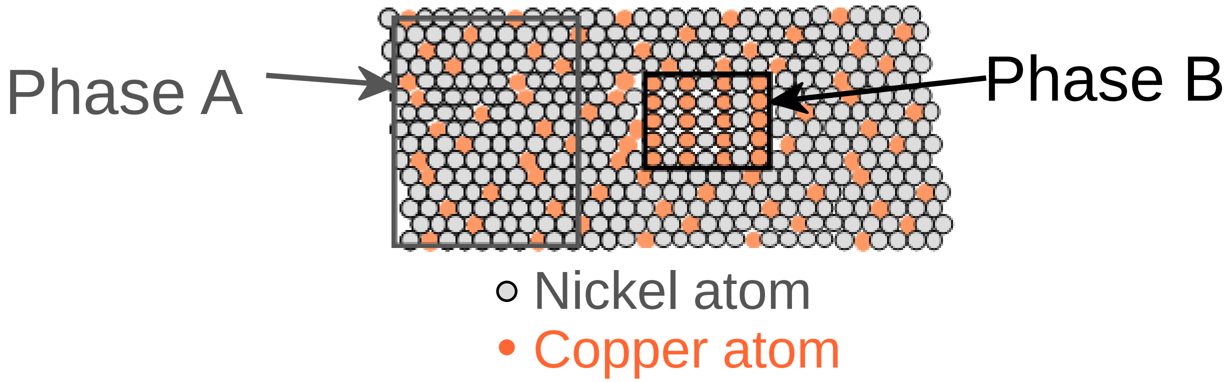
Chapter 9: Phase Diagrams

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. 9.1,
Callister & Rethwisch 8e.

- Solubility Limit:

  Maximum concentration for which only a single phase solution exists.

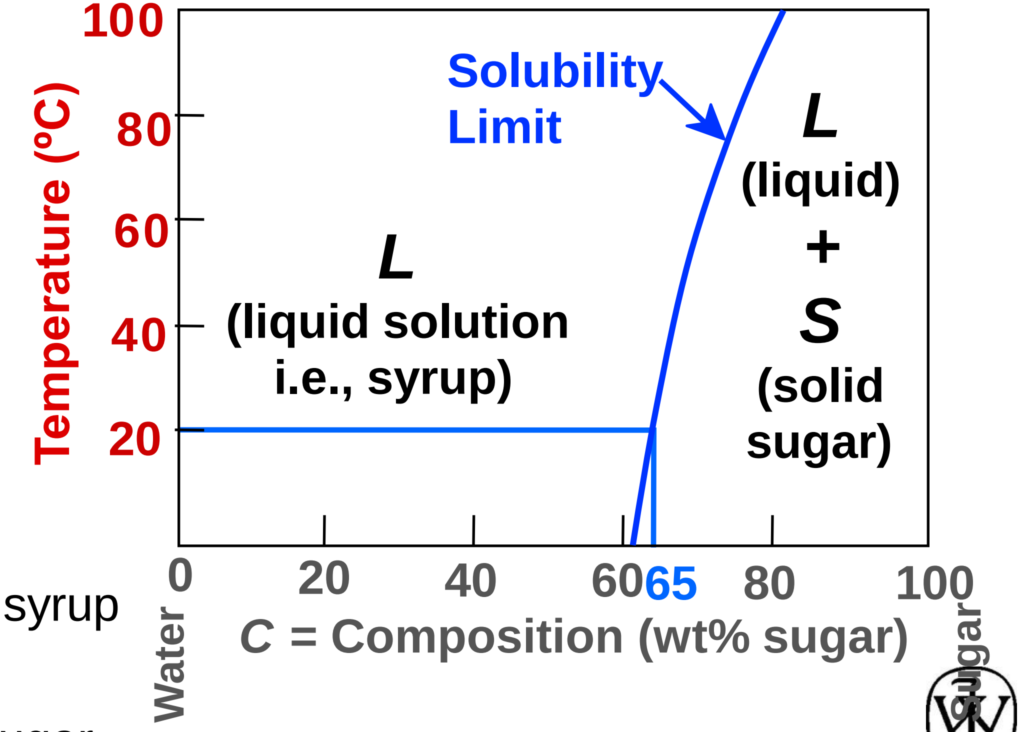
Question: What is the solubility limit for sugar in water at 20ºC?

Answer: 65 wt% sugar.

At 20ºC, if *C* < 65 wt% sugar: syrup

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

Sugar/Water Phase Diagram



Components and Phases

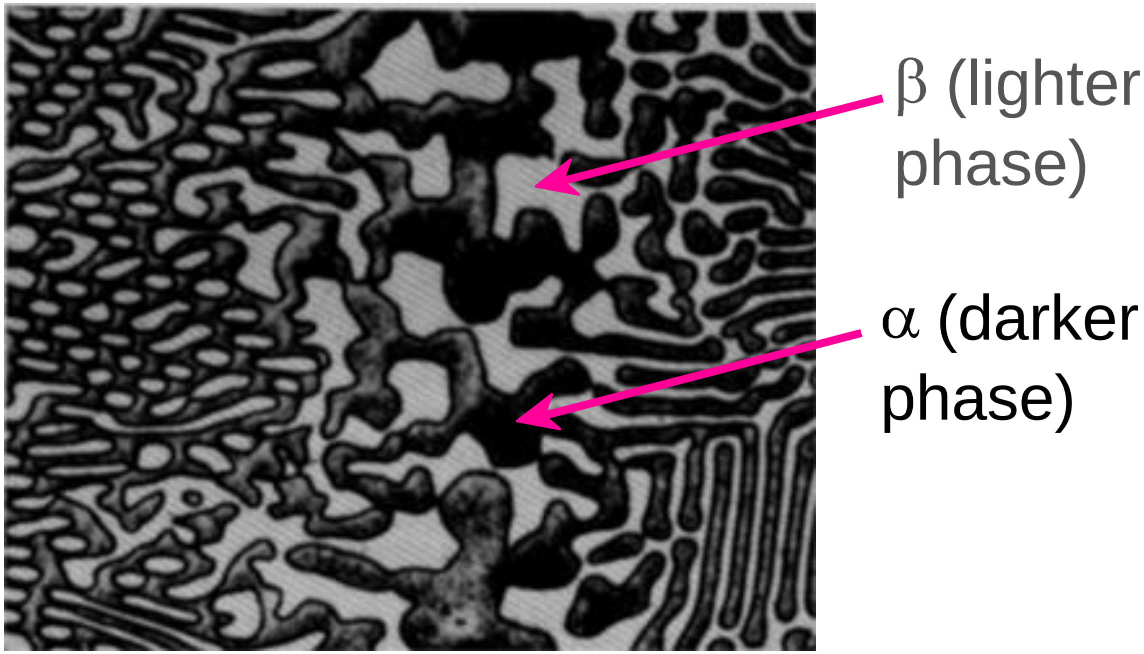
- **Components**:

  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)

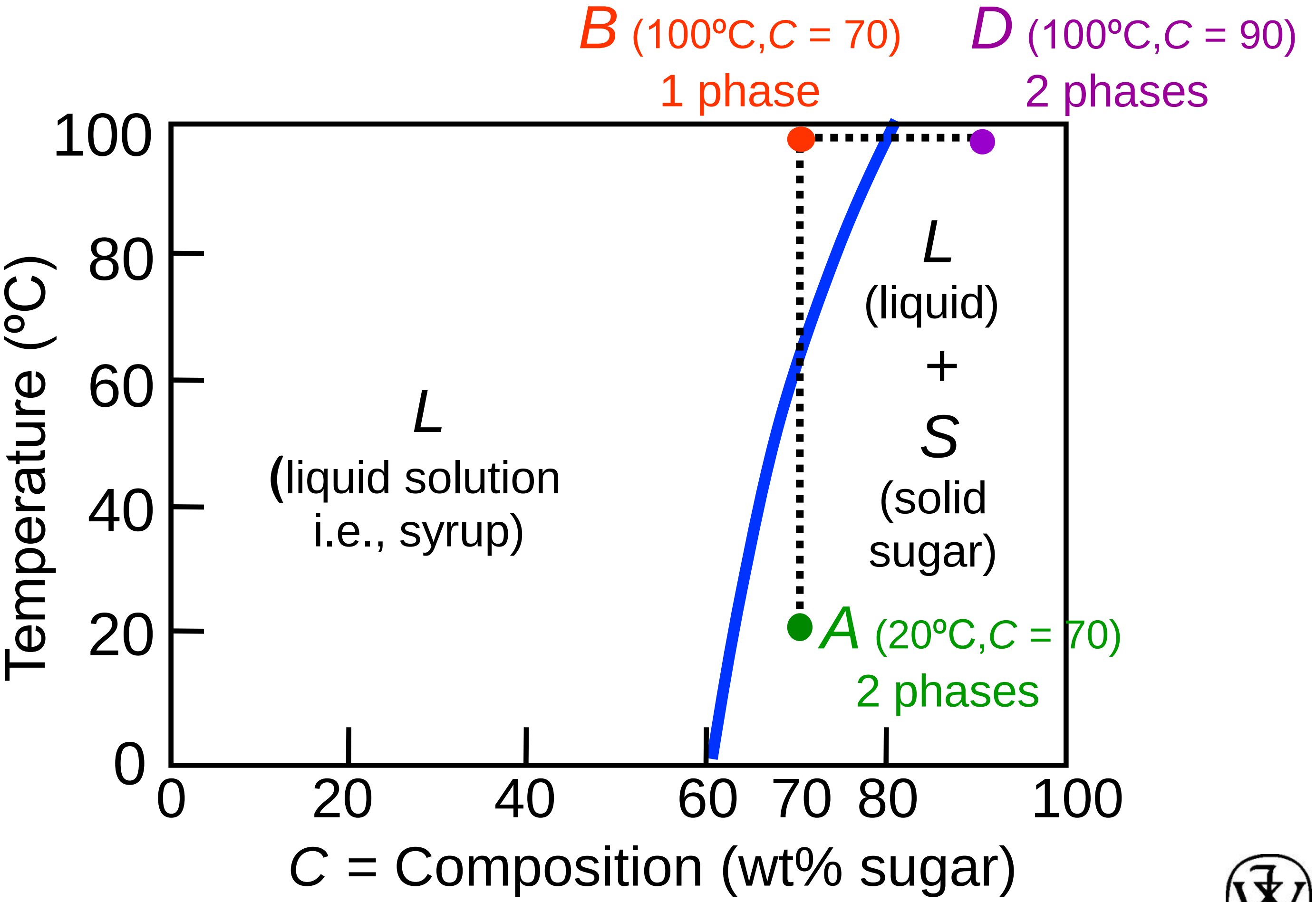
α (darker phase)

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



Adapted from Fig. 9.1,
Callister & Rethwisch 8e.

Criteria for Solid Solubility

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

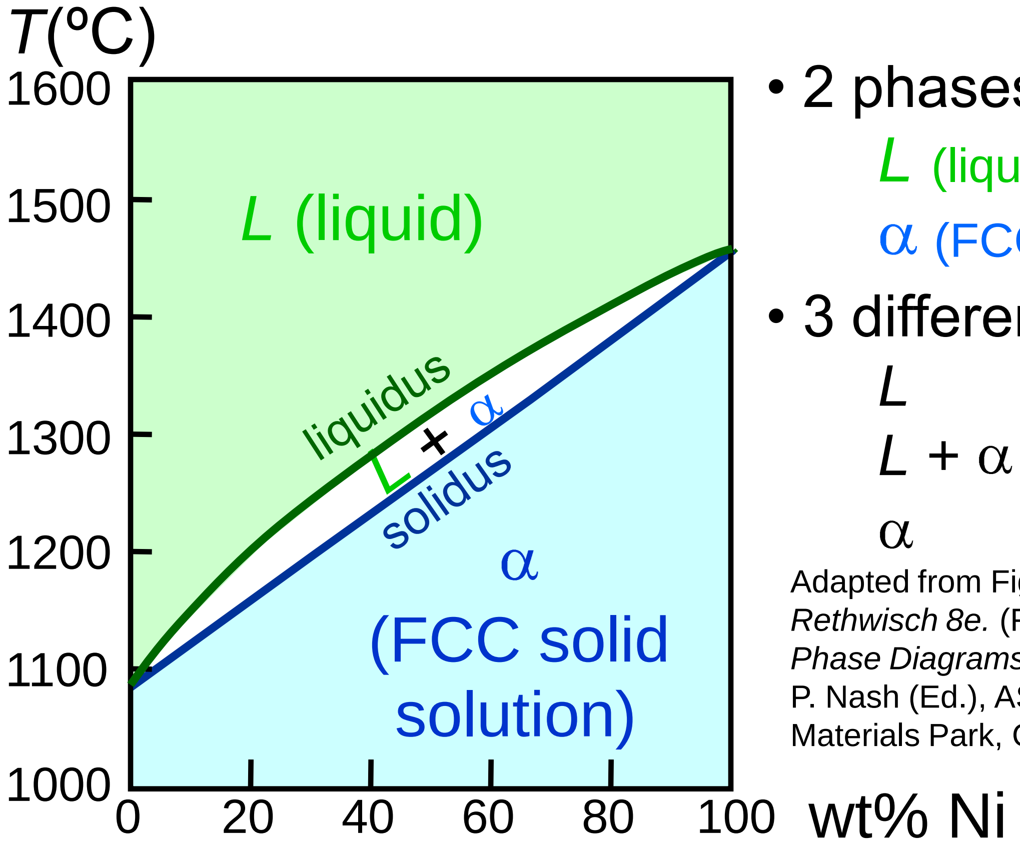
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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

