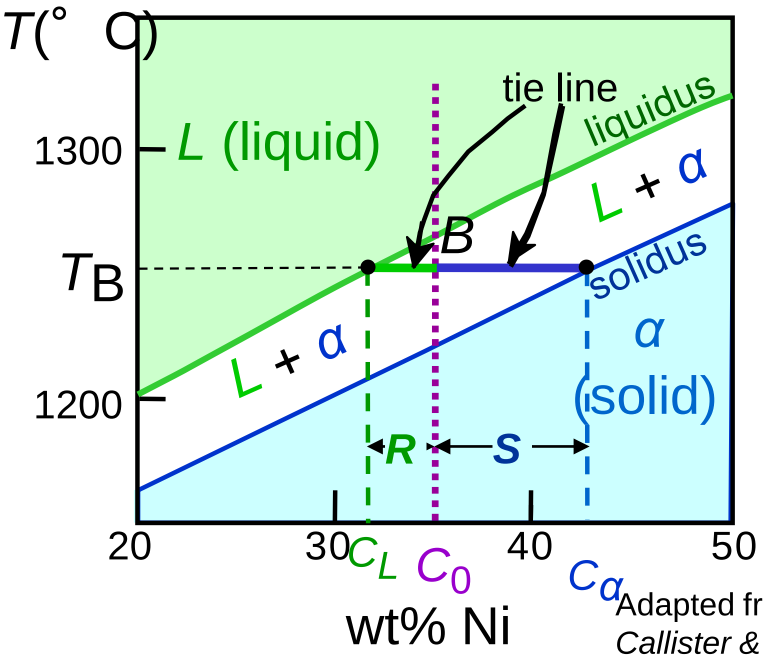


Fig. 11.3(b), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

The Lever Rule

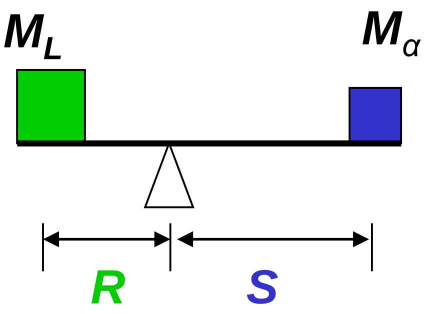
- Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm



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

What fraction of each phase?

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



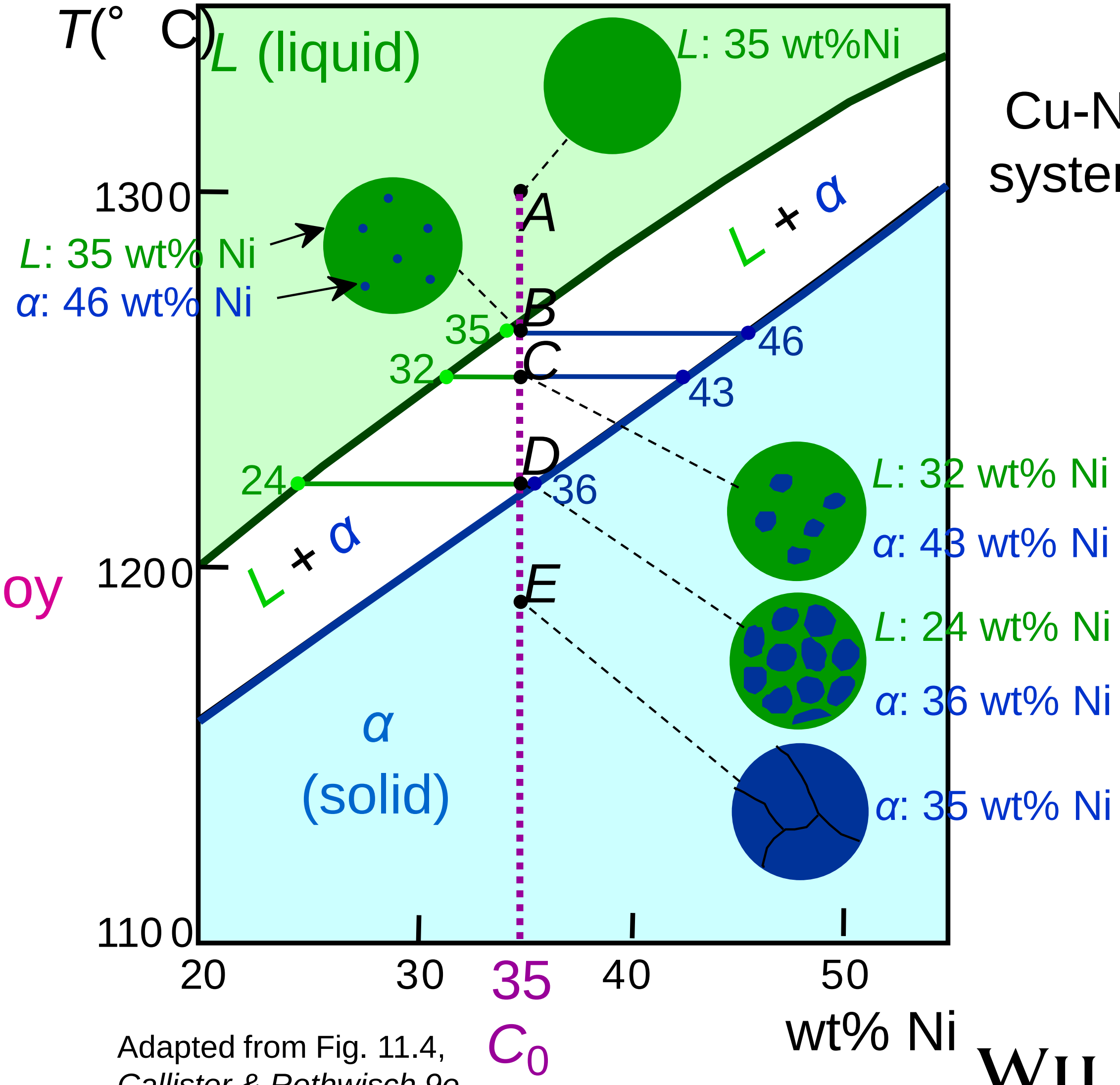
$$M_\alpha \text{ x } S = M_L \text{ x } R$$

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

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

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. 11.4, *Callister & Rethwisch 9e.*

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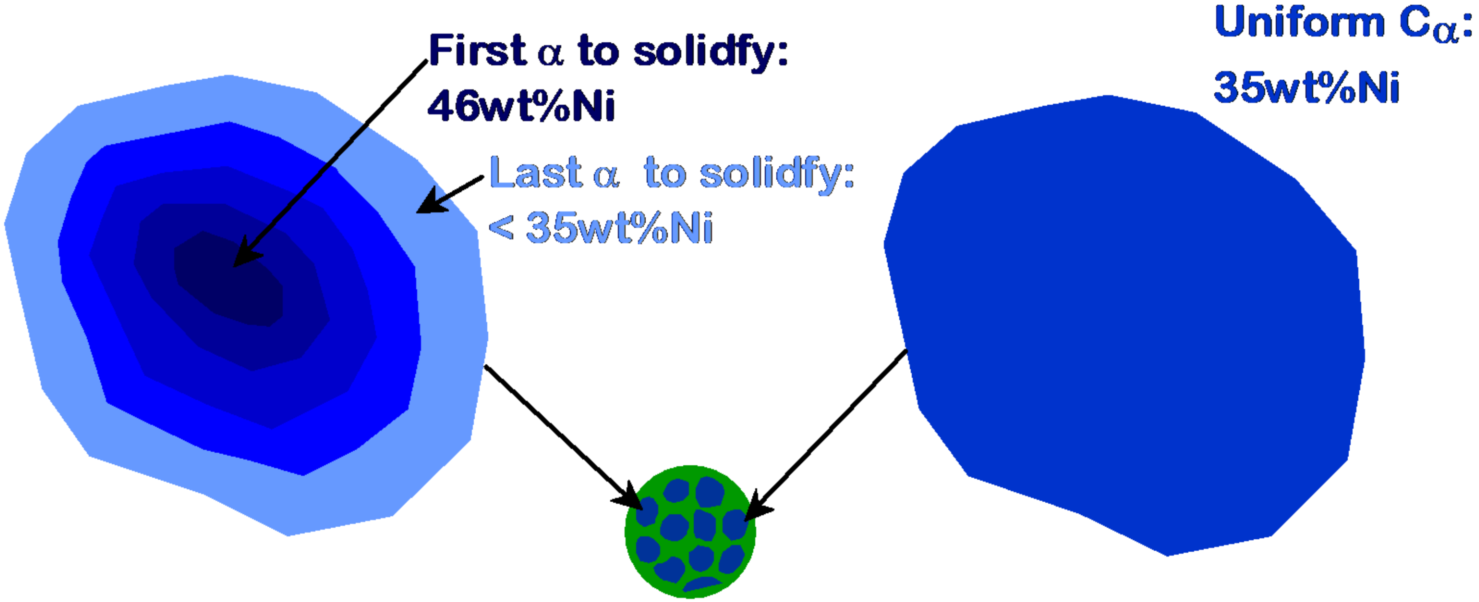
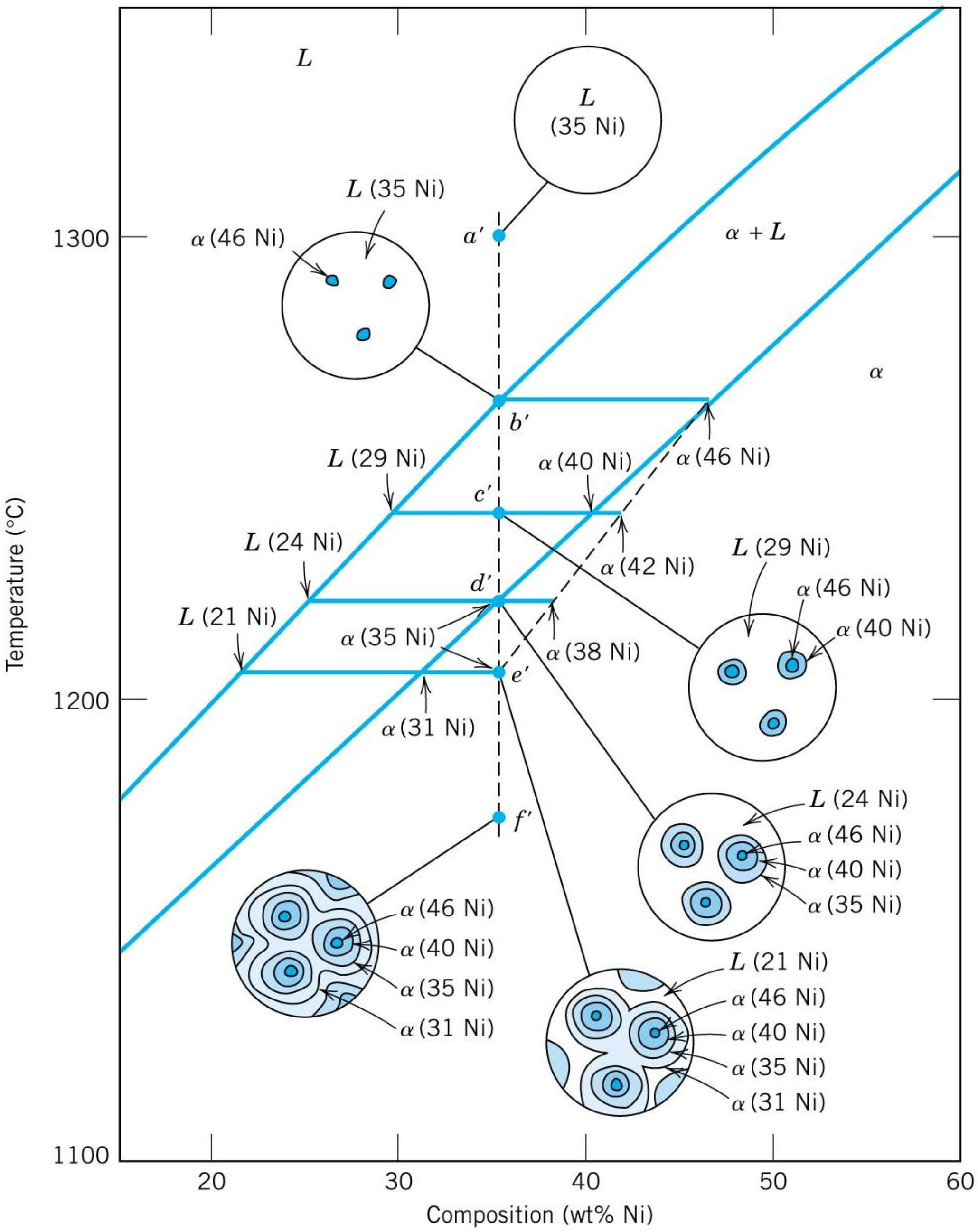
Core vs Equilibrium Phases