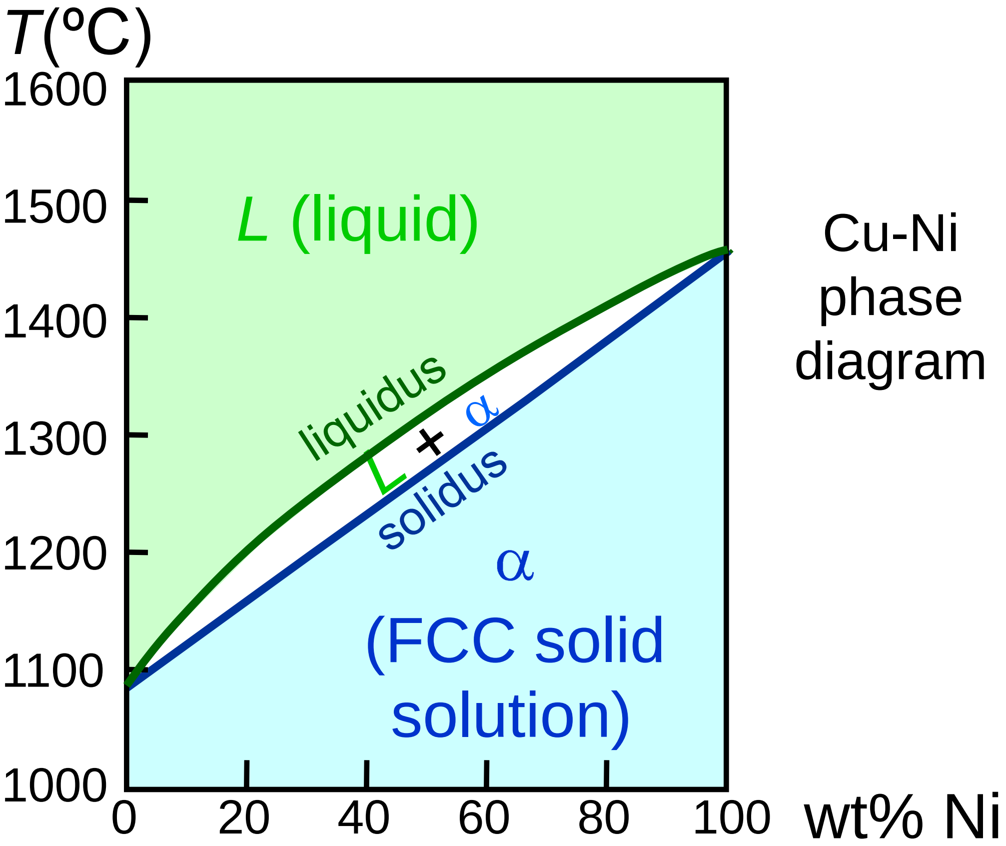


- 2 phases:
  - *L* (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + α
  - α

Adapted from Fig. 9.3(a), *Callister & Rethwisch 8e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

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

Adapted from Fig. 9.3(a), *Callister & Rethwisch 8e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

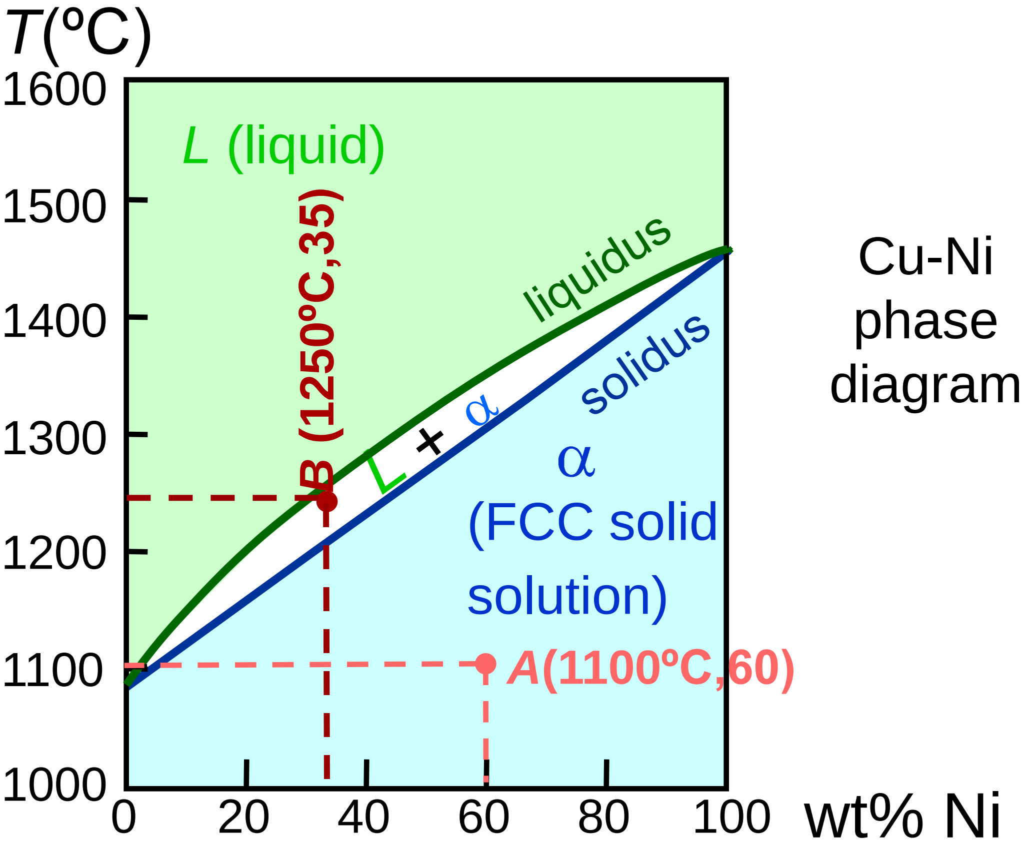
Phase Diagrams:
Determination of phase(s) present

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

- Examples:

  A(1100ºC, 60 wt% Ni):
  1 phase: α

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



Cu-Ni phase diagram

Adapted from Fig. 9.3(a), *Callister & Rethwisch 8e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

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 = 1320ºC:

  Only Liquid (L) present

  $C_L = C_0$ (= 35 wt% Ni)

  At T_D = 1190ºC:

  Only Solid (α) present

  $C_\alpha = C_0$ (= 35 wt% Ni)

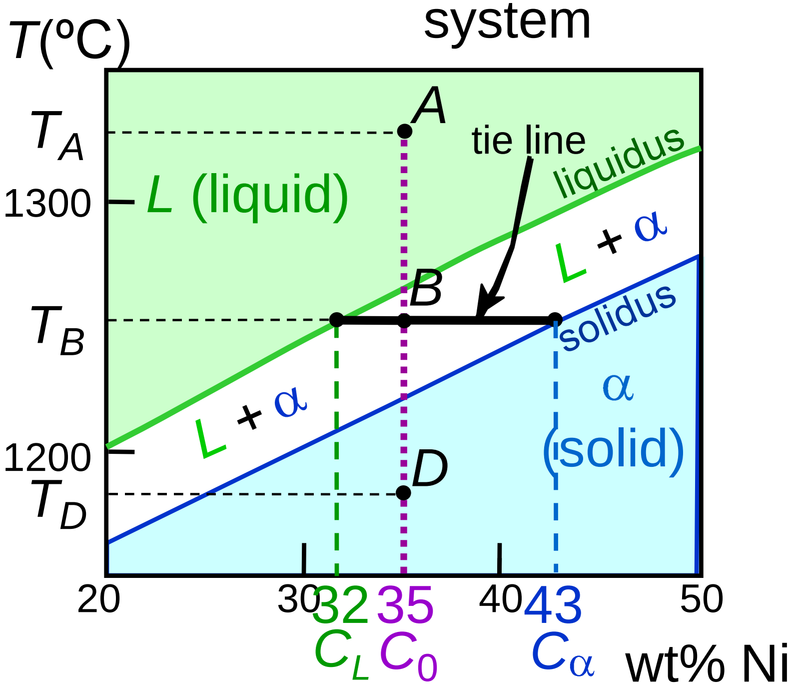
  At T_B = 1250ºC:

  Both α and L present

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

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

Cu-Ni system



Adapted from Fig. 9.3(a), *Callister & Rethwisch 8e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

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

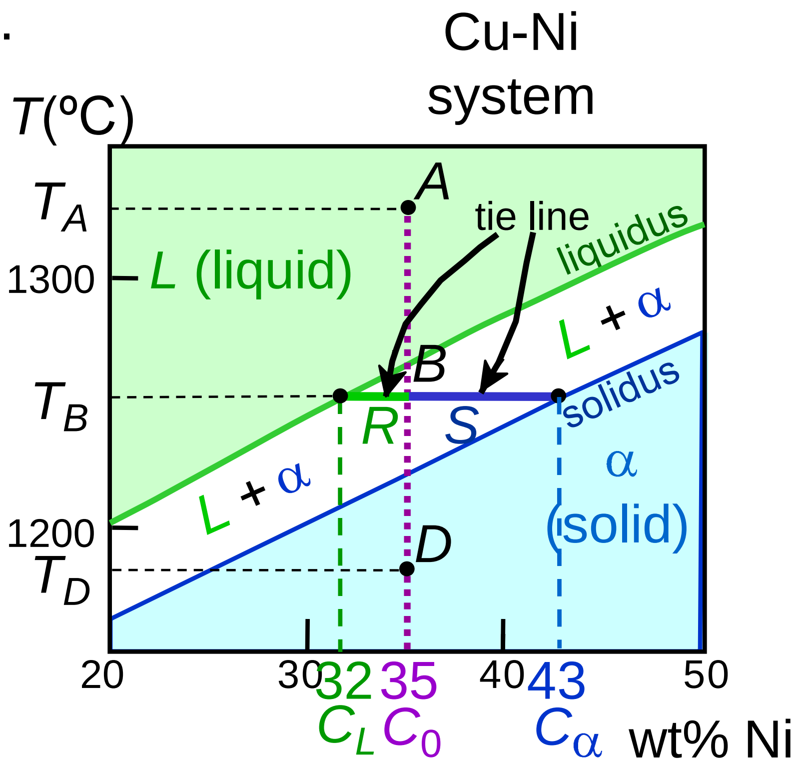
At T_A : Only Liquid (L) present

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

At T_D : Only Solid (α) present

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

At T_B : Both α and L present



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

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

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

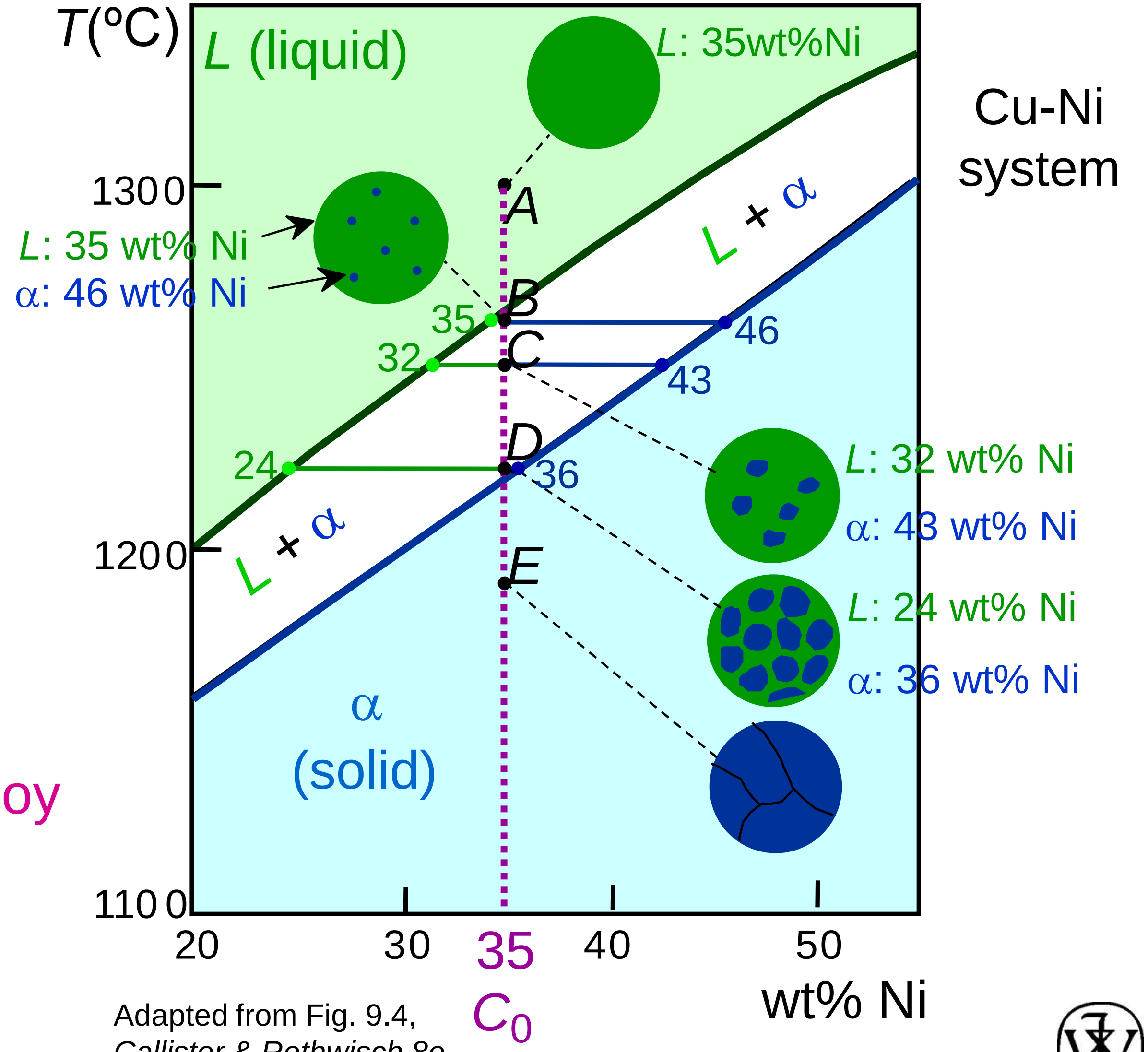
Lever Rule

Development of Microstructure

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

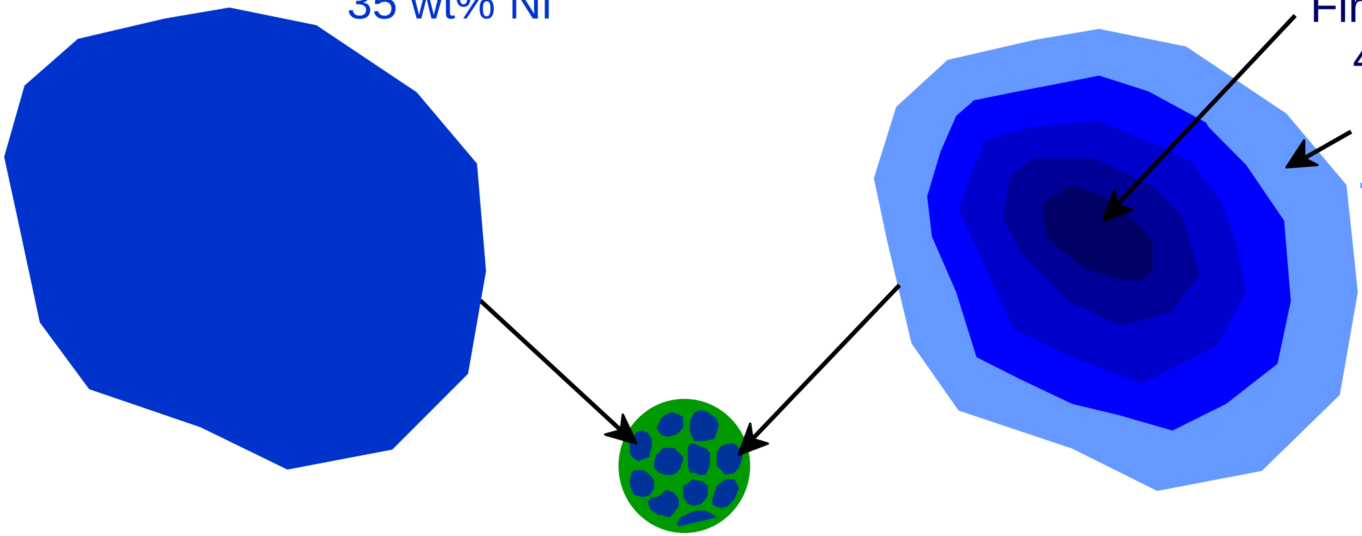


Adapted from Fig. 9.4, *Callister & Rethwisch 8e.*

Cored vs Equilibrium Structures

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

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



Uniform C_α:
35 wt% Ni

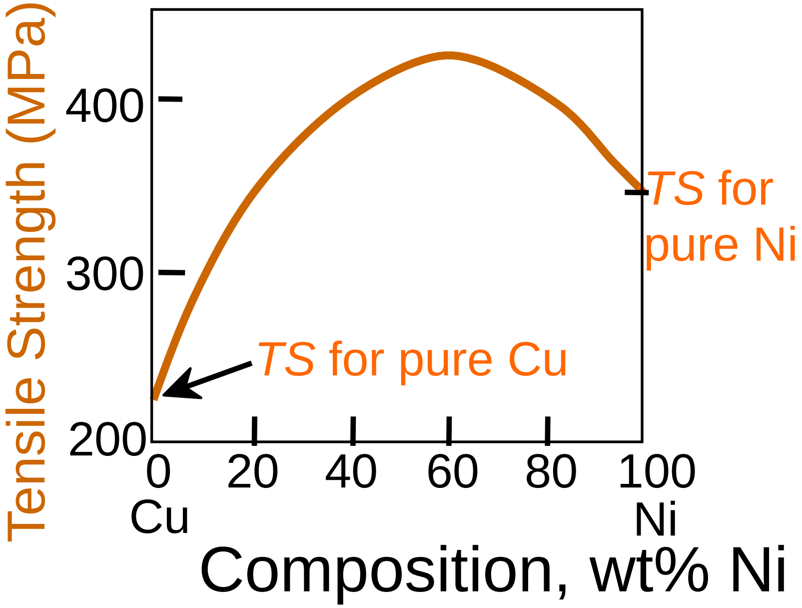
First α to solidify:
46 wt% Ni

Last α to solidify:
< 35 wt% Ni

Mechanical Properties: Cu-Ni System

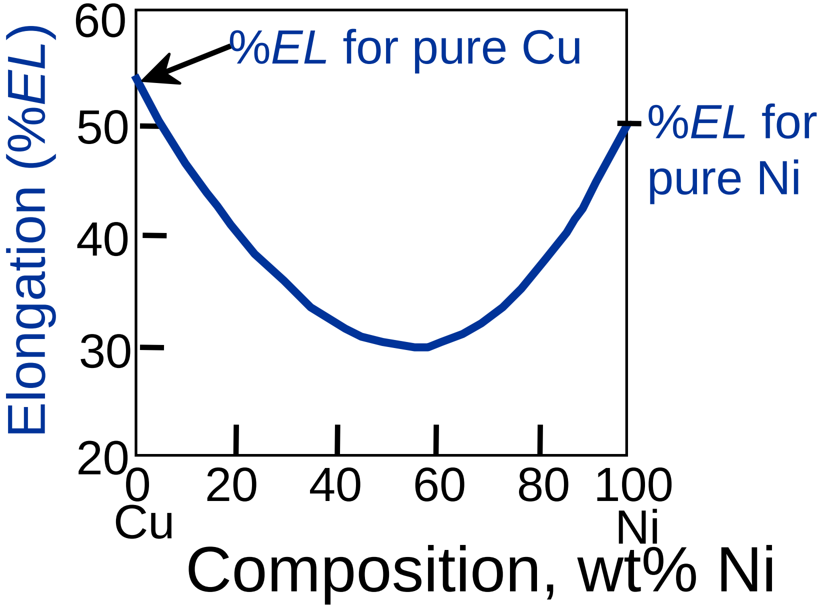
- Effect of solid solution strengthening on:

-- Tensile strength (*TS*)



Adapted from Fig. 9.6(a),
Callister & Rethwisch 8e.

-- Ductility (%*EL*)



Adapted from Fig. 9.6(b),
Callister & Rethwisch 8e.

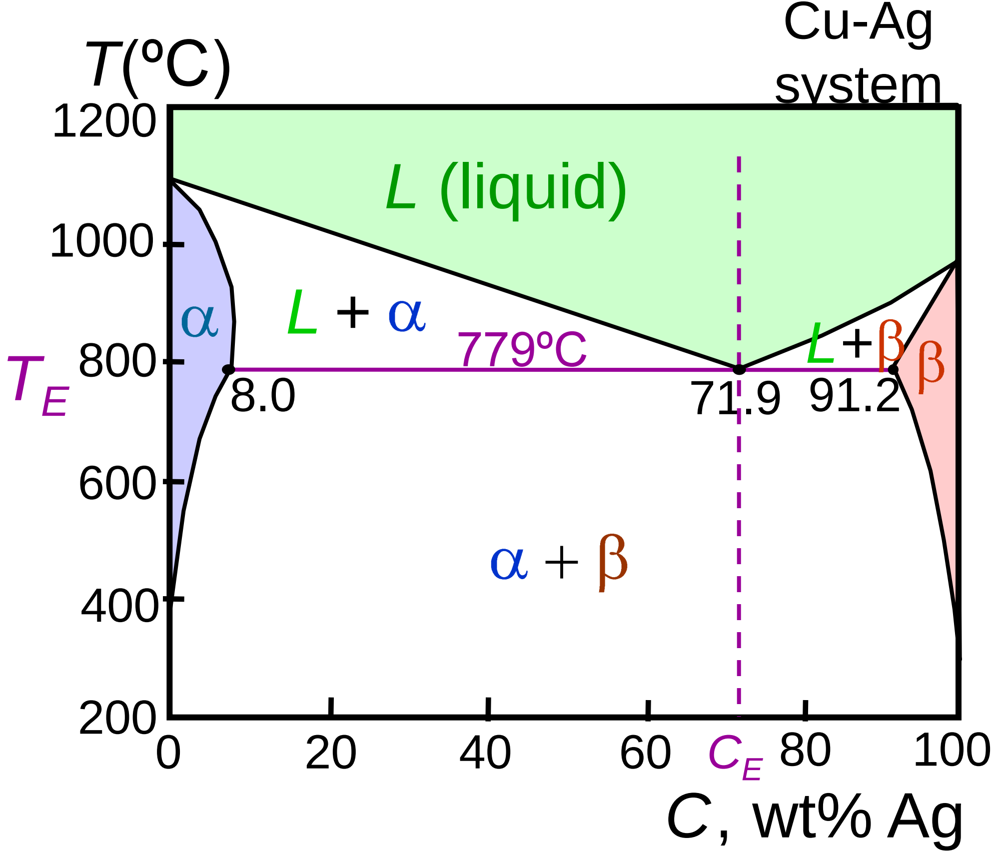
Binary-Eutectic Systems

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



Adapted from Fig. 9.7, *Callister & Rethwisch 8e.*

- **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 150ºC, determine:

  -- the phases present

  Answer: α + β

  -- the phase compositions

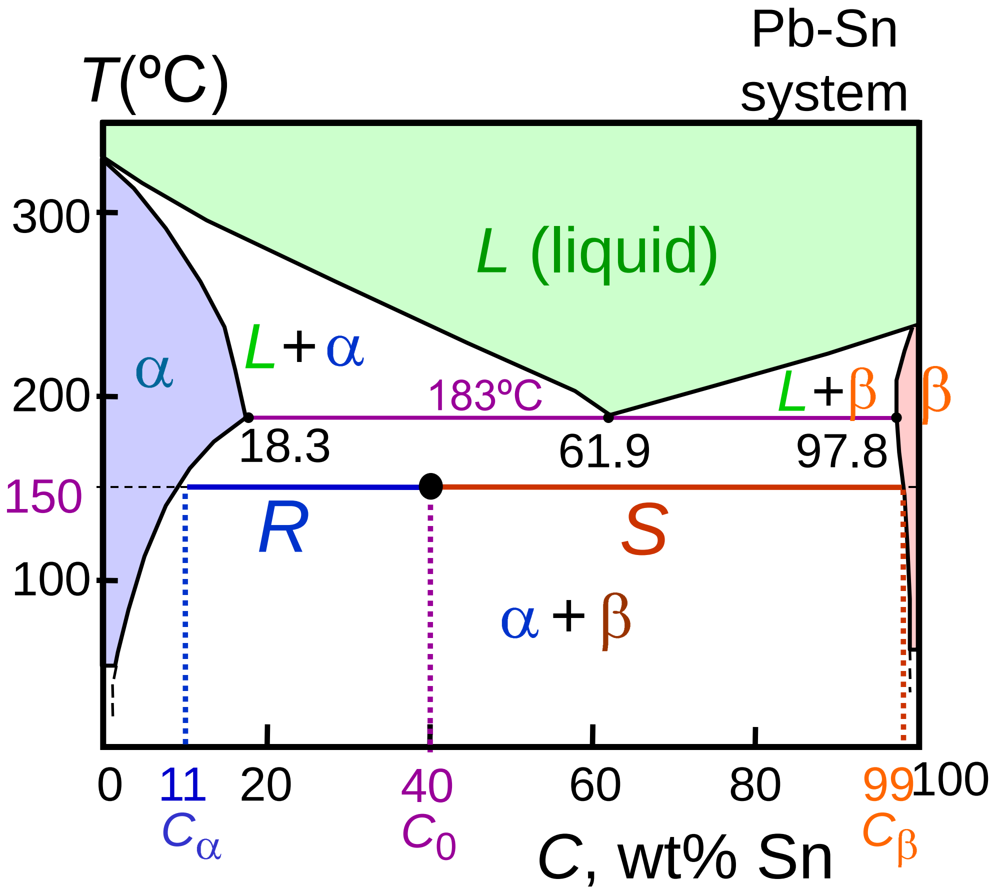
  Answer: C_α = 11 wt% Sn
  C_β = 99 wt% Sn