- C_a changes as we solidify.
- Cu-Ni case: First a to solidify has C_a = 46wt%Ni.
  Last a to solidify has C_a = 35wt%Ni.

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

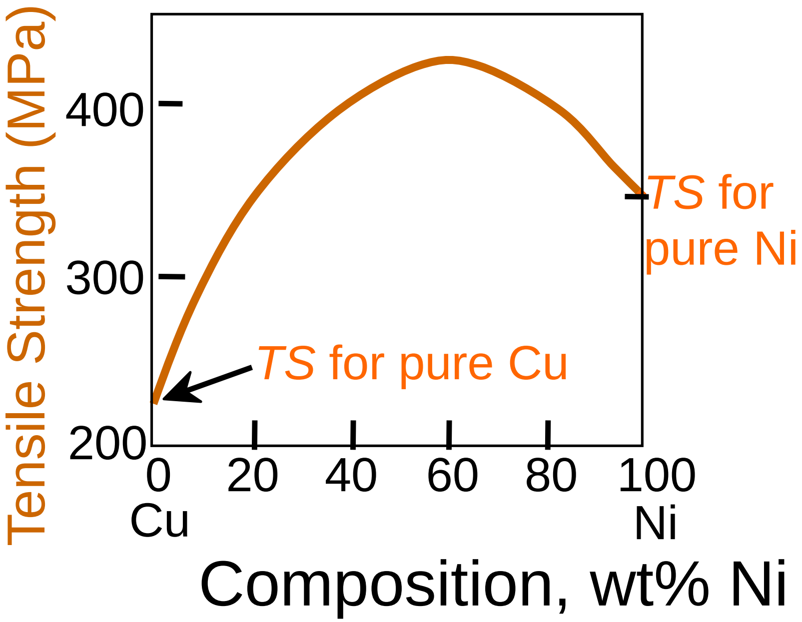



L
L
(35 Ni)
L (35 Ni)
α (46 Ni)
a′
1300
α + L
α
b′
L (29 Ni)
α (40 Ni)
α (46 Ni)
c′
L (24 Ni)
α (42 Ni)
L (29 Ni)
α (46 Ni)
α (40 Ni)
d′
L (21 Ni)
α (35 Ni)
α (38 Ni)
e′
α (31 Ni)
1200
f′
L (24 Ni)
α (46 Ni)
α (40 Ni)
α (35 Ni)
α (46 Ni)
α (40 Ni)
α (35 Ni)
α (31 Ni)
L (21 Ni)
α (46 Ni)
α (40 Ni)
α (35 Ni)
α (31 Ni)
1100
20
30
40
50
60
Temperature (°C)
Composition (wt% Ni)

Mechanical Properties: Cu-Ni System

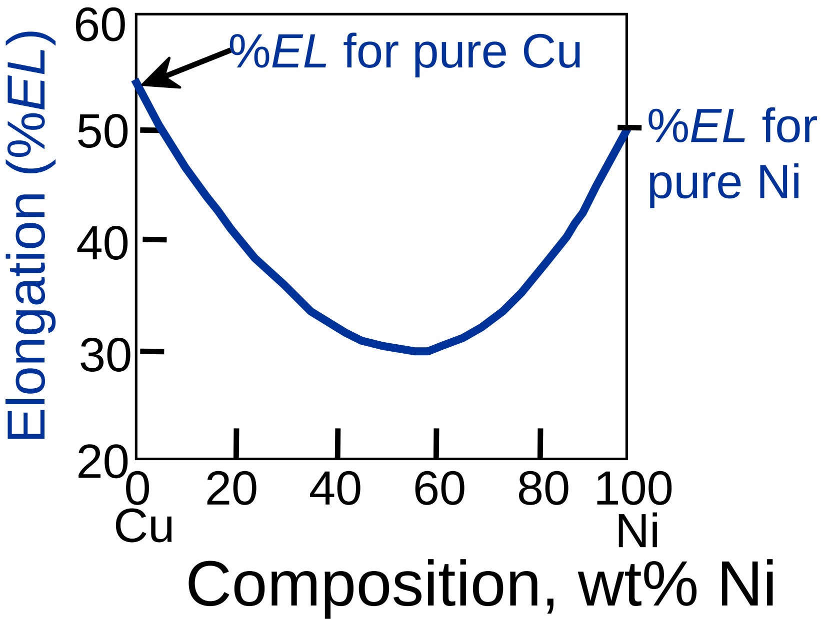
- Effect of solid solution strengthening on:

-- 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

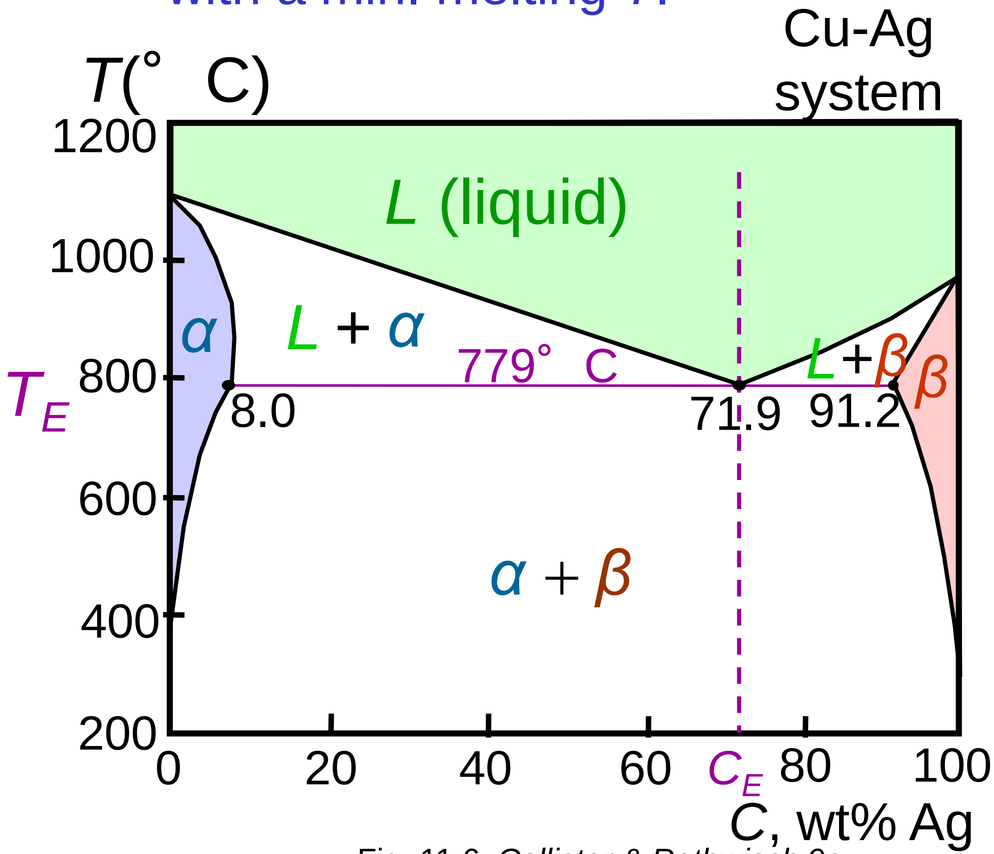


Fig. 11.6, *Callister & Rethwisch 9e*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.].

- **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:

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

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 0.67$$

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

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 0.33$$

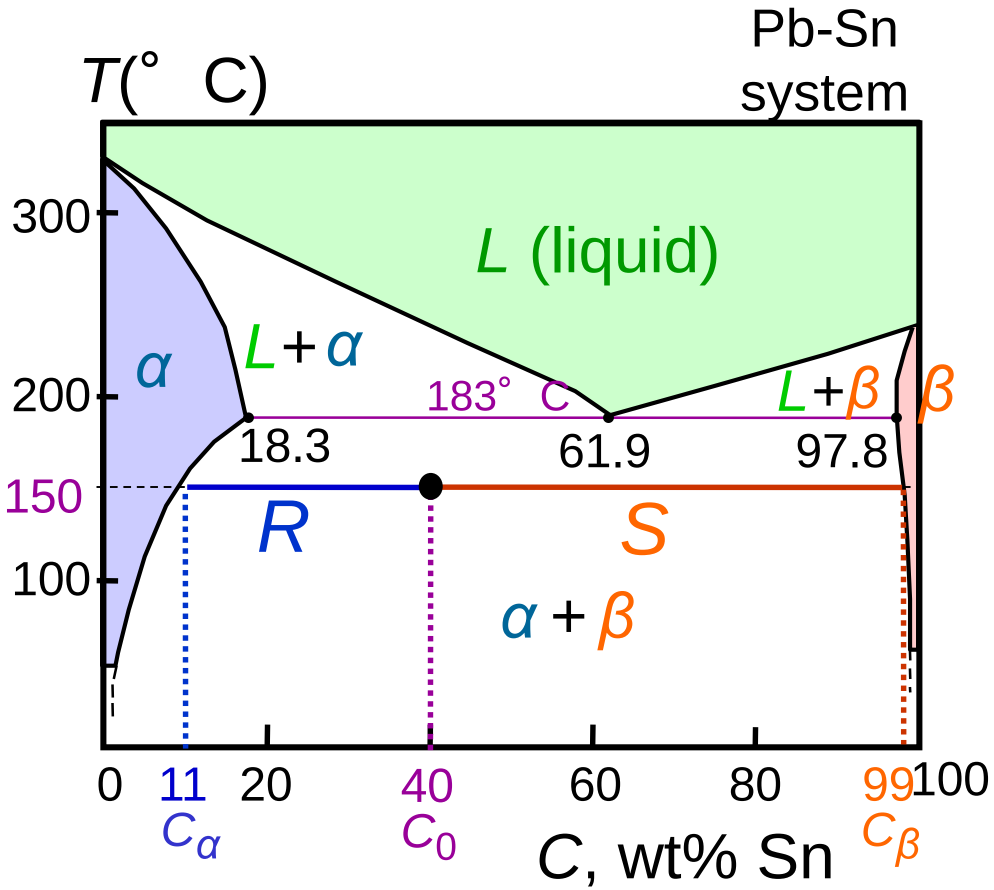


Fig. 11.7, *Callister & Rethwisch 9e.* [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