  -- the relative amount of each phase

  Answer:

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

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



Adapted from Fig. 9.8, *Callister & Rethwisch 8e.*

EX 2: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220ºC, determine:

  -- the phases present:

  Answer: $\alpha + L$

  -- the phase compositions

  Answer: $C_\alpha = 17$ wt% Sn

  $C_L = 46$ wt% Sn

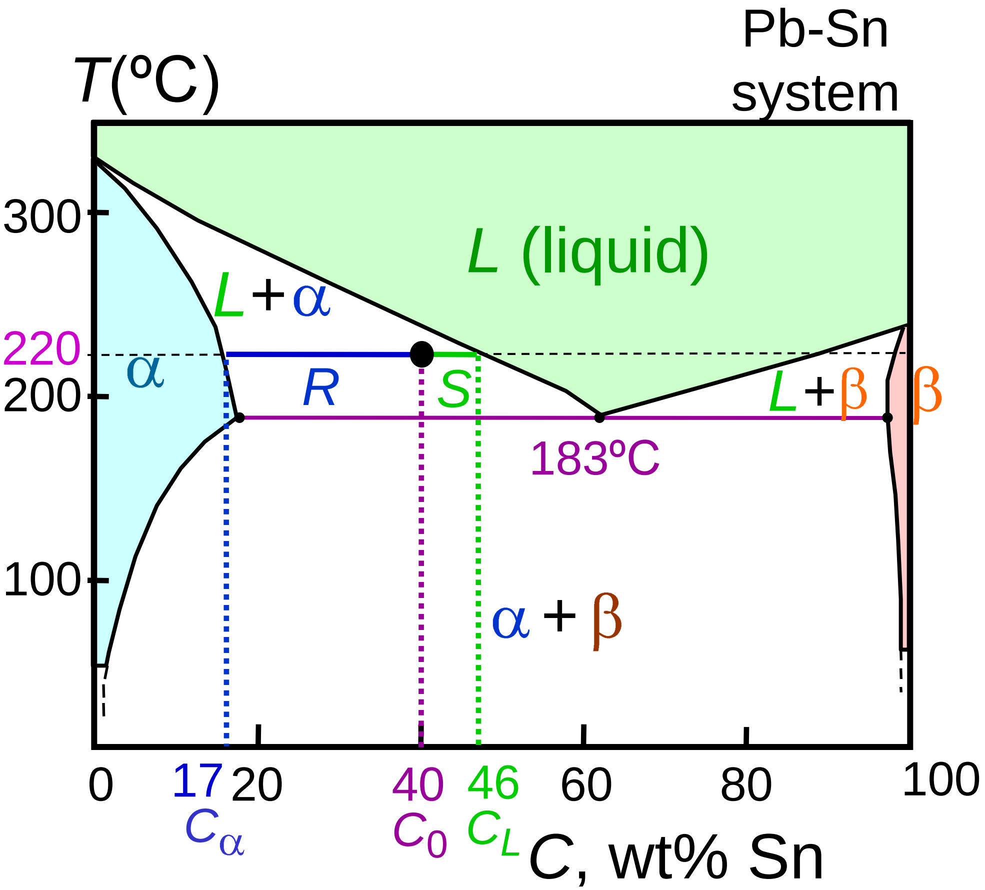
  -- the relative amount of each phase

  Answer:

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

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

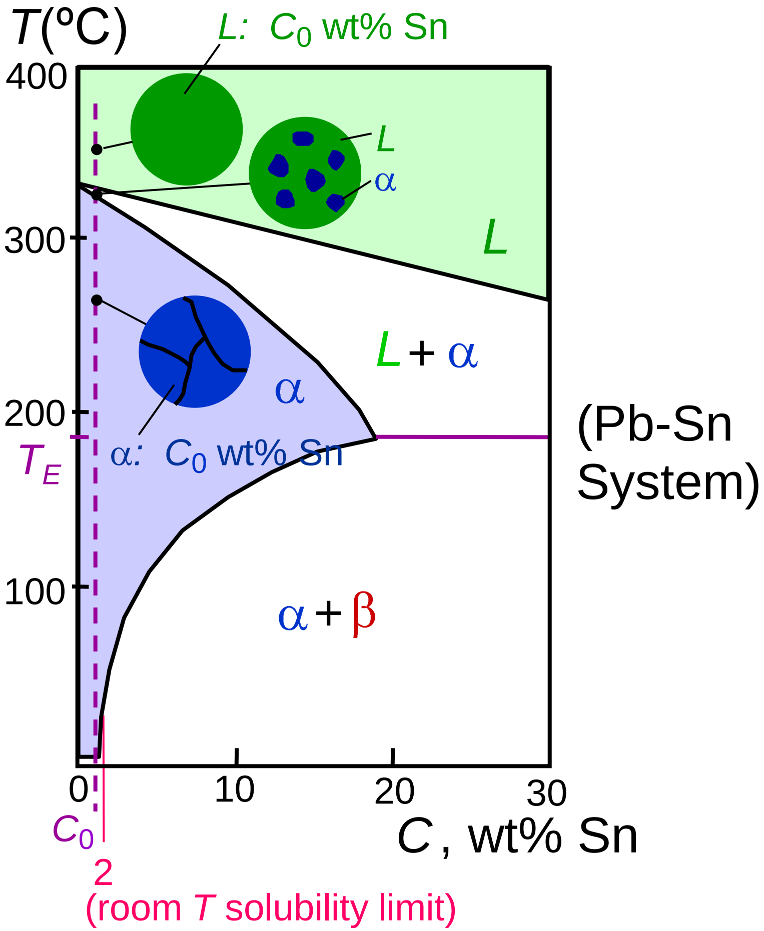
$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$



Adapted from Fig. 9.8, *Callister & Rethwisch 8e.*

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

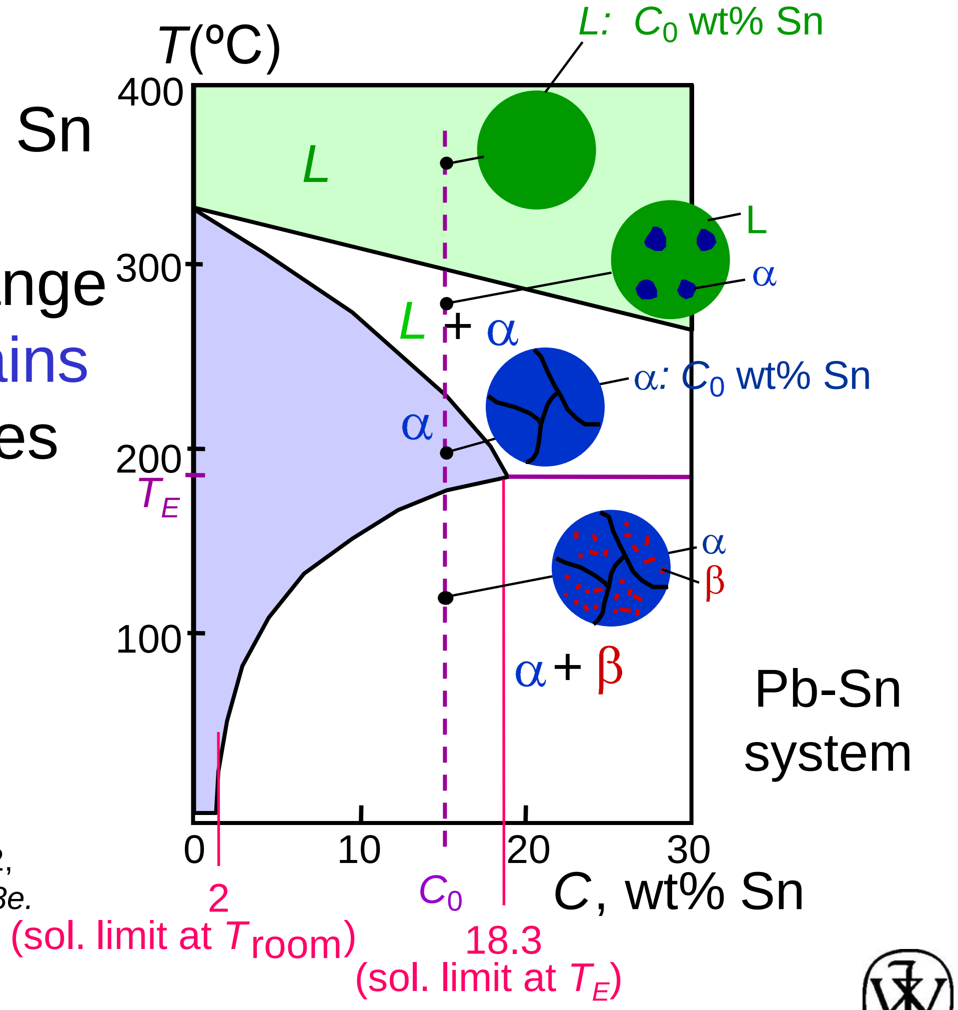


(Pb-Sn System)

Adapted from Fig. 9.11, *Callister & Rethwisch 8e.*

Microstructural Developments in Eutectic Systems II

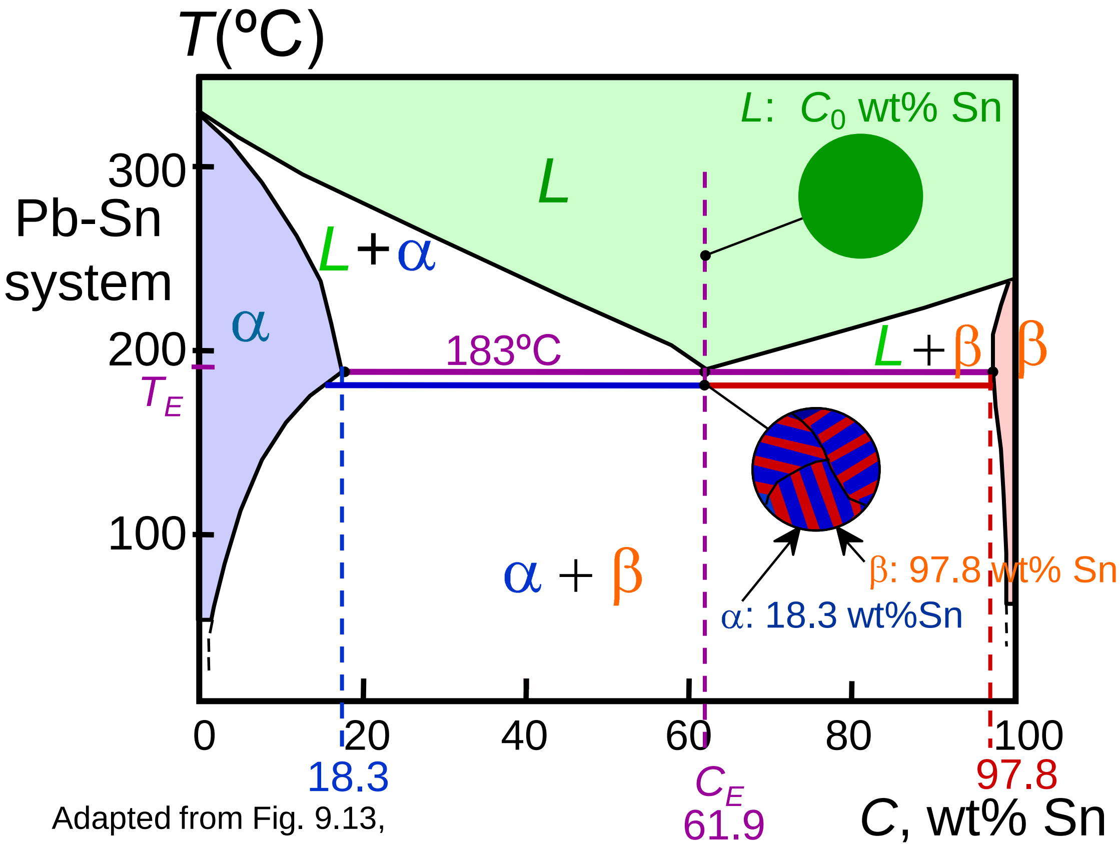
- For alloys for which
  2 wt% Sn < C_0 < 18.3 wt% Sn
- Result:
  at temperatures in α + β range
  -- polycrystalline with α grains
  and small β-phase particles



Adapted from Fig. 9.12, *Callister & Rethwisch 8e.*

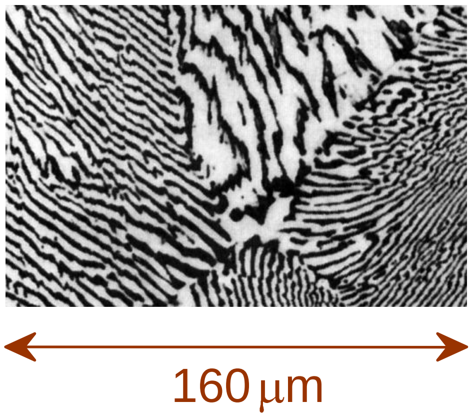
Microstructural Developments in Eutectic Systems III

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



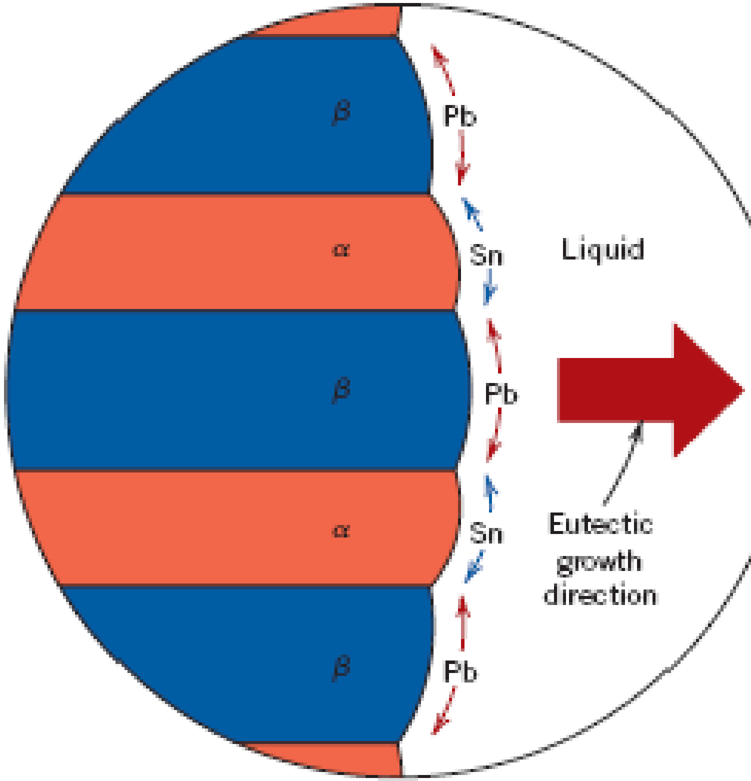
Adapted from Fig. 9.13, *Callister & Rethwisch 8e.*

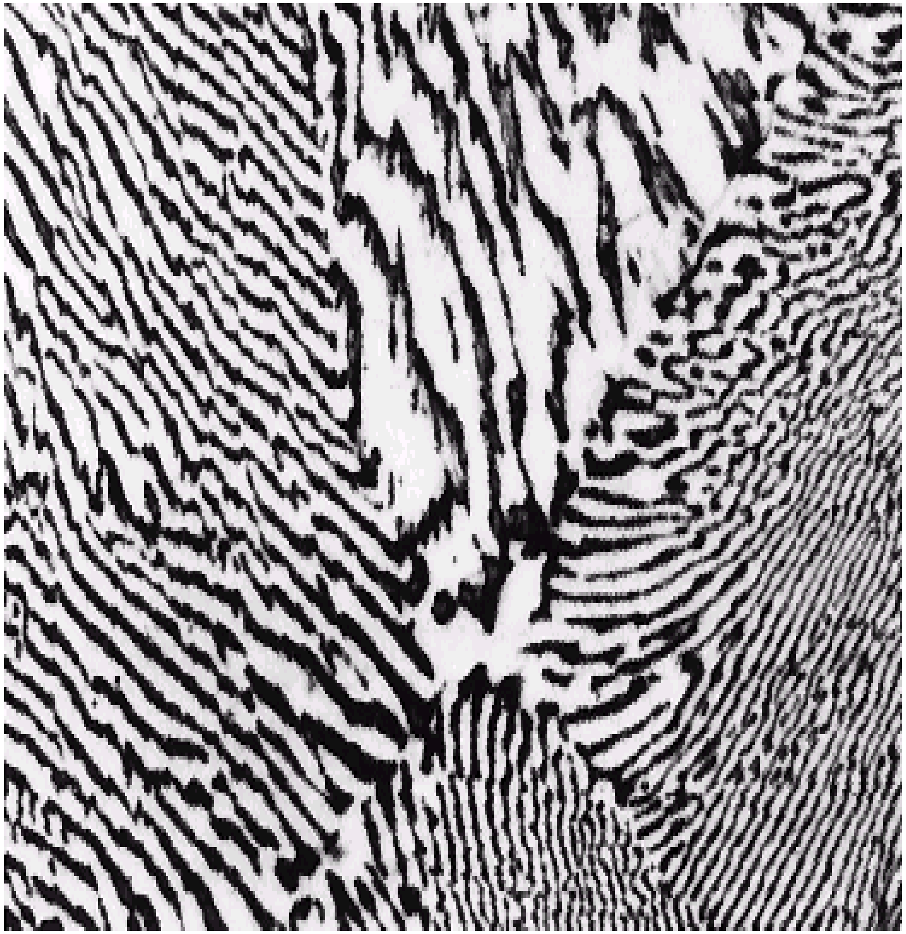
Micrograph of Pb-Sn eutectic microstructure



Adapted from Fig. 9.14, *Callister & Rethwisch 8e.*

Lamellar Eutectic Structure

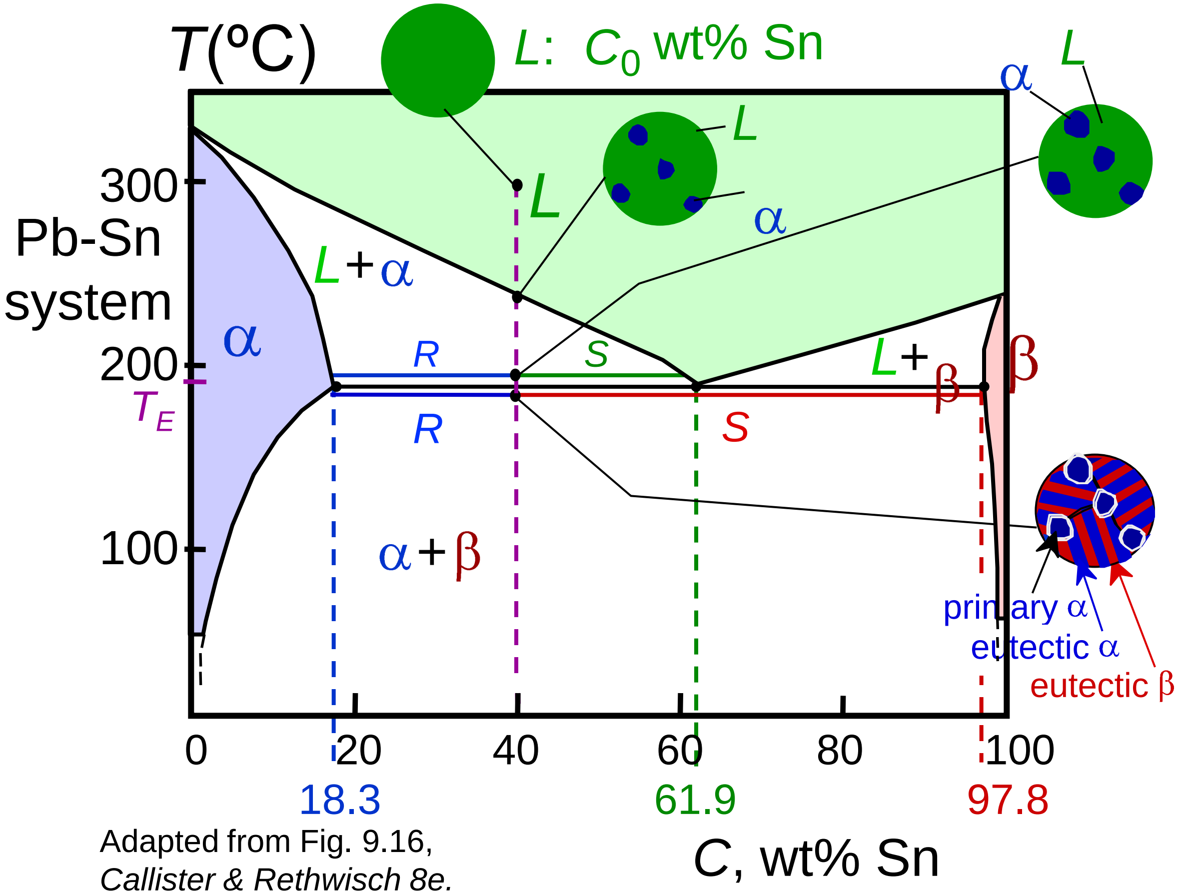




Adapted from Figs. 9.14 & 9.15, *Callister & Rethwisch 8e.*

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



Adapted from Fig. 9.16, *Callister & Rethwisch 8e.*

- 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

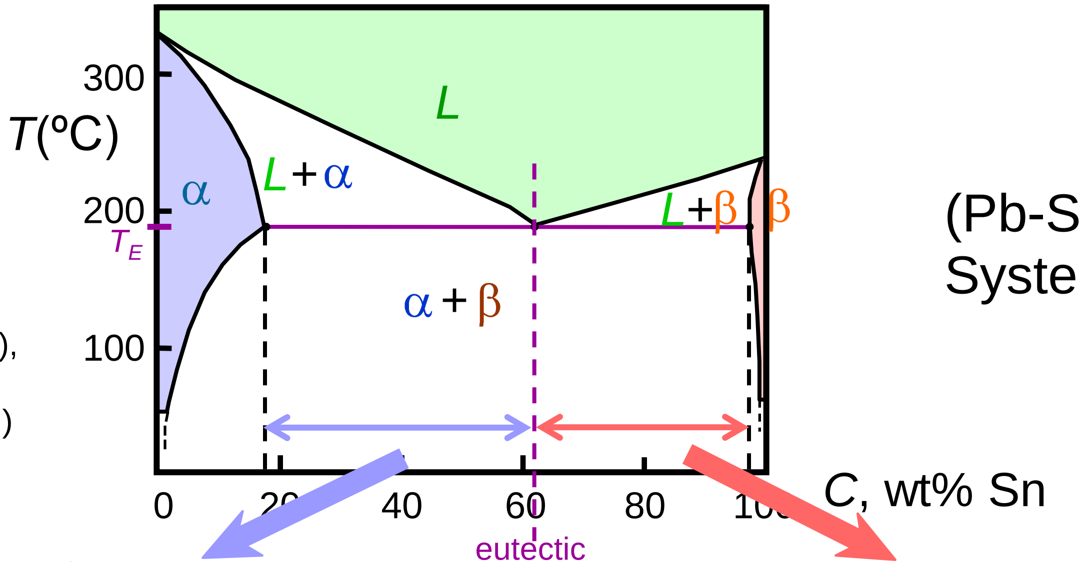
C_β = 97.8 wt% Sn

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

$$W_\beta = 0.27$$

Hypoeutectic & Hypereutectic

Adapted from Fig. 9.8, *Callister & Rethwisch 8e.* (Fig. 10.8 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)



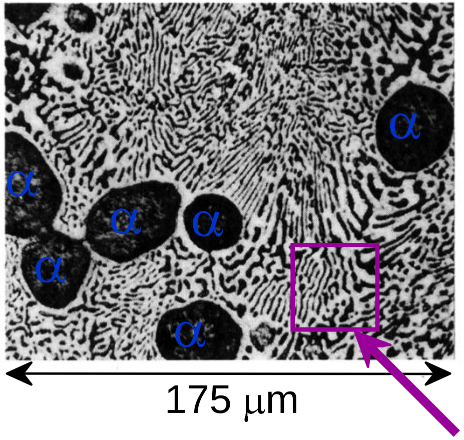
(Pb-Sn System)

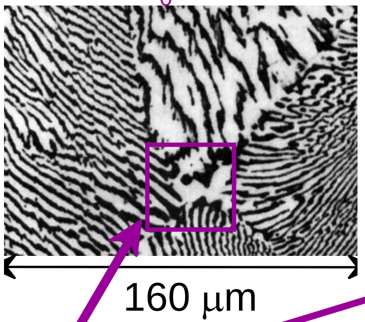
hypoeutectic: C_0 = 50 wt% Sn

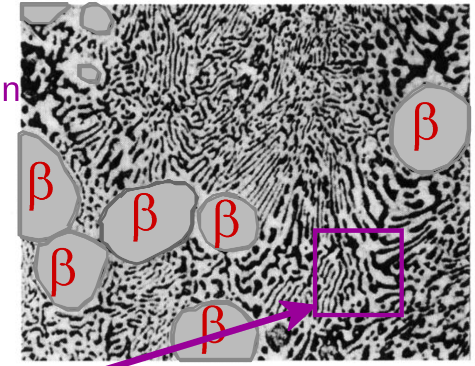
eutectic: C_0 = 61.9 wt% Sn

hypereutectic: (illustration only)

(Figs. 9.14 and 9.17 from *Metals Handbook*, 9th ed., Vol. 9, *Metallography and Microstructures*, American Society for Metals, Materials Park, OH, 1985.)