EX 2: Pb-Sn Eutectic System

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

Answer: $\alpha + L$

-- the phase compositions

Answer: C_α = 17 wt% Sn

C_L = 46 wt% Sn

-- the relative amount of each phase

Answer:

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

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

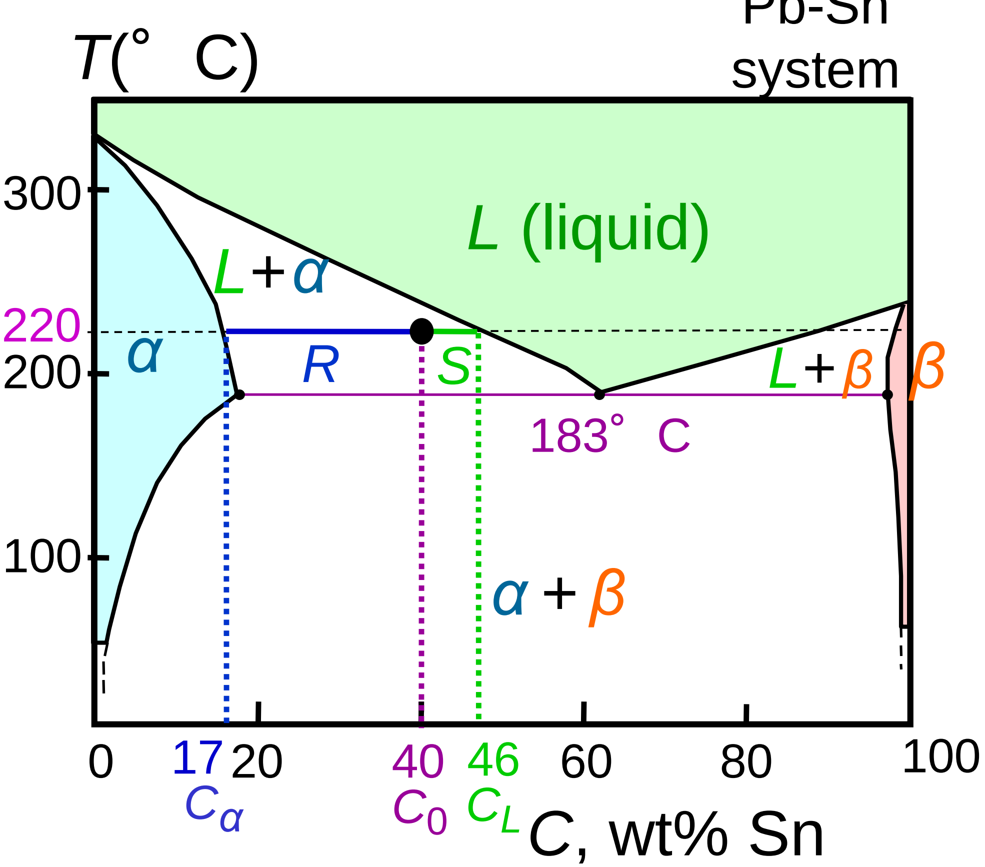


Fig. 11.7, *Callister & Rethwisch 9e.*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

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

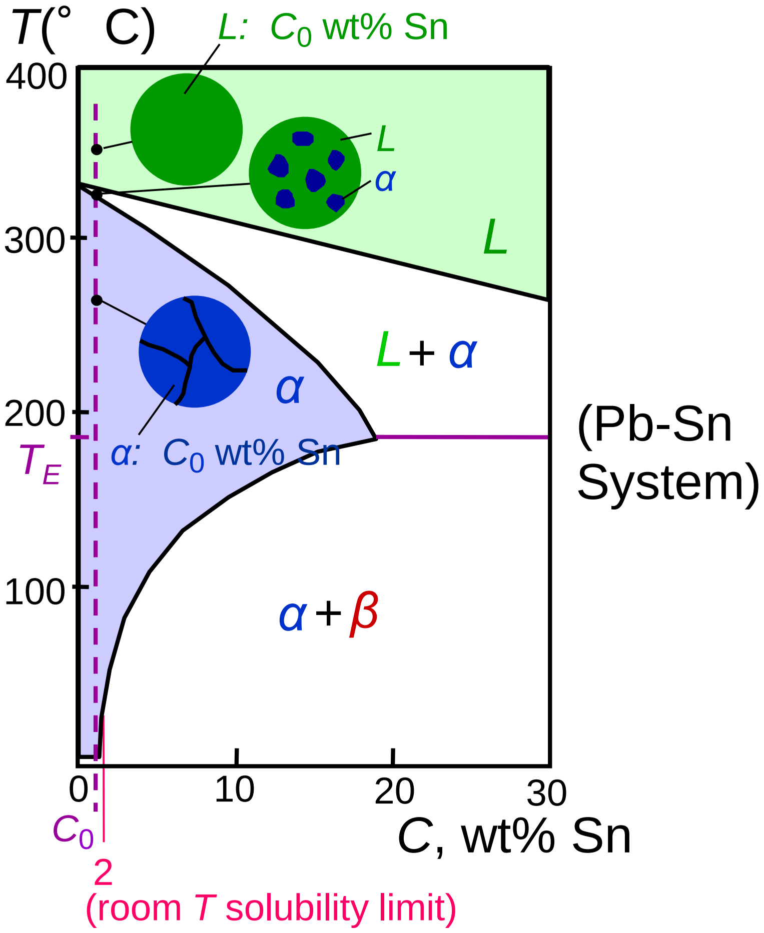
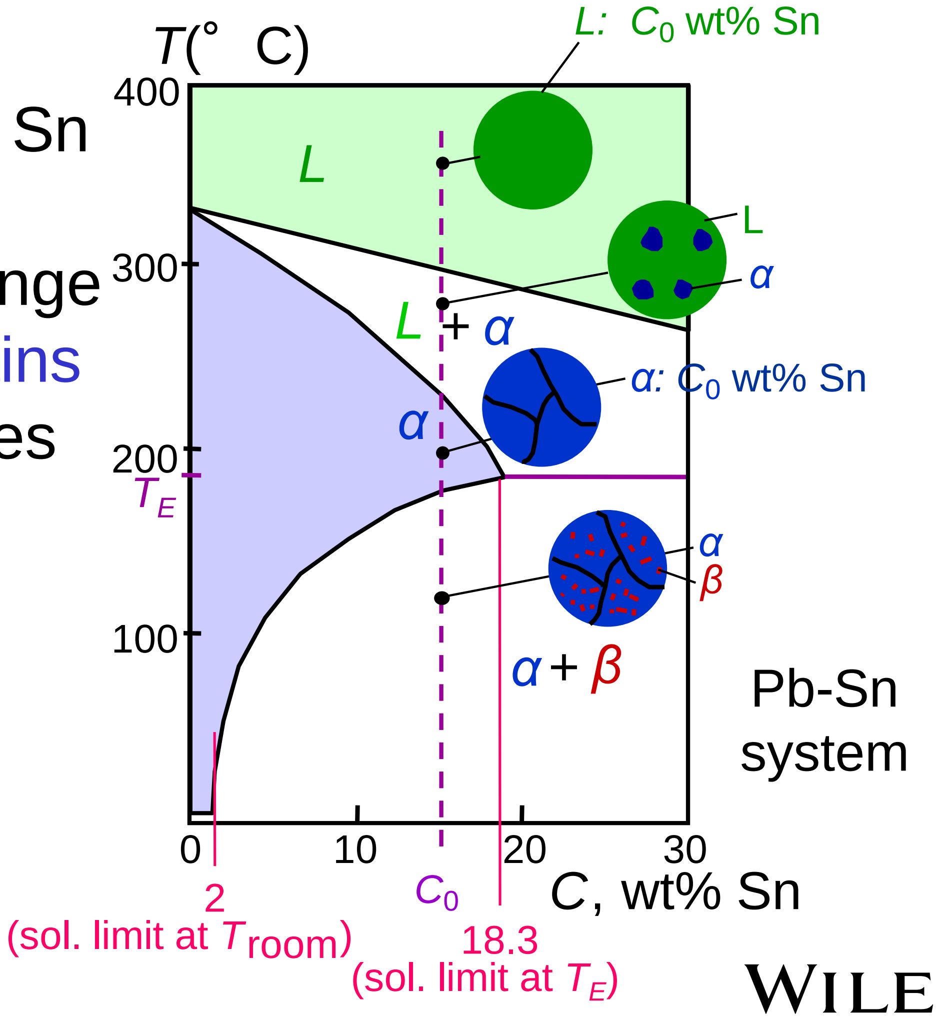


Fig. 11.10, *Callister & Rethwisch 9e.*

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



Pb-Sn system

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

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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.