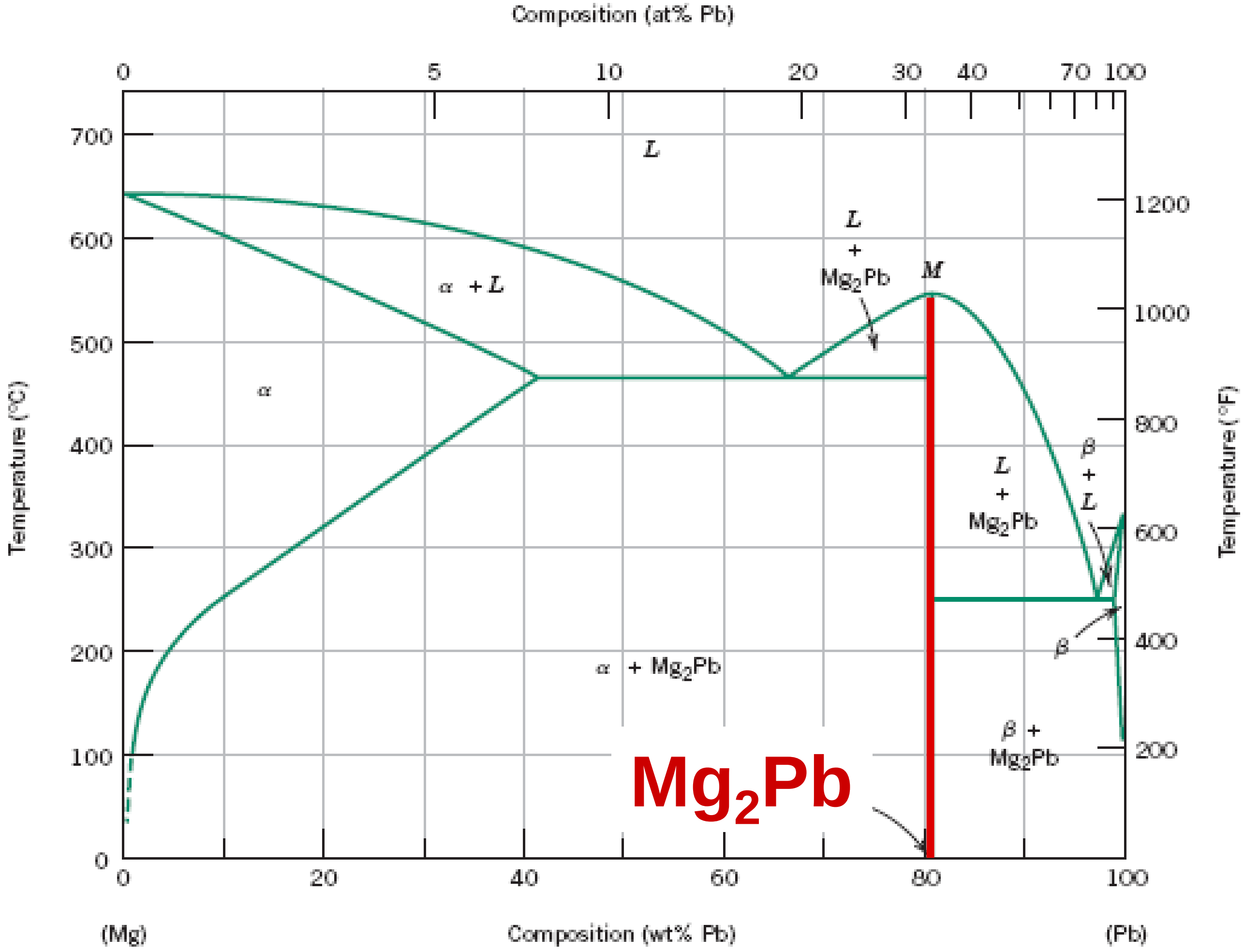
eutectic micro-constituent

Adapted from Fig. 9.17, *Callister & Rethwisch 8e.*

Adapted from Fig. 9.14, *Callister & Rethwisch 8e.*

Adapted from Fig. 9.17, *Callister & Rethwisch 8e.* (Illustration only)

Intermetallic Compounds



Adapted from Fig. 9.20, *Callister & Rethwisch 8e.*

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, 183ºC, 61.9 wt% Sn)

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

$$S_2 \rightleftharpoons S_1 + S_3$$

intermetallic compound - cementite

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

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

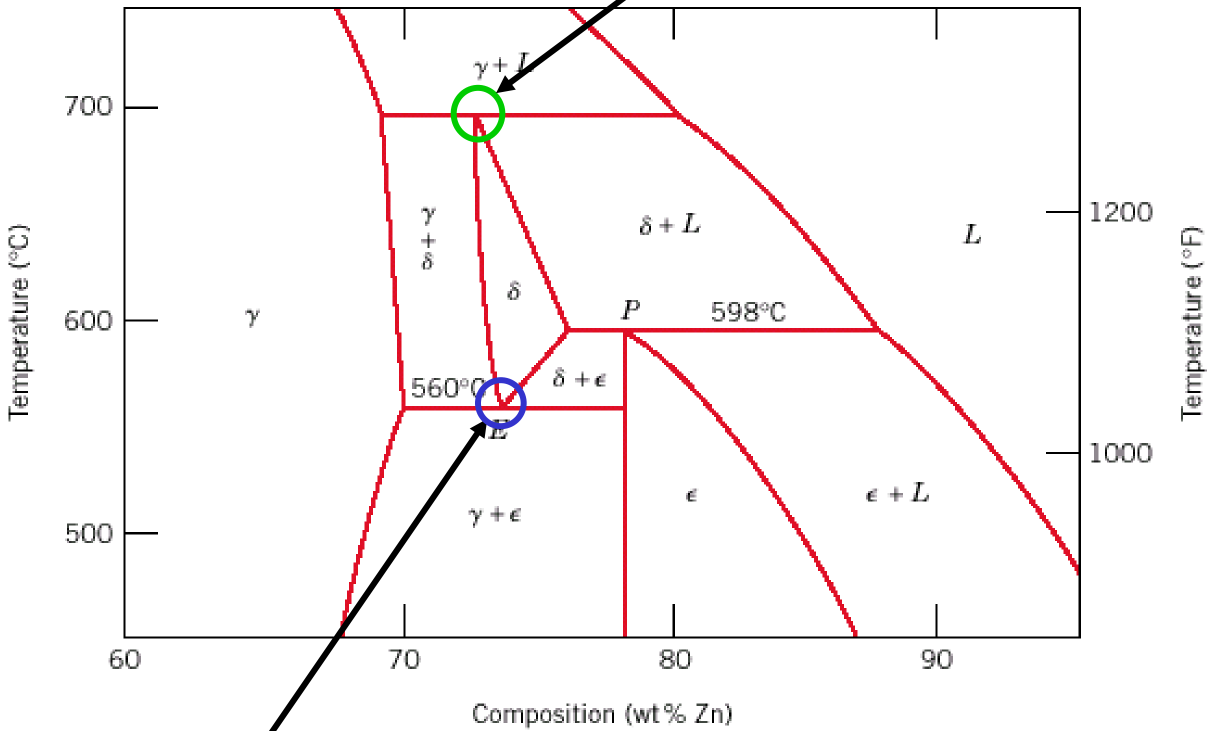
$$S_1 + L \rightleftharpoons S_2$$

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

Eutectoid & Peritectic

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

Cu-Zn Phase diagram

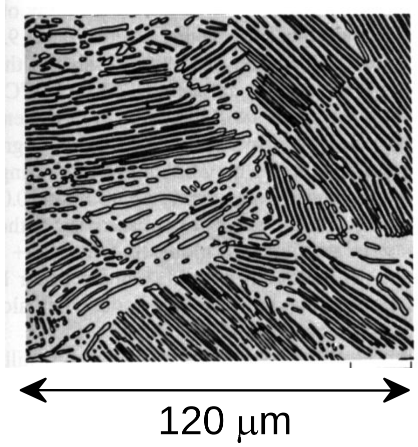


Adapted from Fig. 9.21, *Callister & Rethwisch 8e.*

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

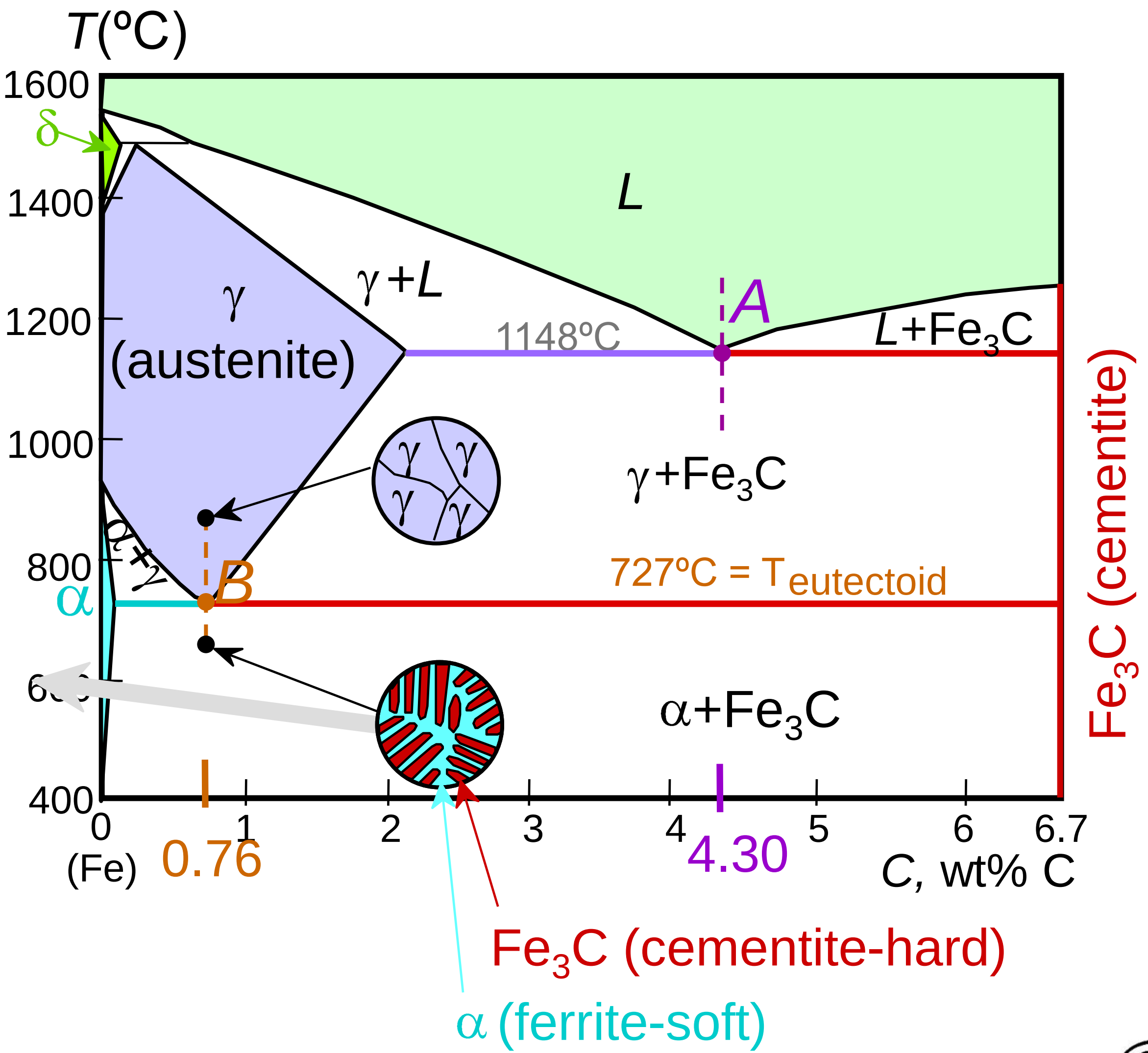
Iron-Carbon (Fe-C) Phase Diagram

- 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

(Adapted from Fig. 9.27, *Callister & Rethwisch 8e.*)