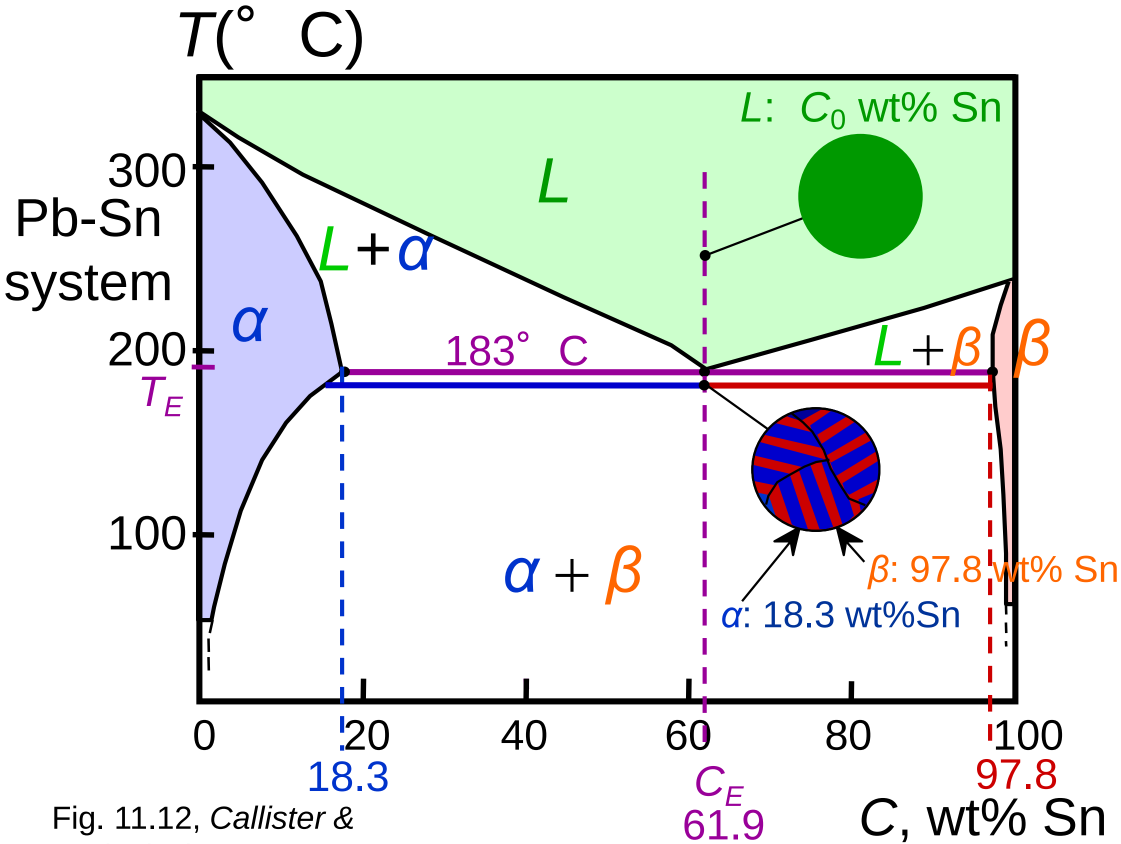


Fig. 11.12, *Callister & Rethwisch 9e.*

Micrograph of Pb-Sn eutectic microstructure

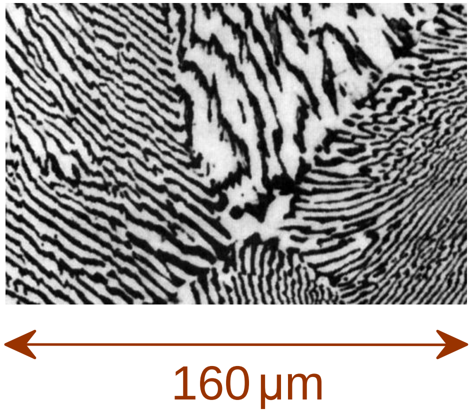
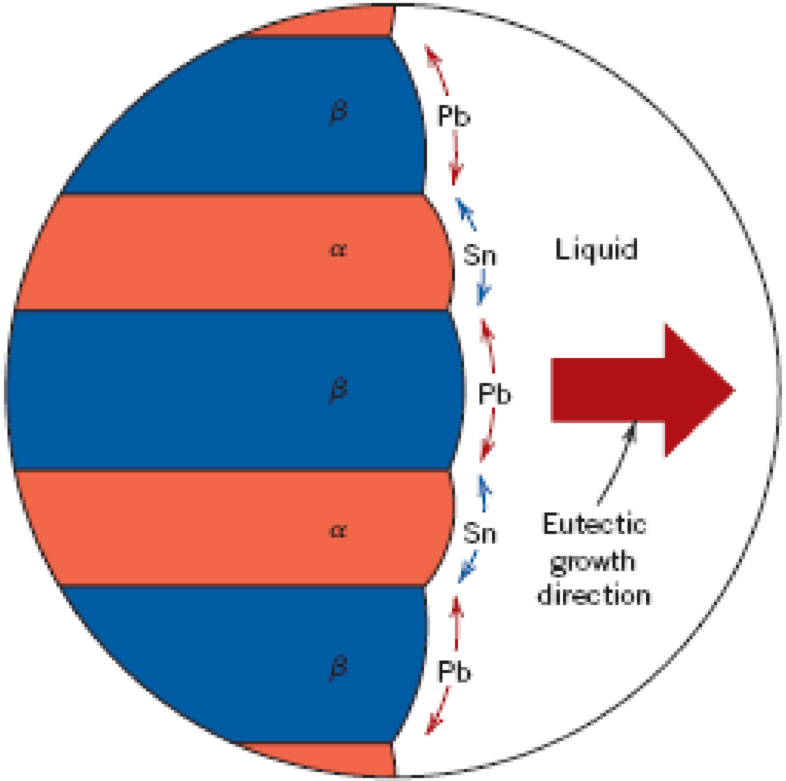
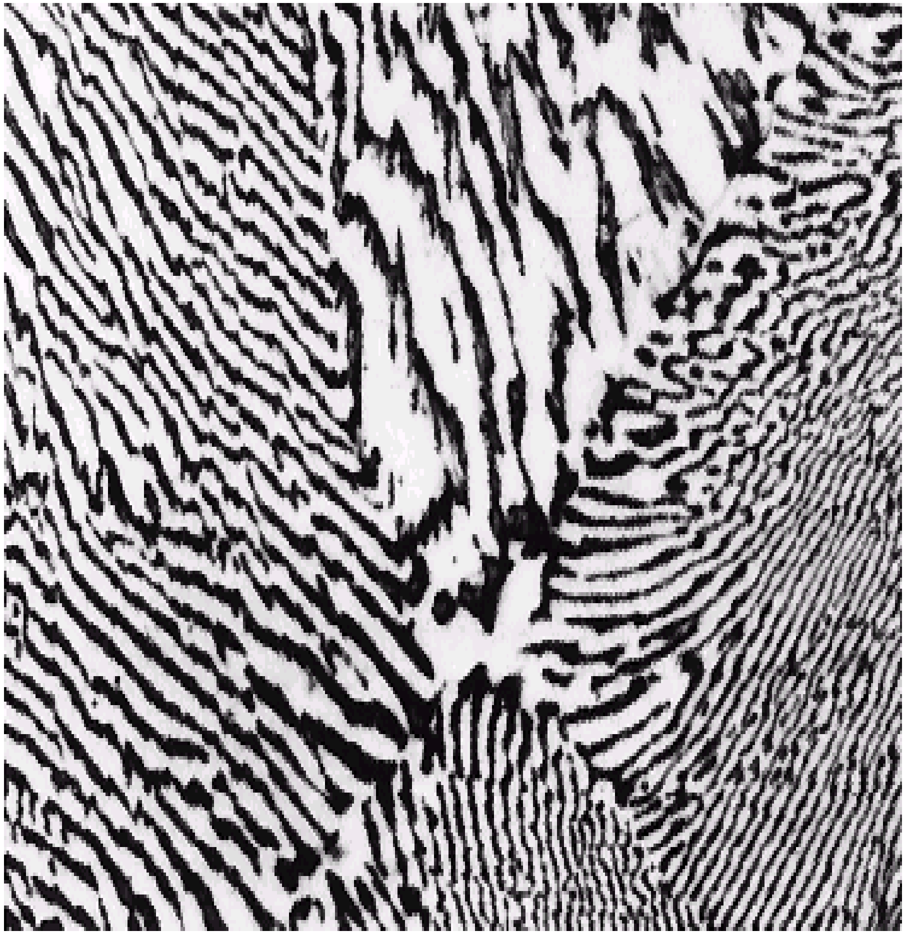


Fig. 11.13, *Callister & Rethwisch 9e.* (From *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

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

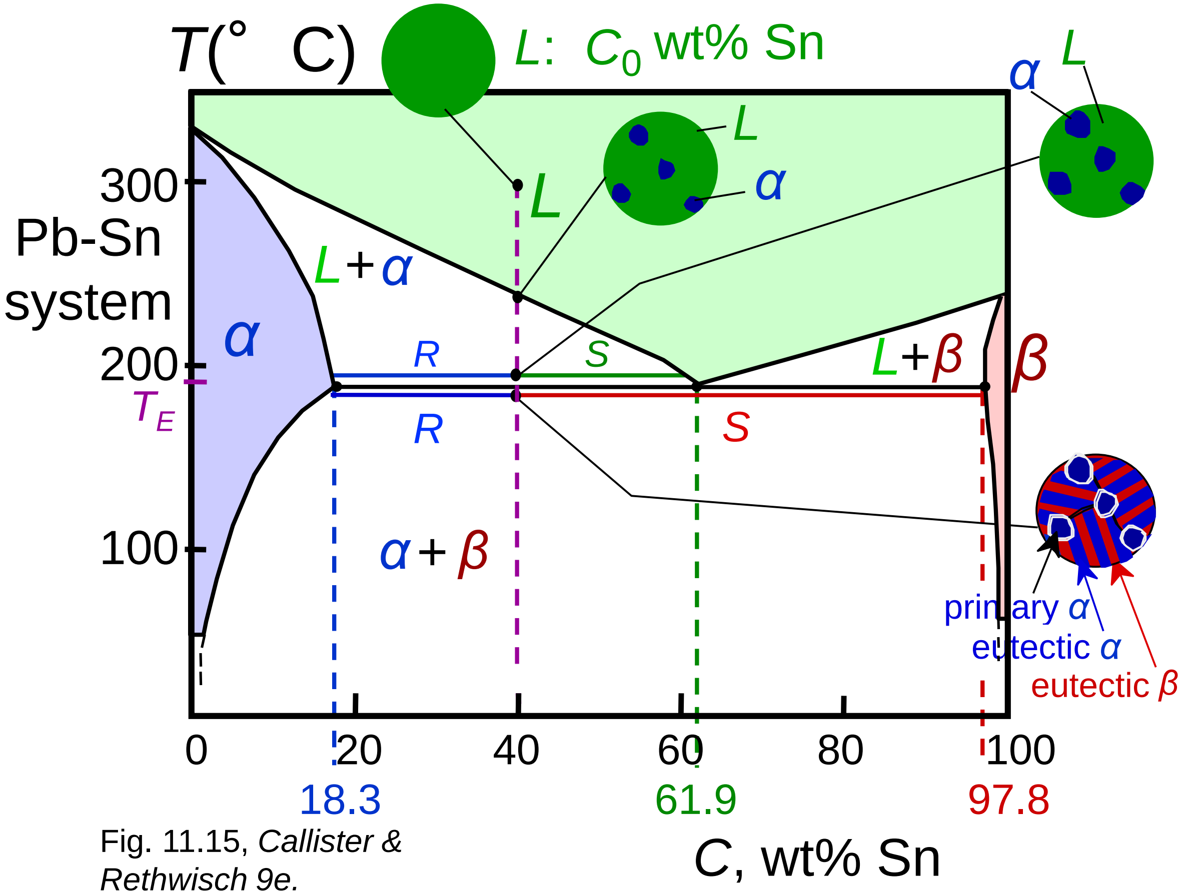


Fig. 11.15, *Callister & Rethwisch 9e.*

- 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

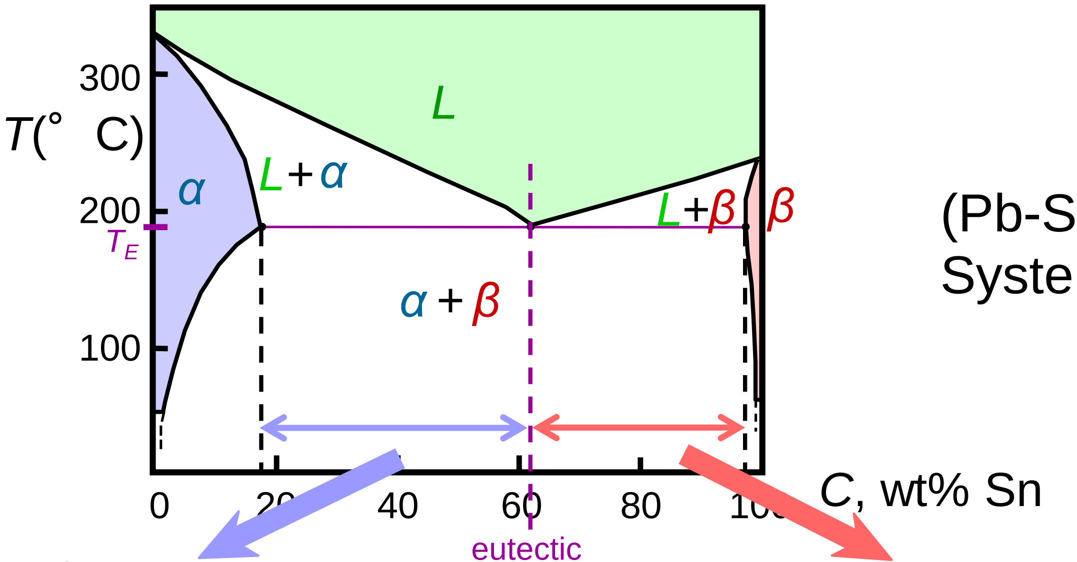
  C_β = 97.8 wt% Sn

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

  $W_\beta = 0.27$

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)

hypoeutectic: C_0 = 50 wt% Sn

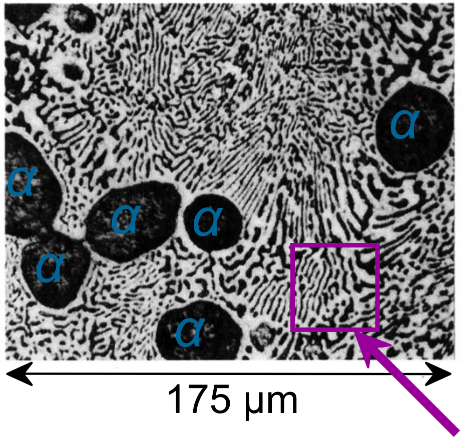


Fig. 11.16, *Callister & Rethwisch 9e.*

eutectic: C_0 = 61.9 wt% Sn

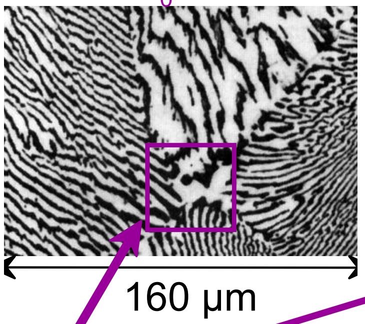
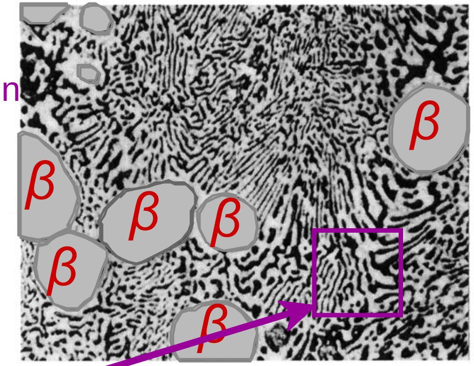


Fig. 11.13, *Callister & Rethwisch 9e.*

hypereutectic: (illustration only)



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

eutectic micro-constituent

(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.)

Intermetallic Compounds

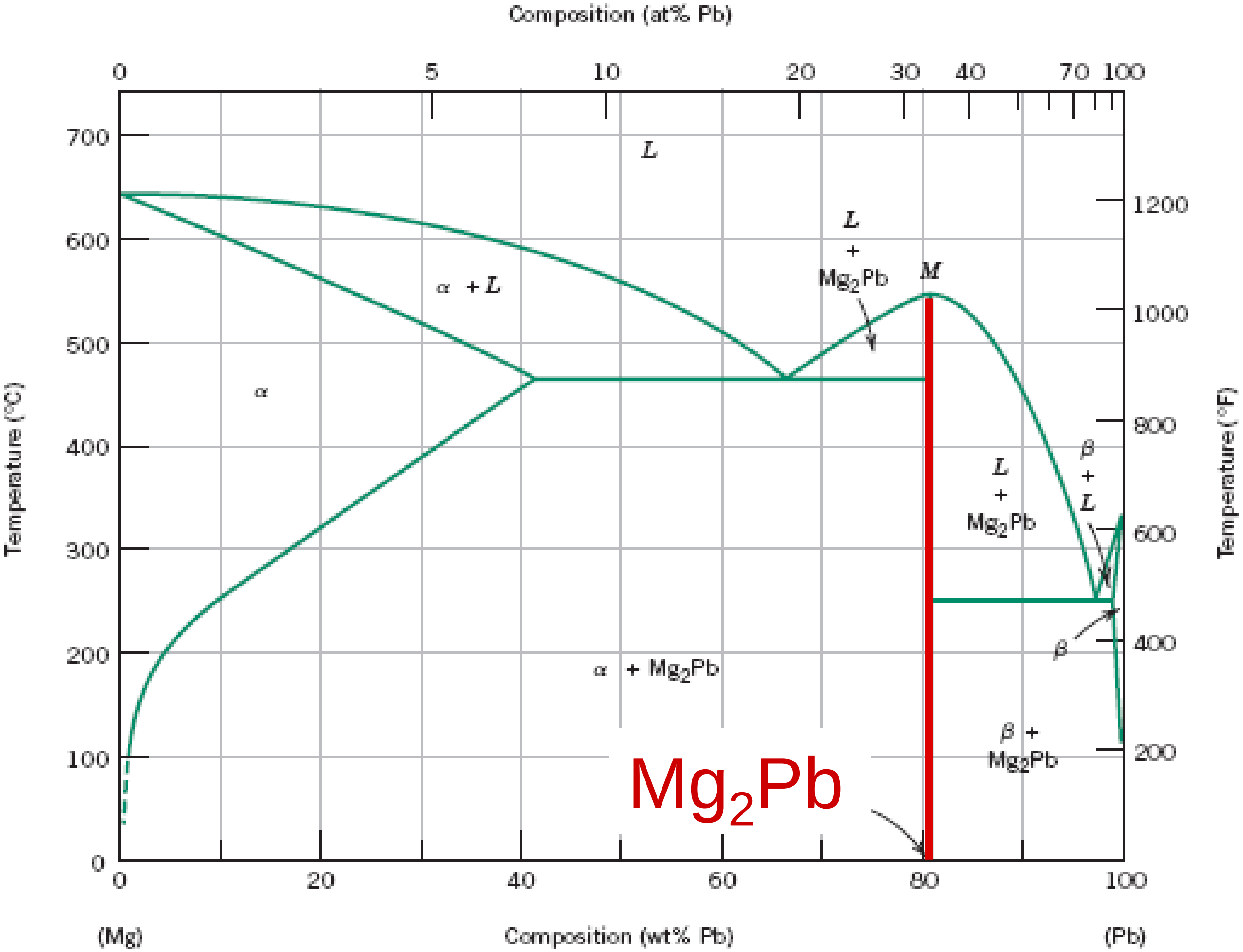


Fig. 11.19, *Callister & Rethwisch 9e.*
[Adapted from *Phase Diagrams of Binary Magnesium Alloys*, A. A. Nayeb-Hashemi and J. B. Clark (Editors), 1988. Reprinted by permission of ASM International, Materials Park, OH.]

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).

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

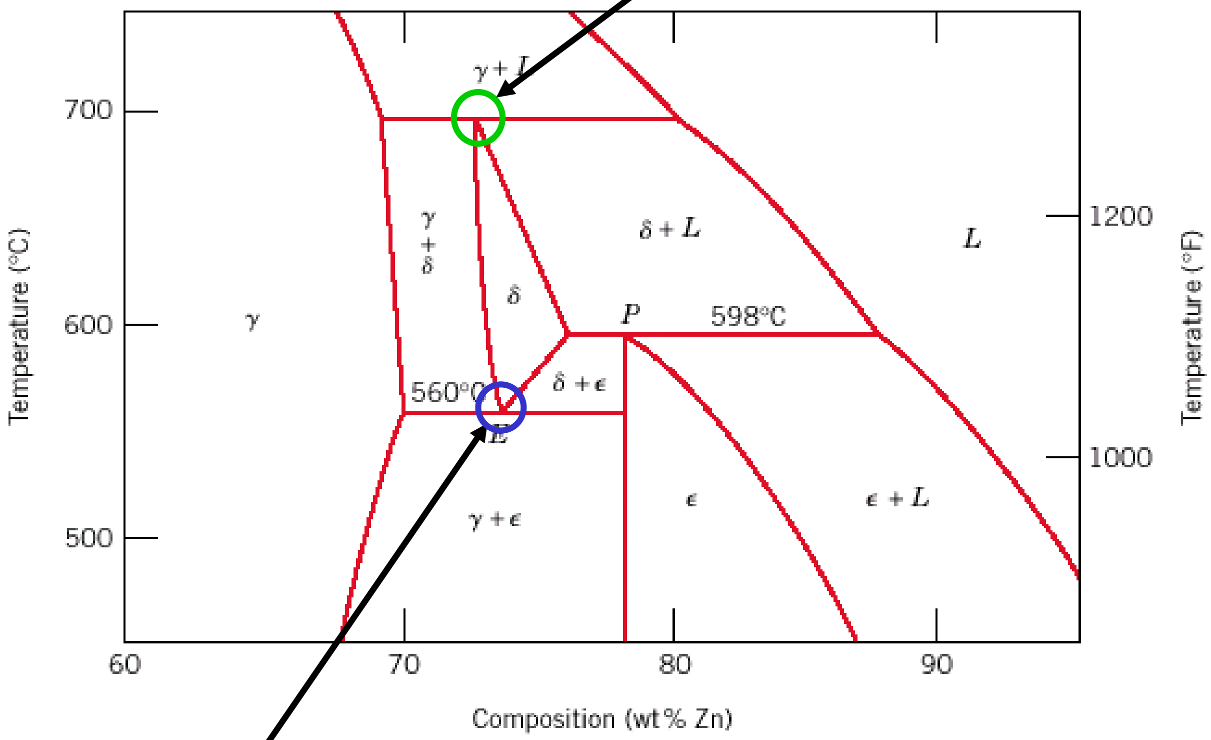
$$S_1 + L \rightleftharpoons S_2$$

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

Eutectoid & Peritectic

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

Cu-Zn Phase diagram

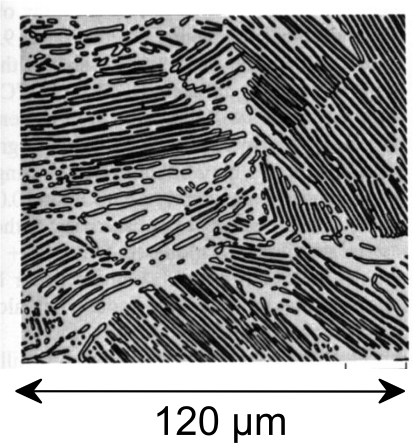


Eutectoid transformation $\delta \rightleftharpoons \gamma + e$

Fig. 11.20, *Callister & Rethwisch 9e.*
[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.]