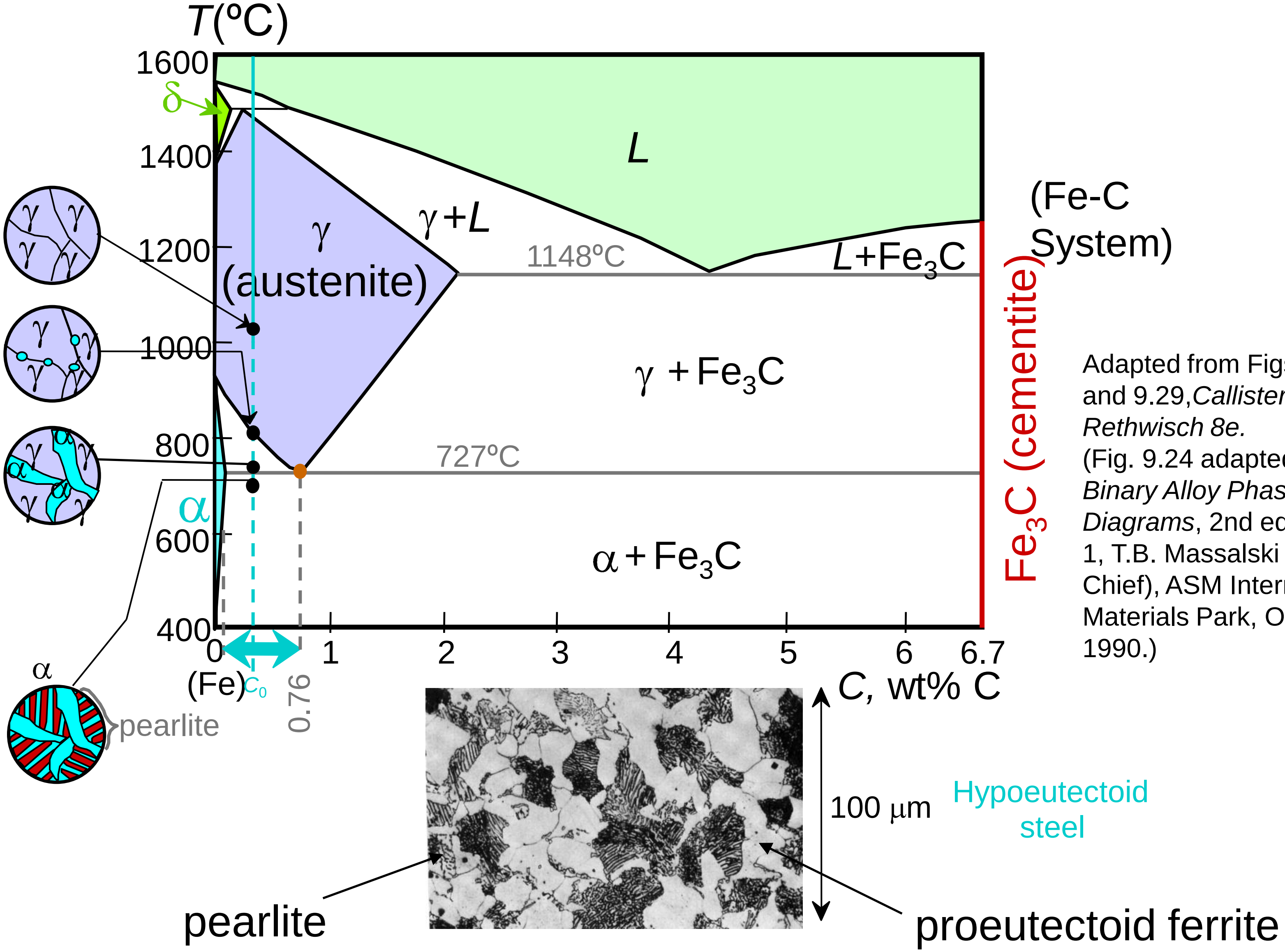


Fe_3C (cementite-hard)

α (ferrite-soft)

Adapted from Fig. 9.24, *Callister & Rethwisch 8e.*

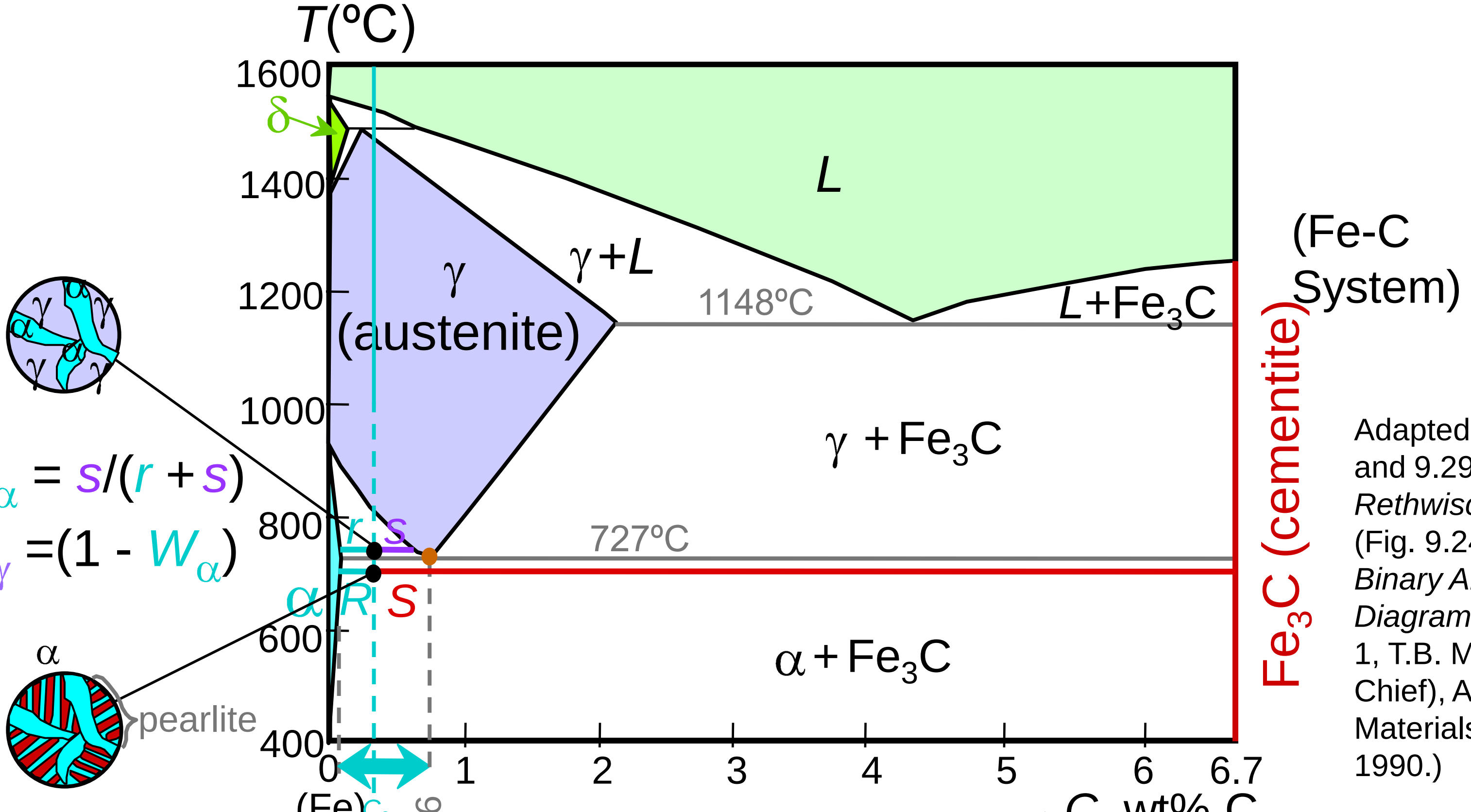
Hypoeutectoid Steel



Adapted from Figs. 9.24 and 9.29, *Callister & Rethwisch 8e.* (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

Adapted from Fig. 9.30, *Callister & Rethwisch 8e.*

Hypoeutectoid Steel



(Fe-C System)

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

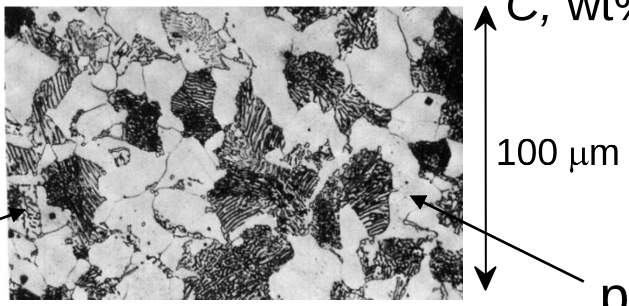
$W_\gamma = (1 - W_\alpha)$

$W_{pearlite} = W_\gamma$

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

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

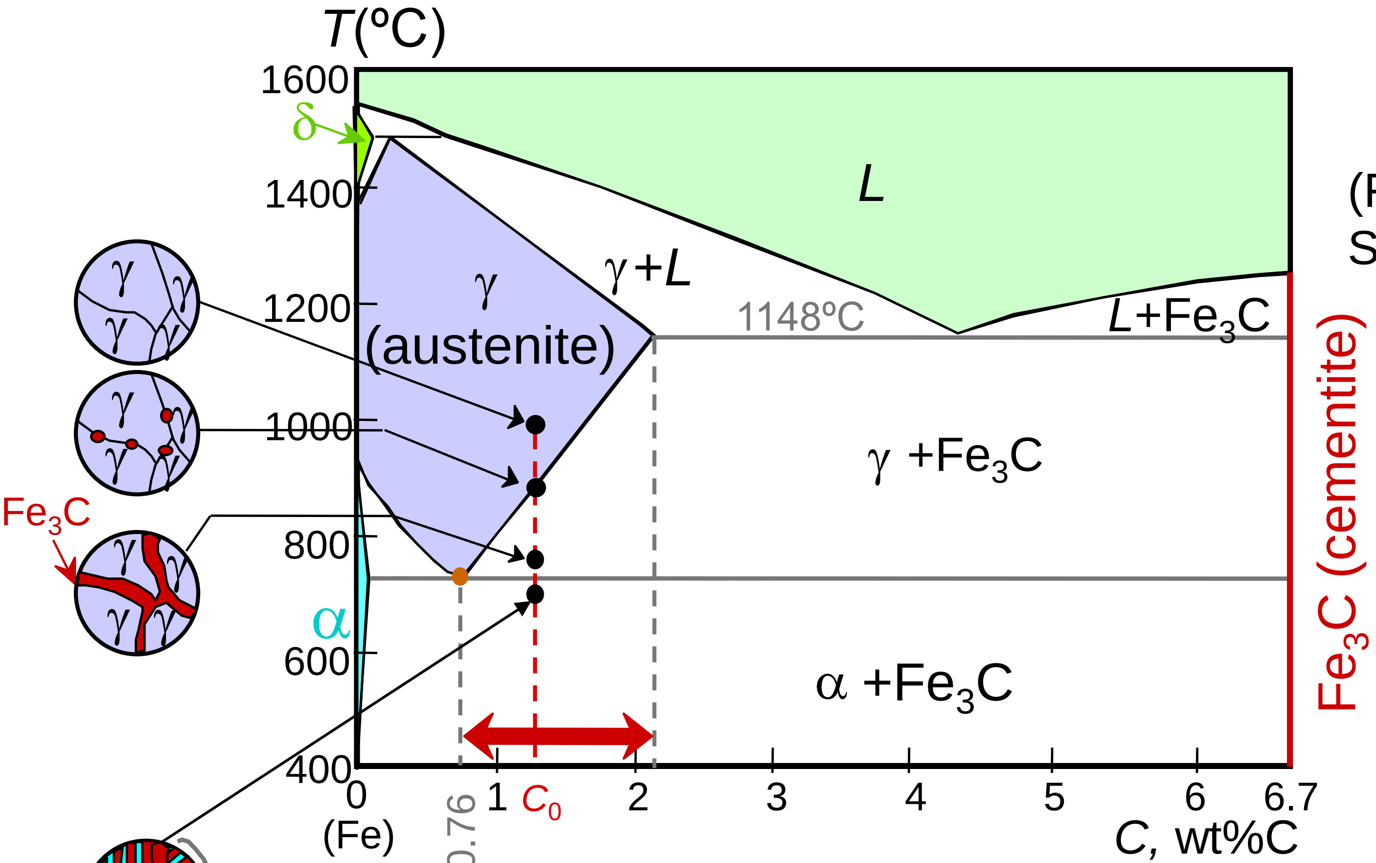
Adapted from Figs. 9.24 and 9.29, *Callister & Rethwisch 8e.* (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



Hypoeutectoid steel

Adapted from Fig. 9.30, *Callister & Rethwisch 8e.*

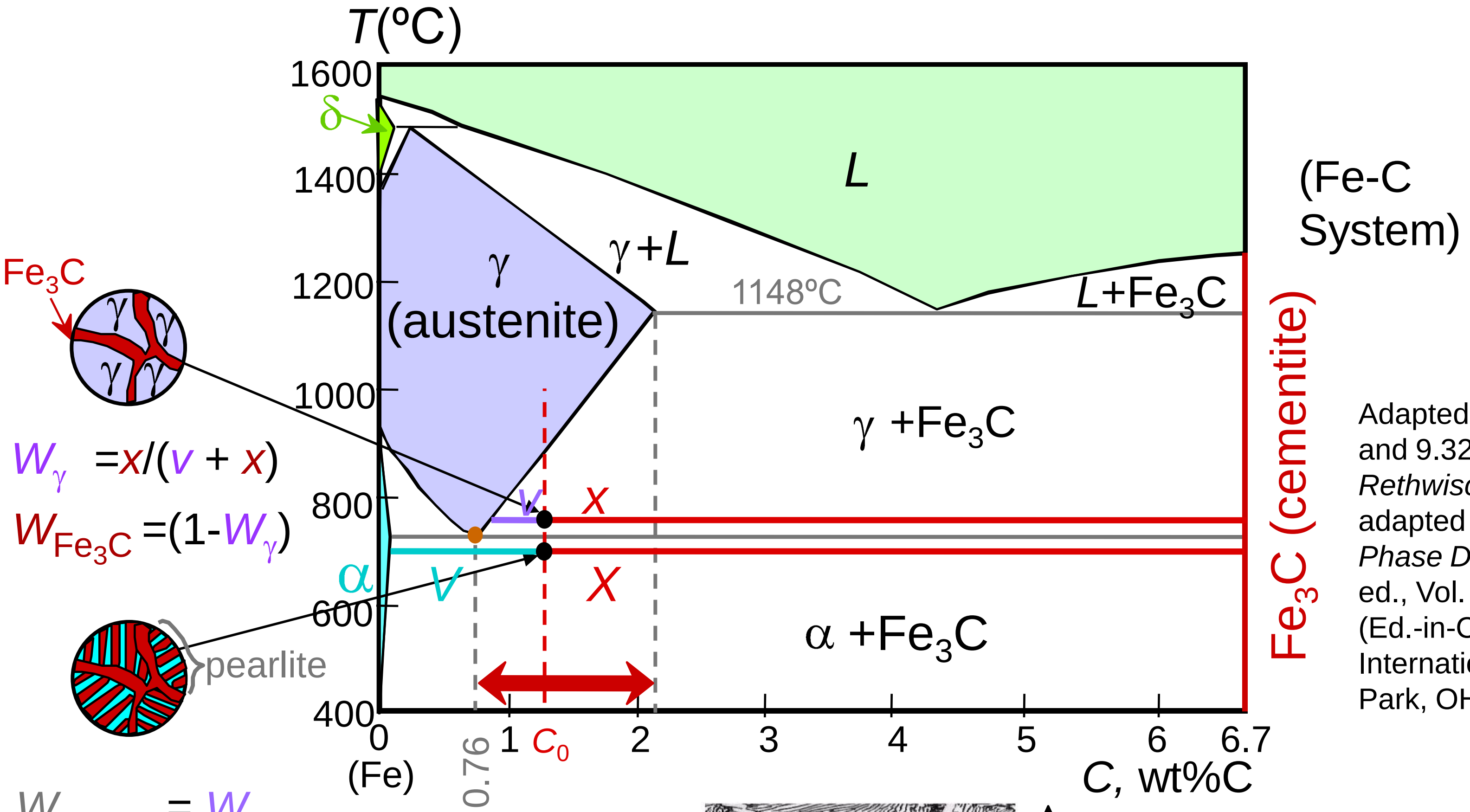
Hypereutectoid Steel



Adapted from Figs. 9.24 and 9.32, *Callister & Rethwisch 8e.* (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

Adapted from Fig. 9.33, *Callister & Rethwisch 8e*.

Hypereutectoid Steel



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

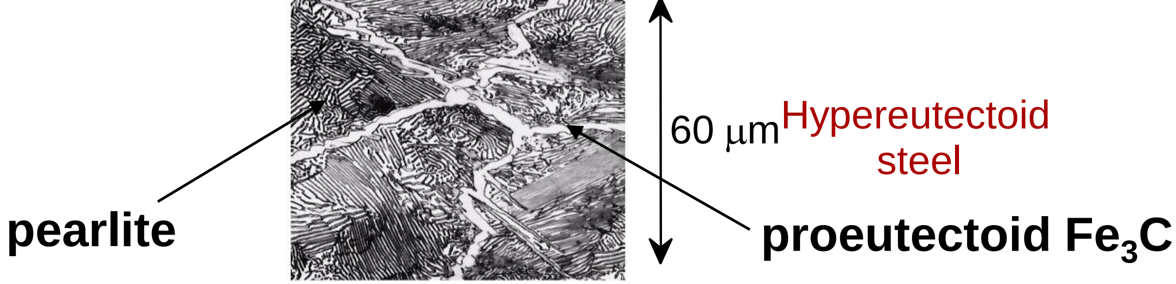
$W_{Fe_3C} = (1 - W_\gamma)$

$W_{pearlite} = W_\gamma$

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

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

Adapted from Figs. 9.24 and 9.32, *Callister & Rethwisch 8e.* (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



Adapted from Fig. 9.33, *Callister & Rethwisch 8e*.

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

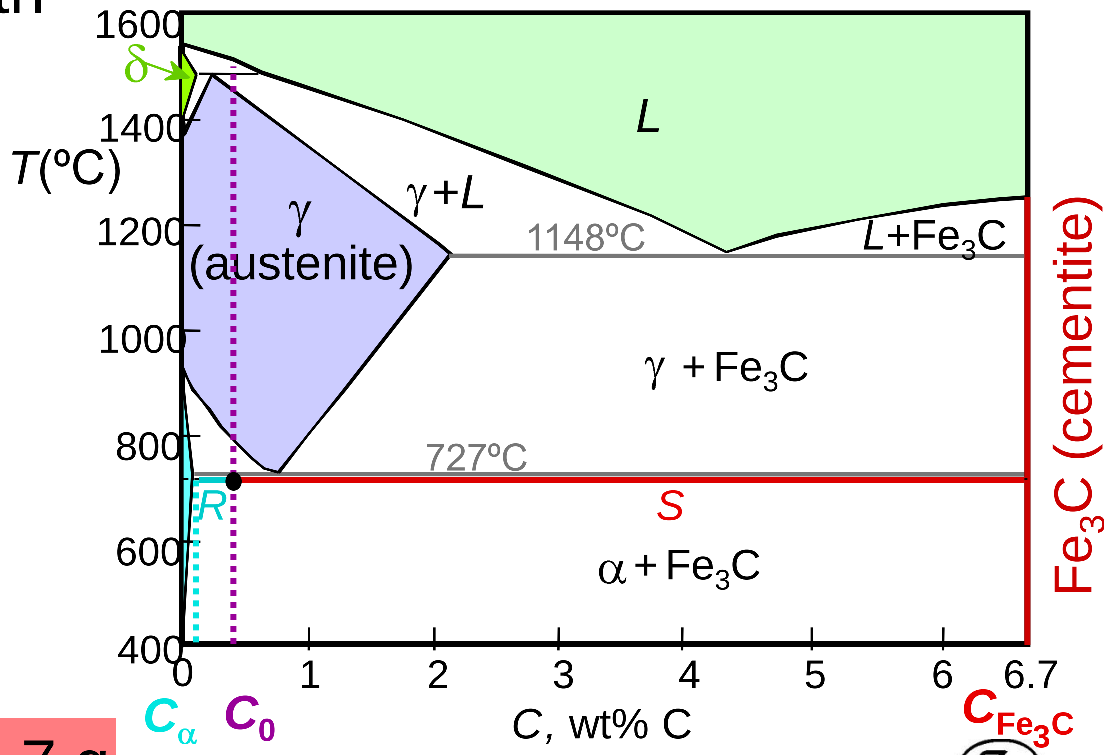
C_α = 0.022 wt% C

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

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

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

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

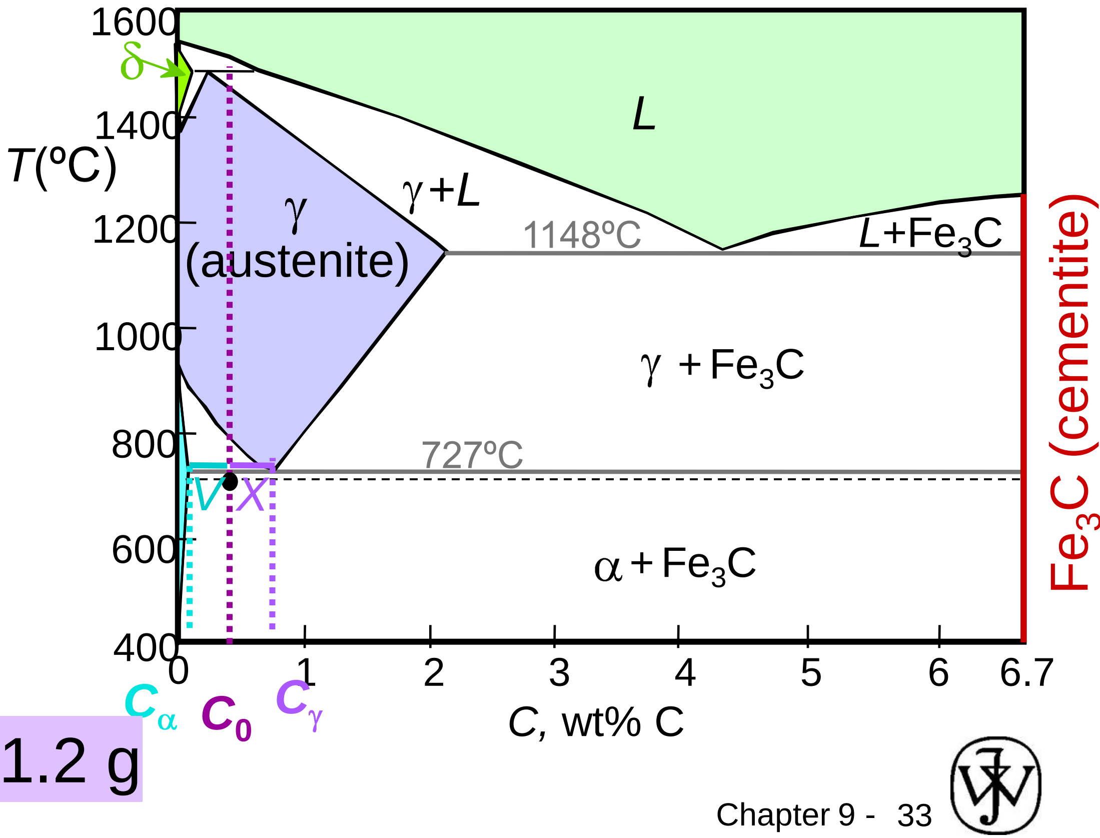
$$W_{\text{pearlite}} = \frac{V}{V+X} = \frac{C_0 - C_\alpha}{C_\gamma - C_\alpha}$$

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

Amount of pearlite in 100 g

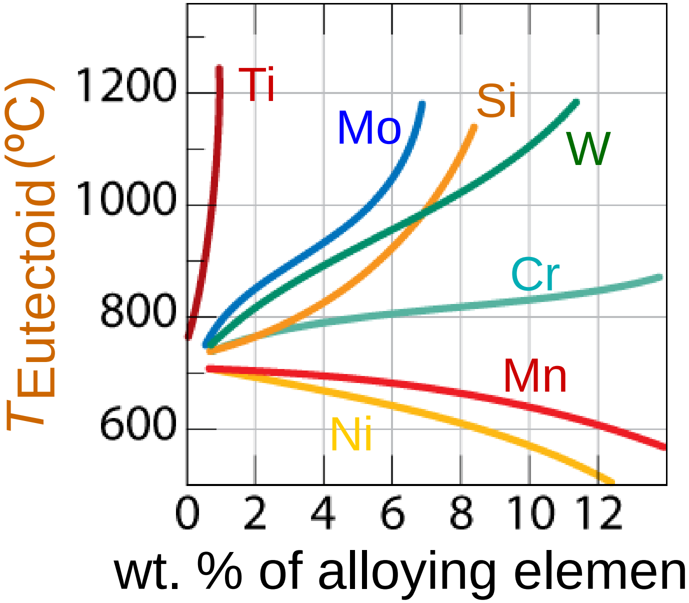
$= (100 \text{ g})W_{\text{pearlite}}$

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



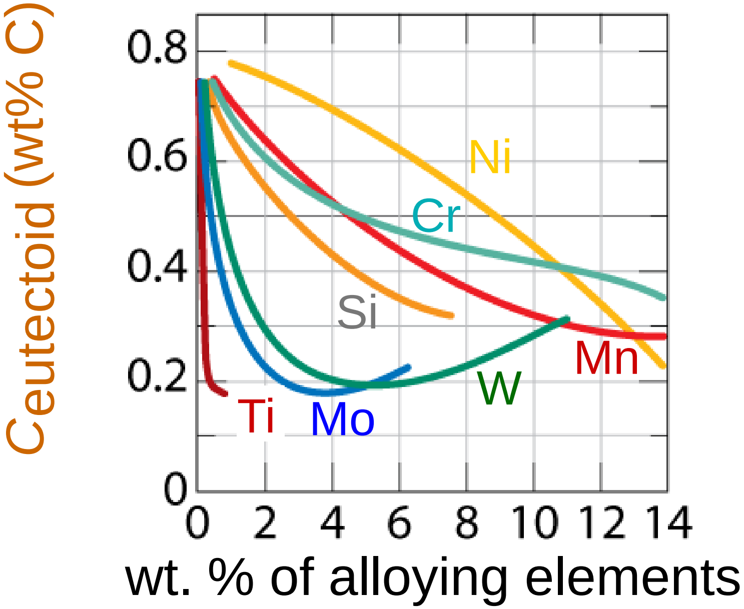
Alloying with Other Elements

- $T_{eutectoid}$ changes:



Adapted from Fig. 9.34,*Callister & Rethwisch 8e*. (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 & Rethwisch 8e*. (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 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.