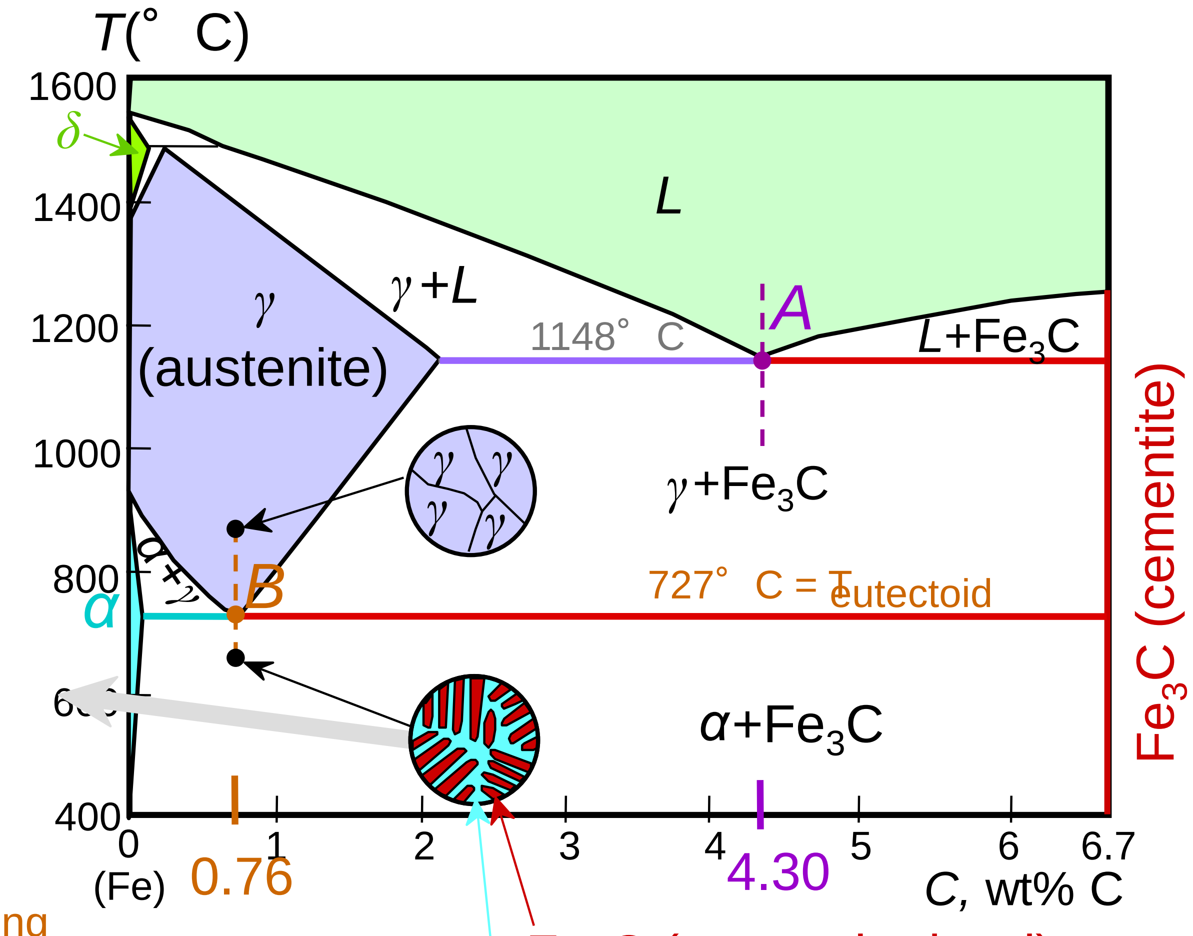
Iron-Carbon (Fe-C) Phase Diagram

- 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.)

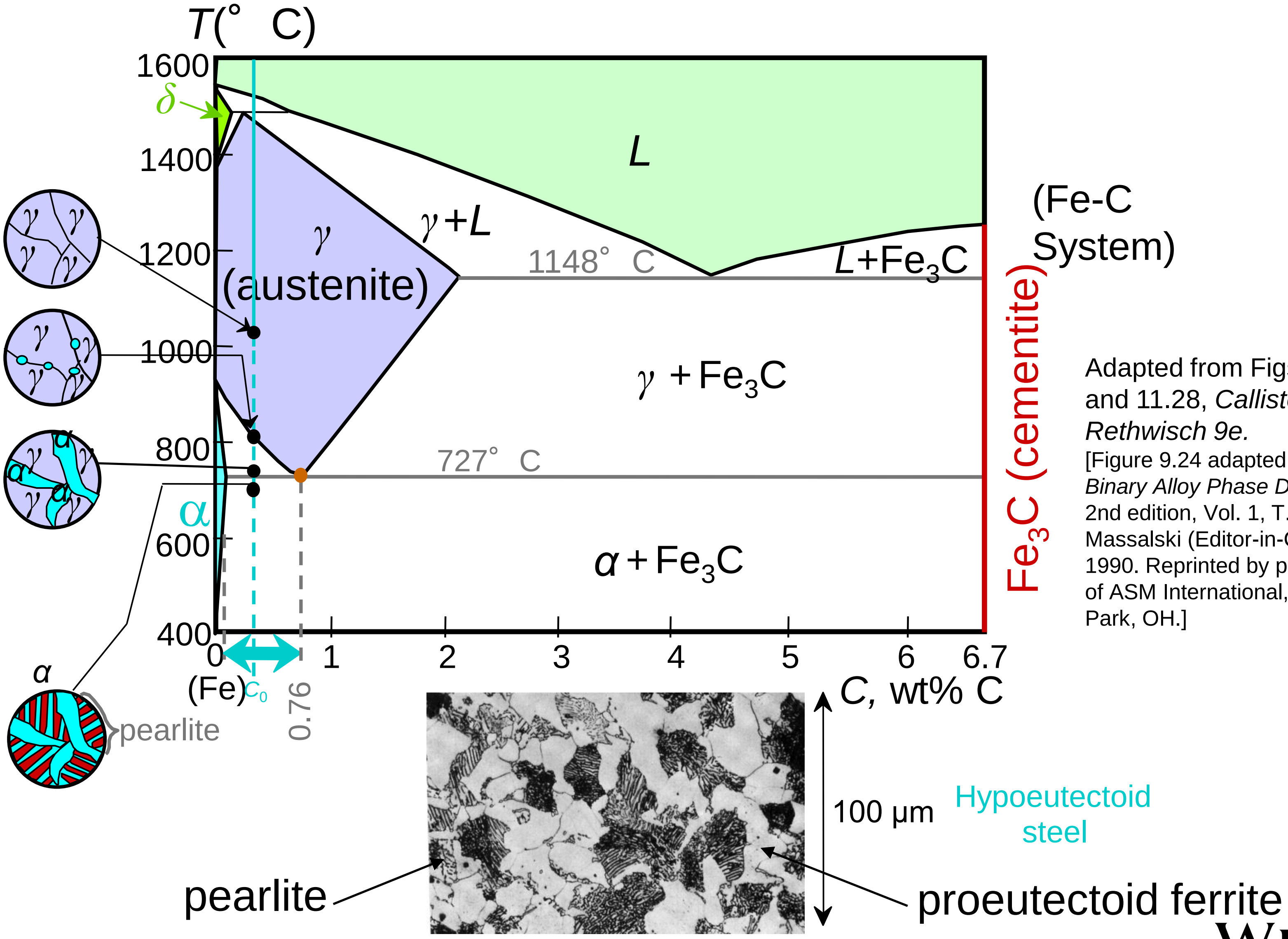


Fe_3C (cementite-hard)

α (ferrite-soft)

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.)

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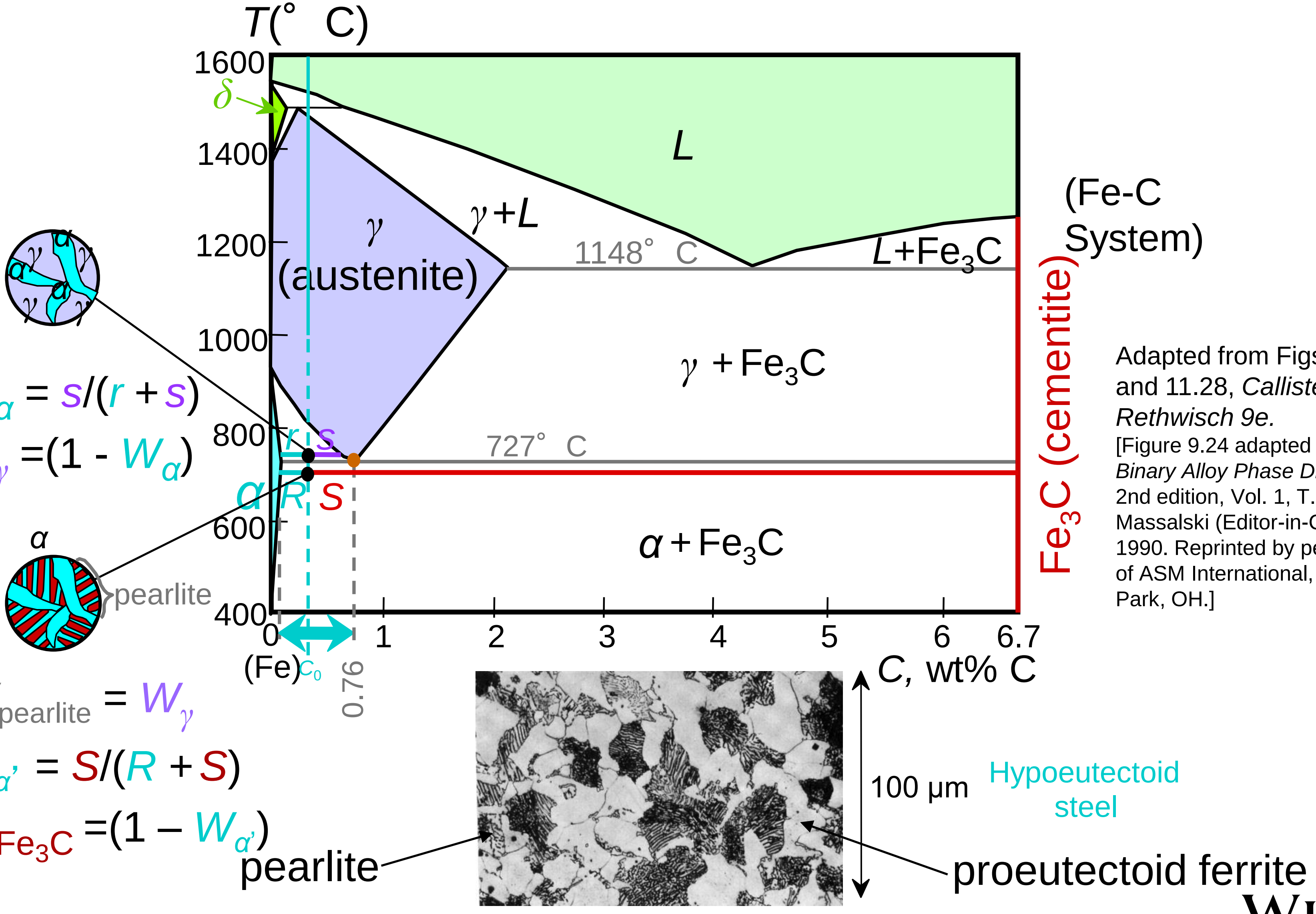
Hypoeutectoid Steel



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

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

$W_{pearlite} = W_\gamma$

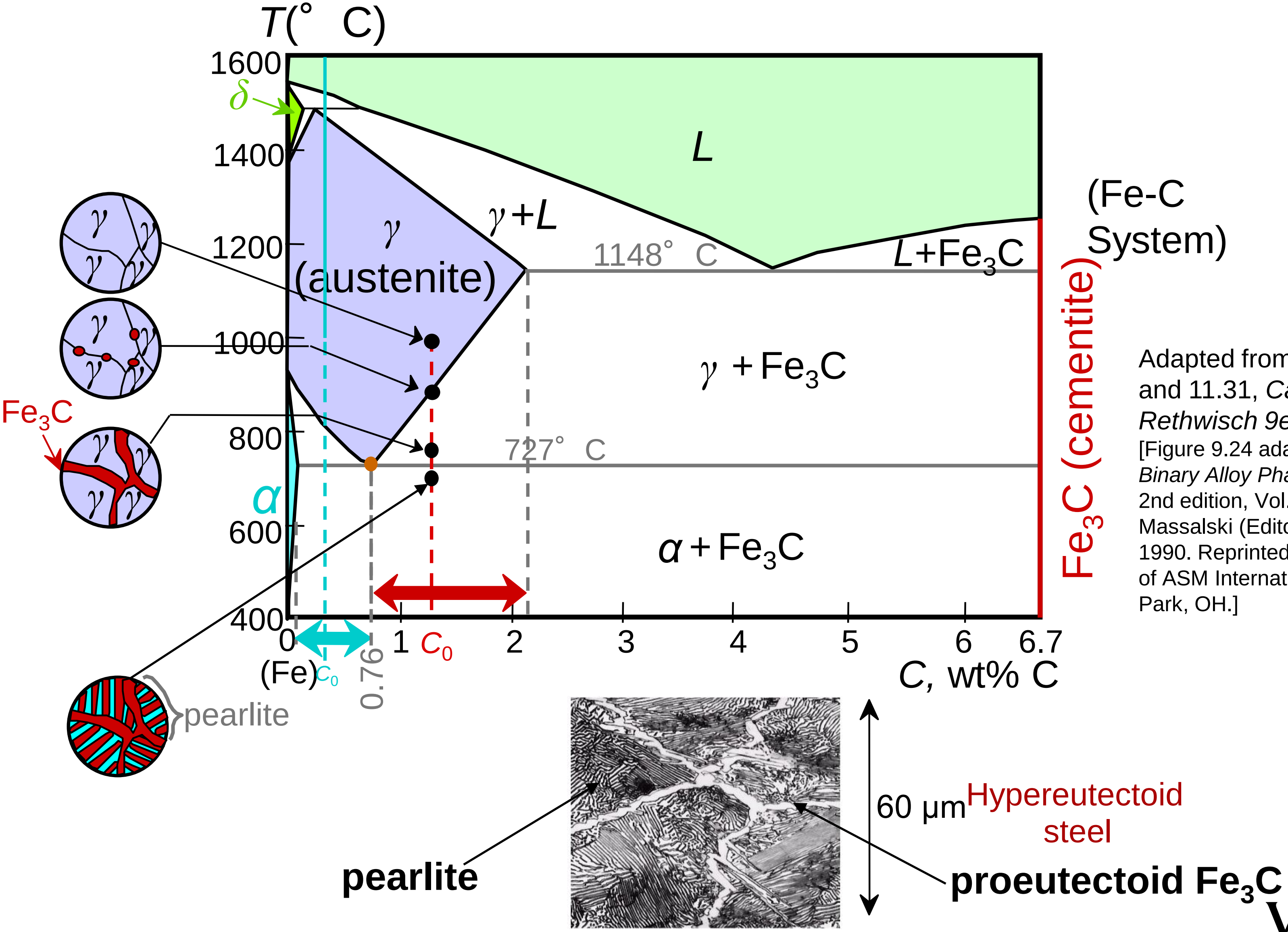
$W_{\alpha'} = S/(R+S)$

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

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.]

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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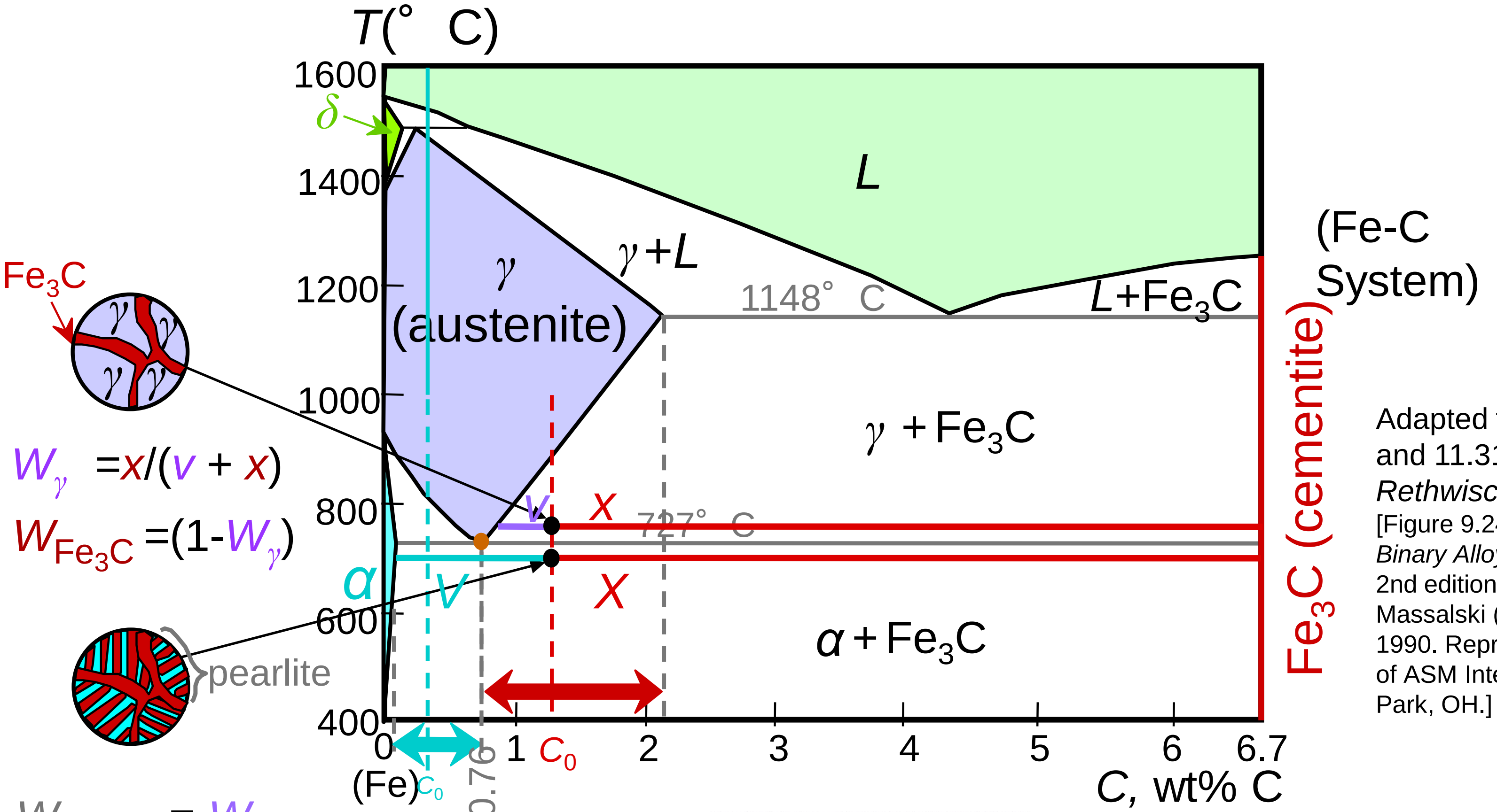
Hypereutectoid Steel



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

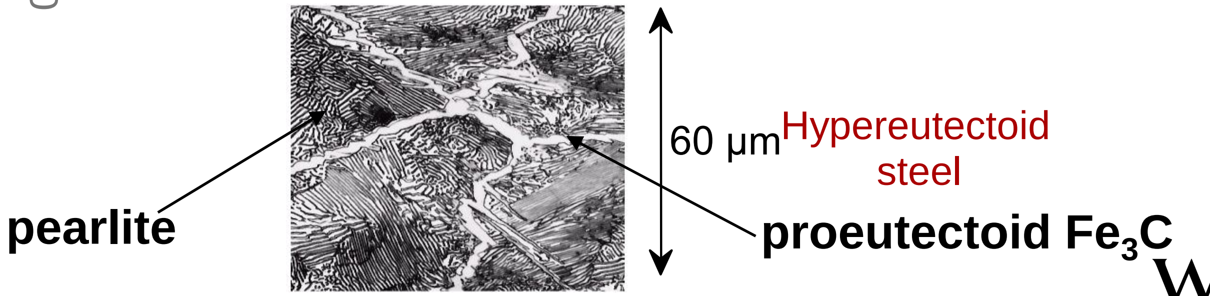
$W_{Fe_3C} = (1 - W_\gamma)$

$W_{pearlite} = W_\gamma$

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

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

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

$C_\alpha = 0.022$ wt% C

$C_{Fe_3C} = 6.70$ wt% C

b) Using the lever rule with the tie line shown

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

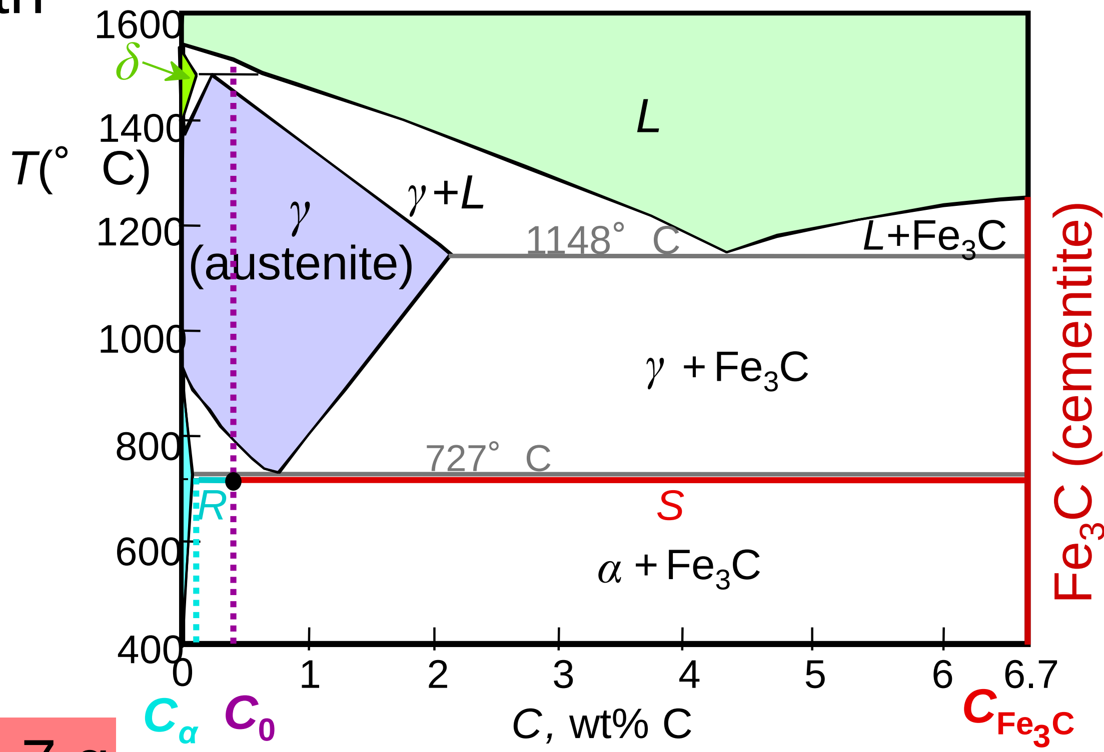
$$= \frac{0.40 - 0.022}{6.70 - 0.022} = 0.057$$

Amount of Fe_3C in 100 g

$= (100\text{ g})W_{Fe_3C}$

$= (100\text{ g})(0.057) = 5.7\text{ g}$

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.]



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

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

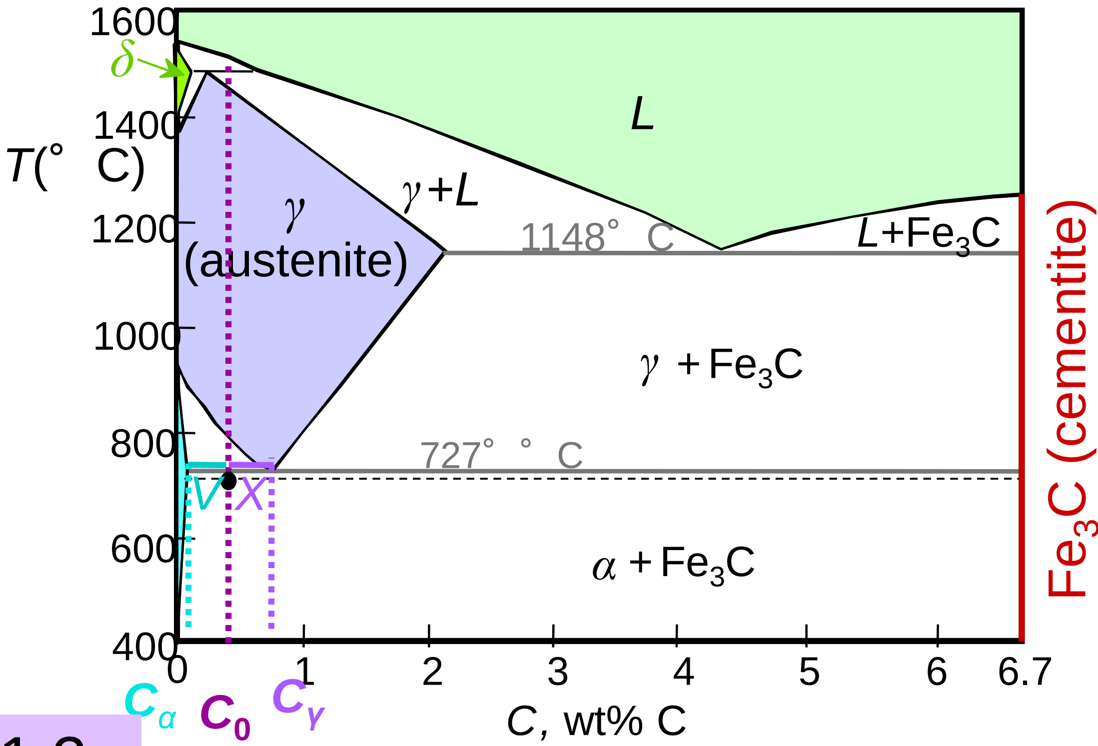
$$= \frac{0.40 - 0.022}{0.76 - 0.022} = 0.512$$

Amount of pearlite in 100 g

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

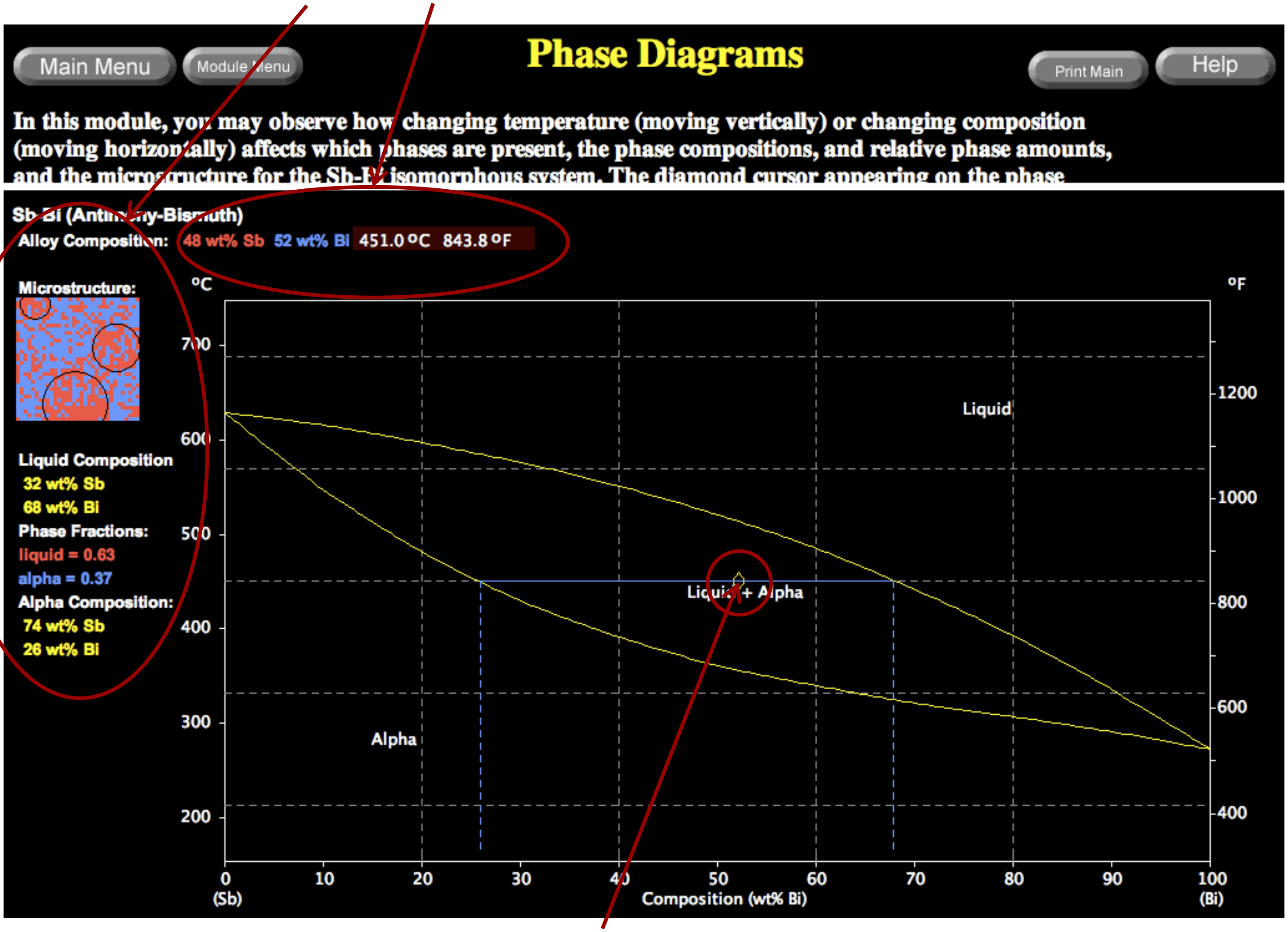
$= (100 \text{ g})(0.512) =$ **51.2 g**

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.]



VMSE: Interactive Phase Diagrams

Microstructure, phase compositions, and phase fractions respond interactively



Phase Diagrams

In this module, you may observe how changing temperature (moving vertically) or changing composition (moving horizontally) affects which phases are present, the phase compositions, and relative phase amounts, and the microstructure for the Sb-Bi isomorphous system. The diamond cursor appearing on the phase

Sb-Bi (Antimony-Bismuth)

Alloy Composition: 48 wt% Sb 52 wt% Bi 451.0 °C 843.8 °F

Microstructure:

Liquid Composition
32 wt% Sb
68 wt% Bi

Phase Fractions:
liquid = 0.63
alpha = 0.37

Alpha Composition:
74 wt% Sb
26 wt% Bi

Change alloy composition

Alloying with Other Elements

- $T_{\text{eutectoid}}$ changes:

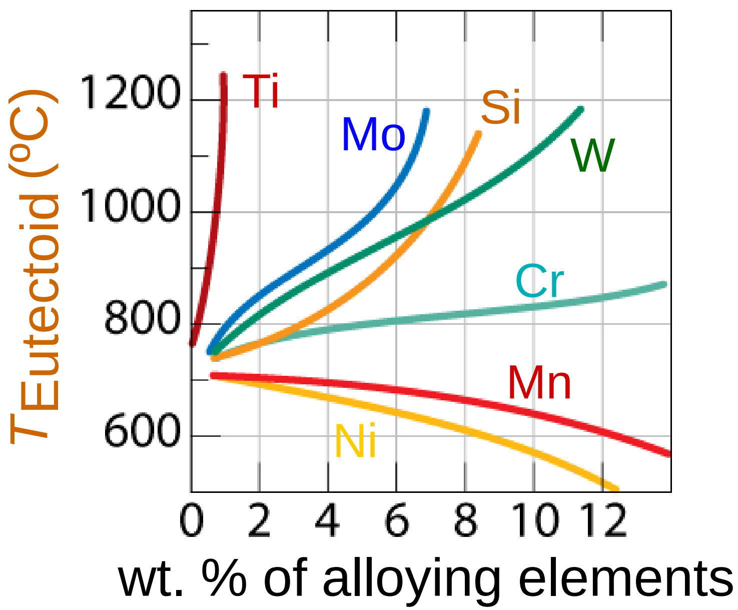


Fig. 11.33, *Callister & Rethwisch 9e*.

(From Edgar C. Bain, *Functions of the Alloying Elements in Steel,* 1939. Reproduced by permission of ASM International, Materials Park, OH.)

- $C_{\text{eutectoid}}$ changes:

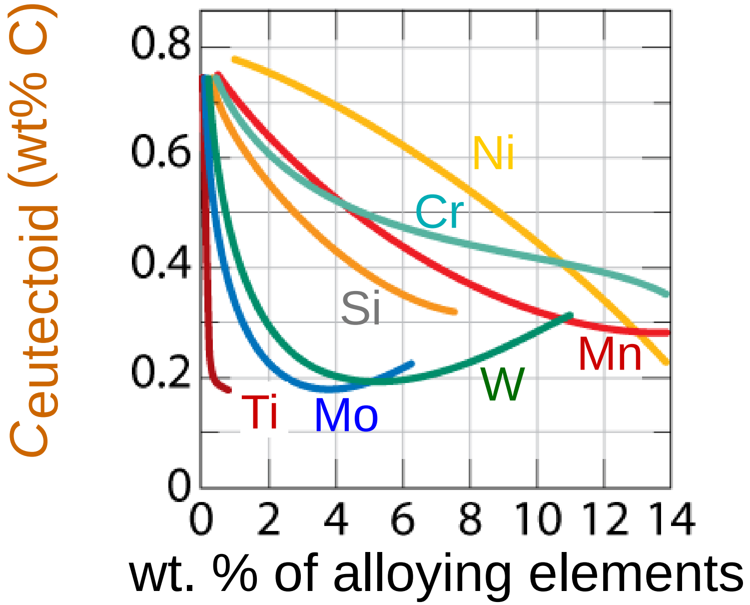


Fig. 11.34,*Callister & Rethwisch 9e*.

(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.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: