Chapter 9: Phase Diagrams

ISSUES TO ADDRESS...

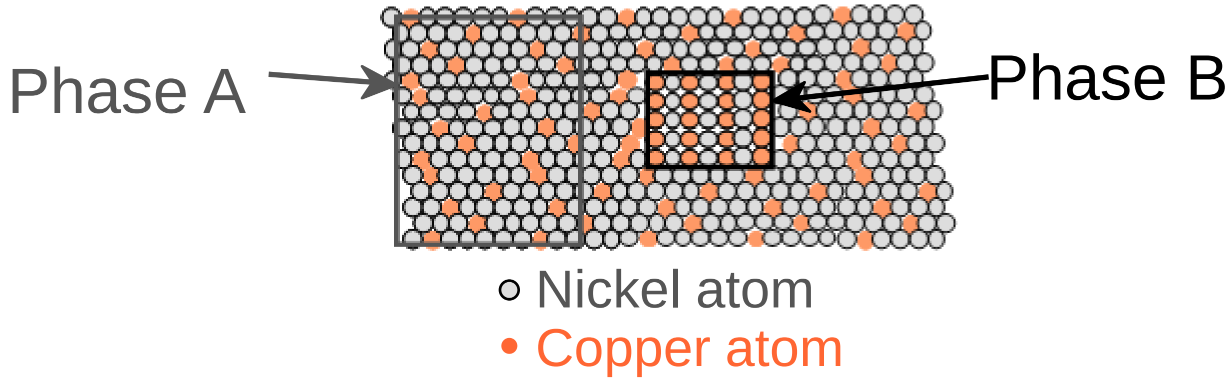
- When we combine two elements...
  what equilibrium state do we get?
- In particular, if we specify...
  --a composition (e.g., wt% Cu - wt% Ni), and
  --a temperature (*T*)

then...

How many phases do we get?

What is the composition of each phase?

How much of each phase do we get?



Phase Equilibria: Solubility Limit

Introduction

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

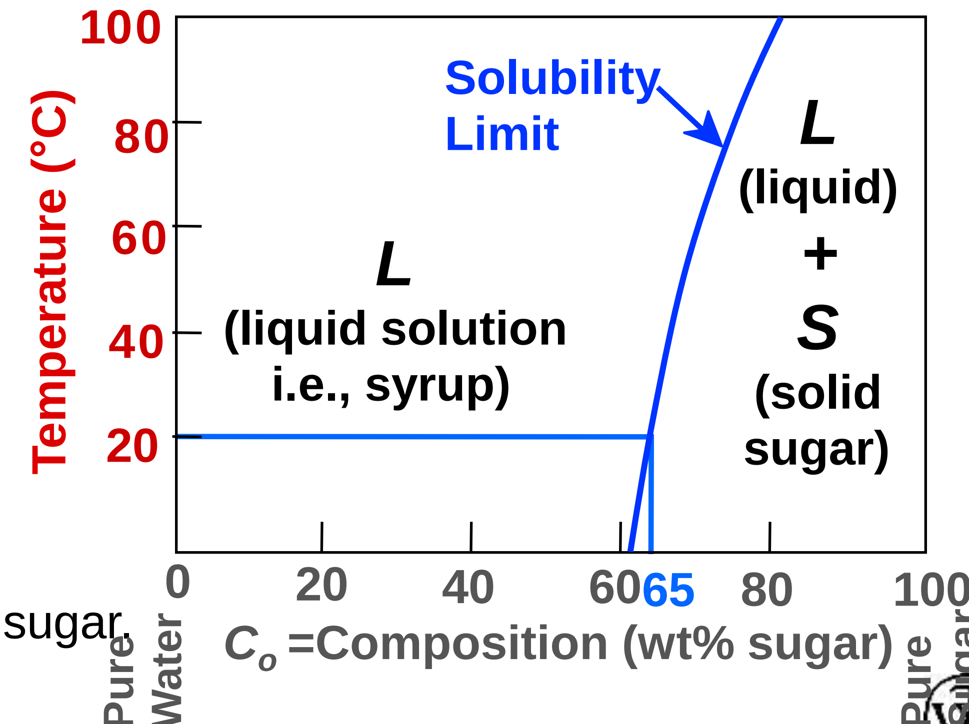
Adapted from Fig. 9.1, *Callister 7e.*

- 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.

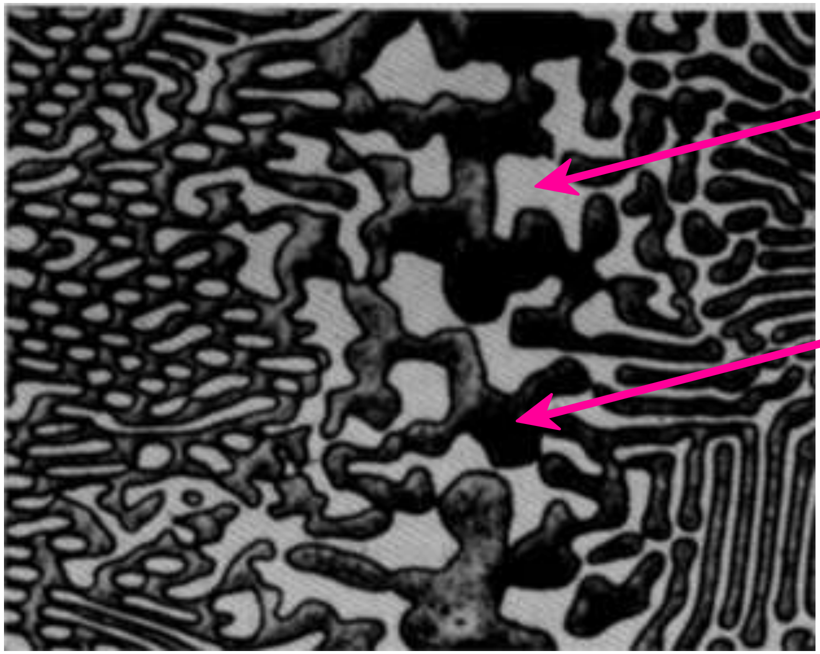
Sucrose/Water Phase Diagram



Components and Phases

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

Aluminum-Copper Alloy



β (lighter phase)

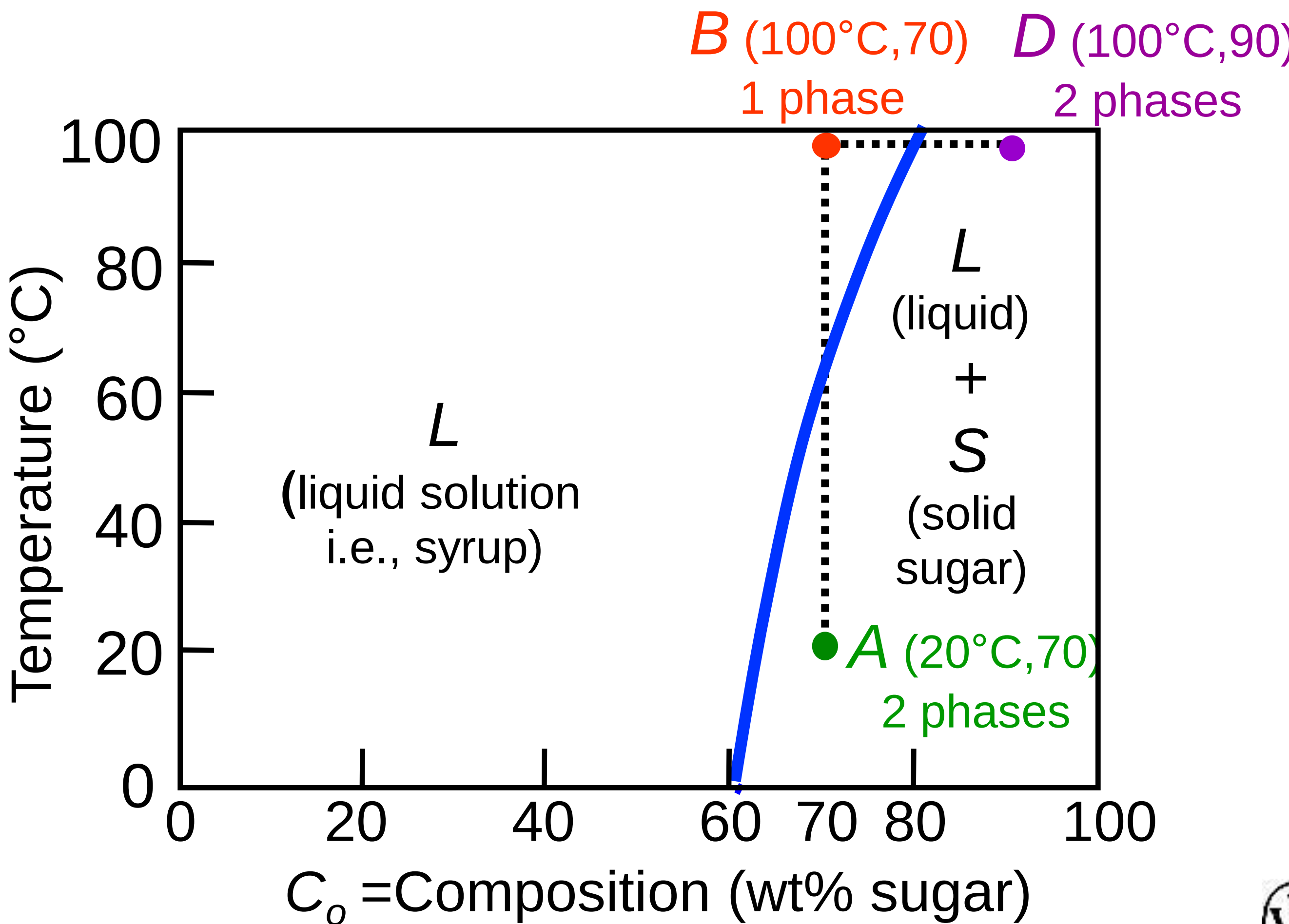
α (darker phase)

Adapted from chapter-opening photograph, Chapter 9, *Callister 3e.*

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 Equilibria

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

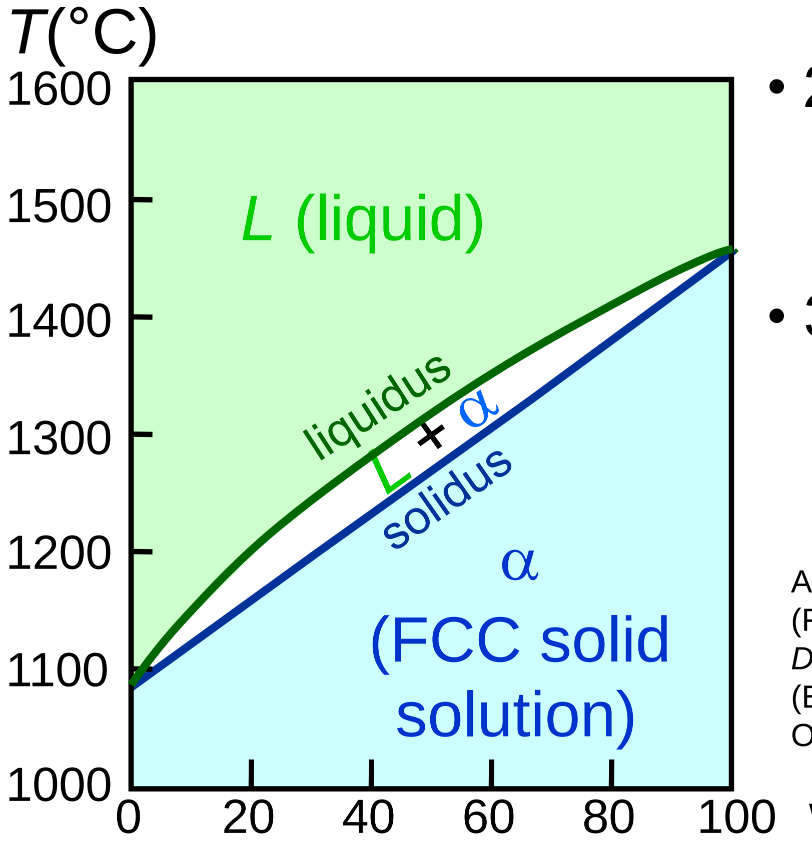
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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 miscible in all proportions.

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)
  - α (FCC solid solution)
- 3 phase fields:
  - *L*
  - *L* + α
  - α

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).

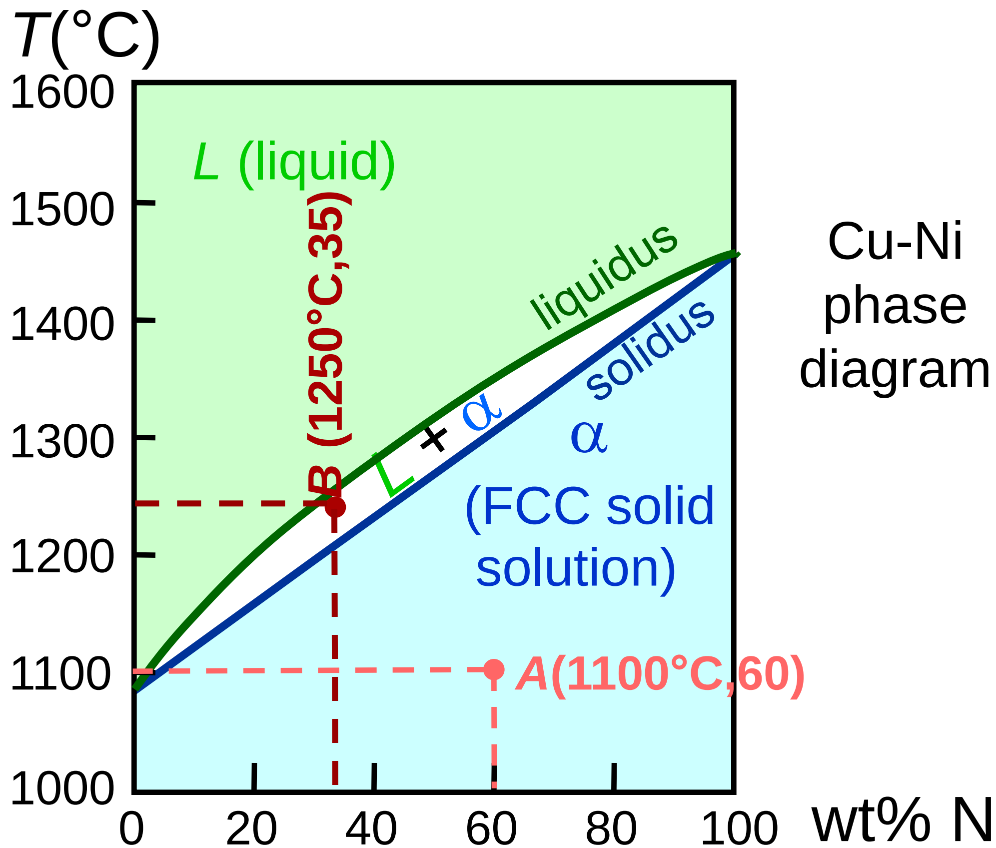
Phase Diagrams:
and types of phases

- 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: $L + \alpha$



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)

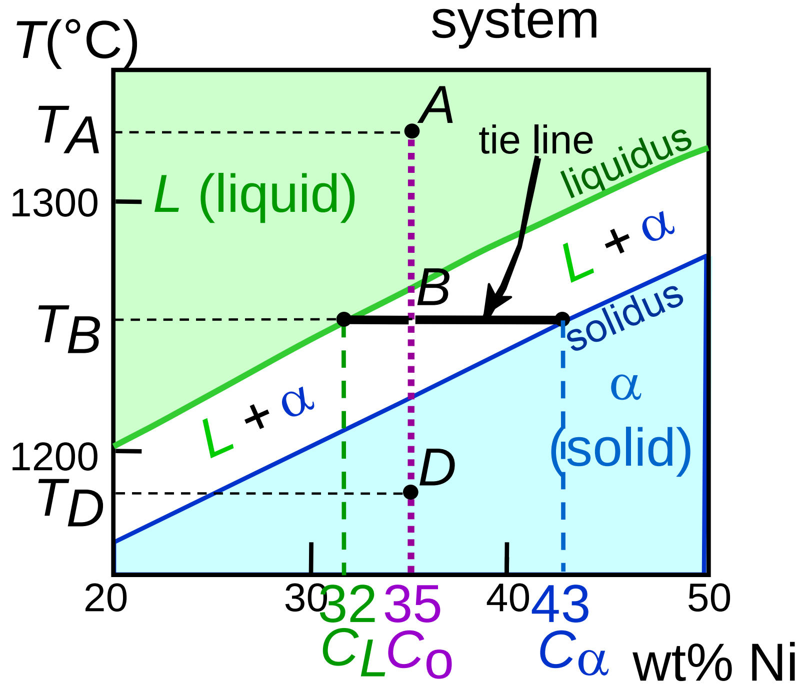
$C_\alpha = C_o$ (= 35 wt% Ni)

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)



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_α = 0

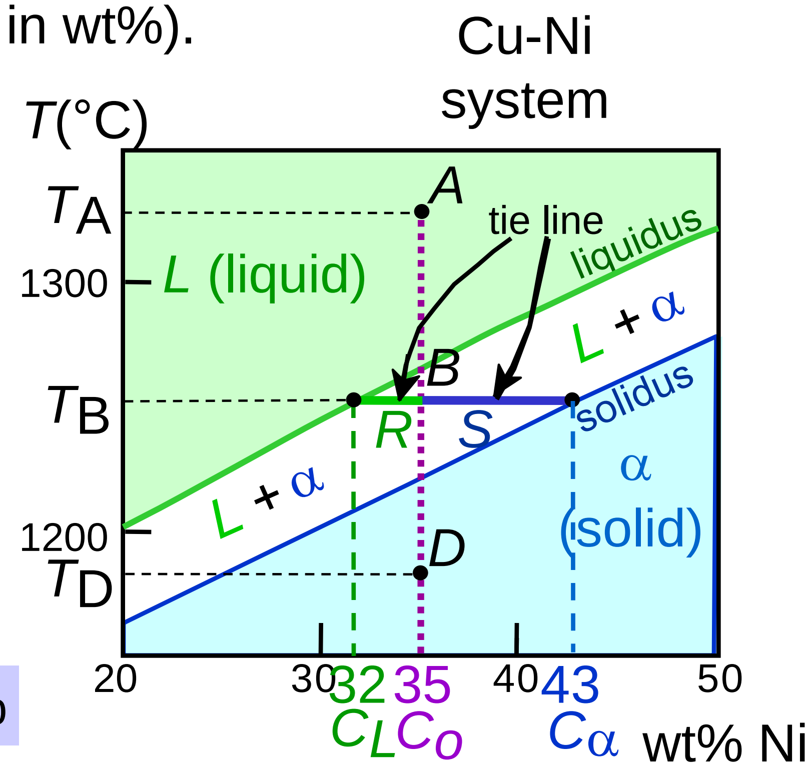
At T_D: Only Solid (α)

W_L = 0, W_α = 100 wt%

At T_B: Both α and L

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

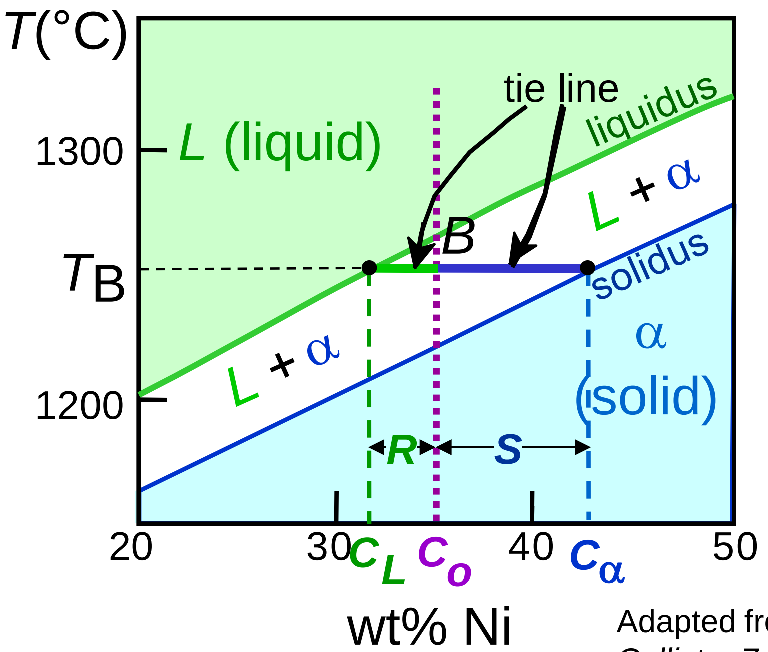
$$W_\alpha = \frac{R}{R+S} = 27\text{ wt\%}$$



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.)

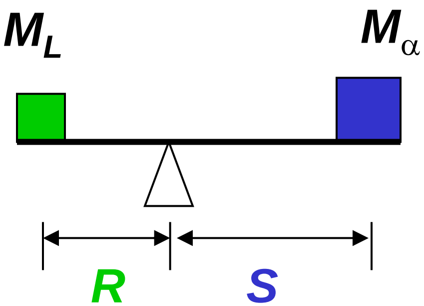
The Lever Rule

- 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)



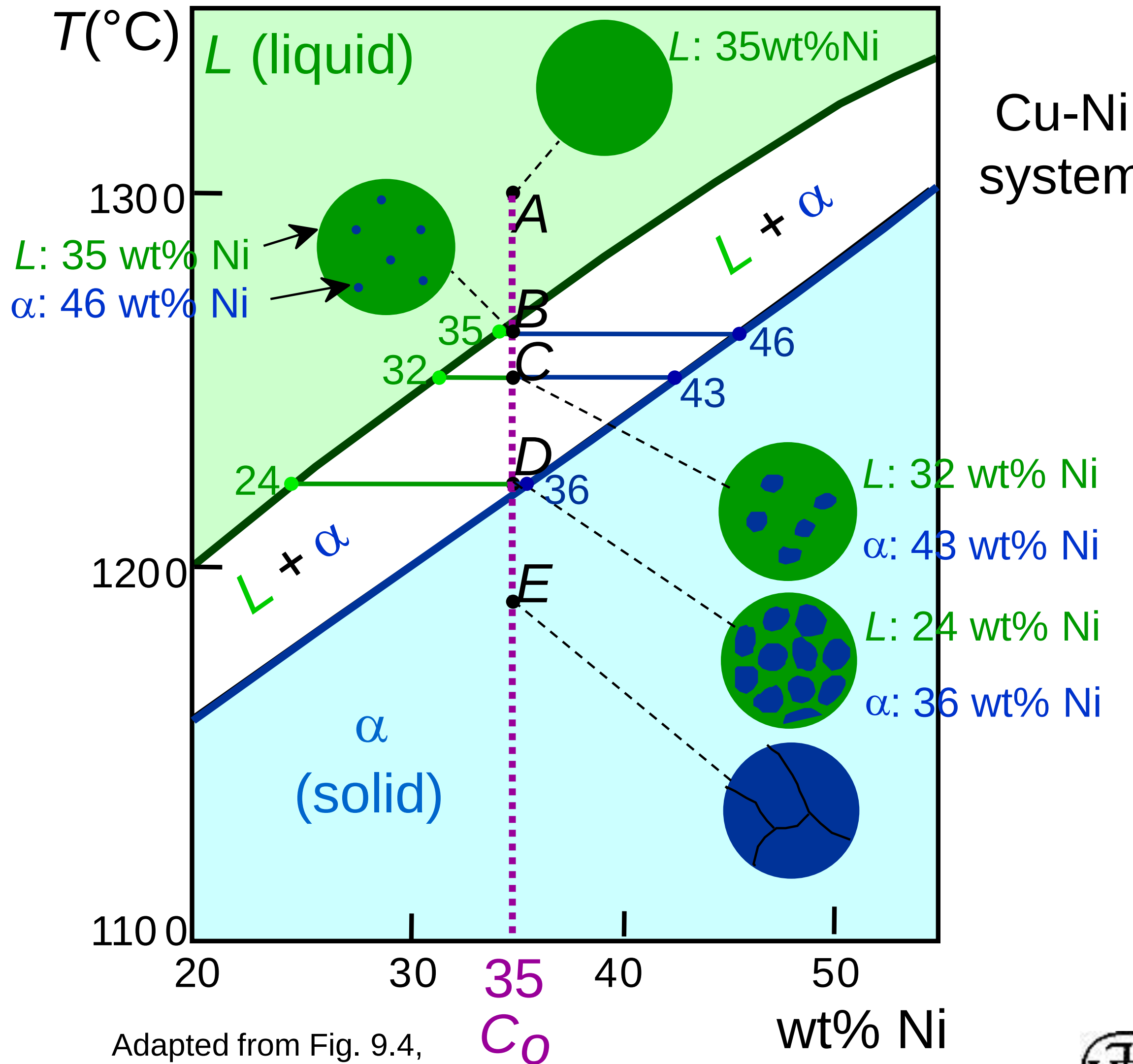
$$M_\alpha \cdot S = M_L \cdot R$$

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

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

Ex: 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; α phase
  field extends from
  0 to 100 wt% Ni.
- Consider
  C_o = 35 wt%Ni.



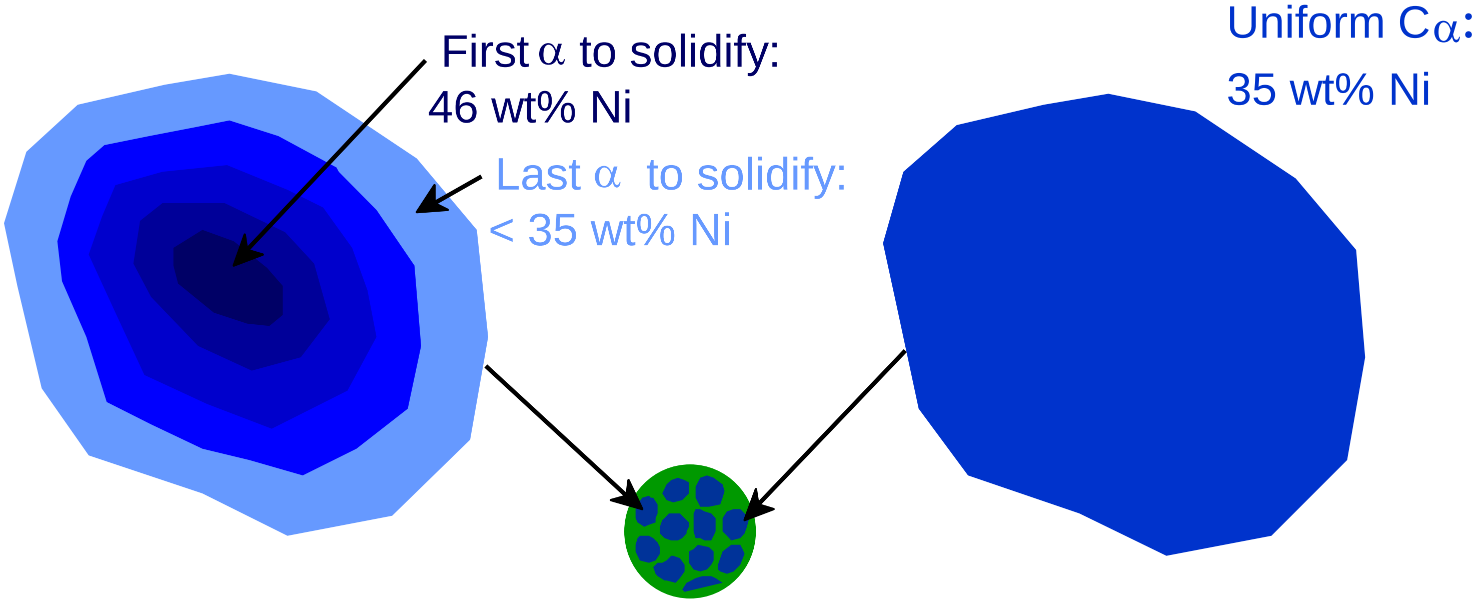
Adapted from Fig. 9.4, *Callister 7e.*

Cored vs Equilibrium Phases

- 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.

- Fast rate of cooling:
  Cored structure

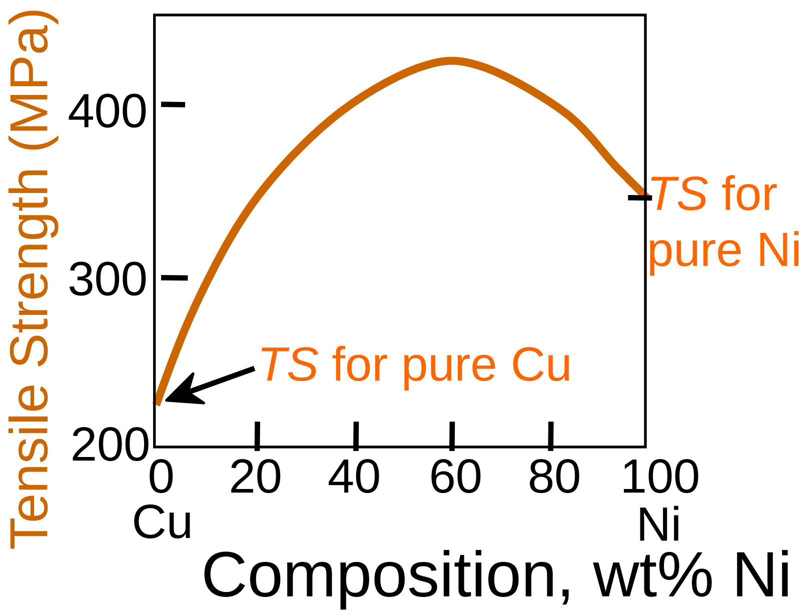
- Slow rate of cooling:
  Equilibrium structure



Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

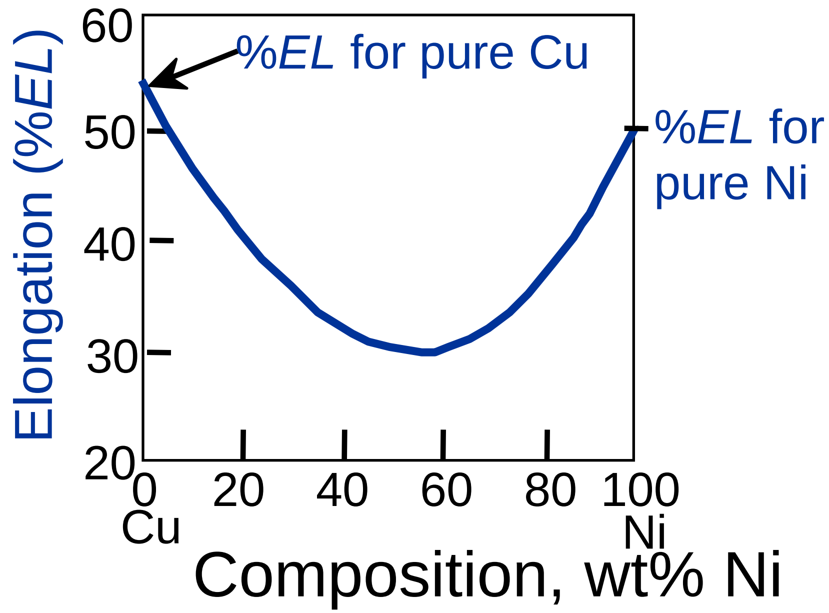
--Tensile strength (*TS*)



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

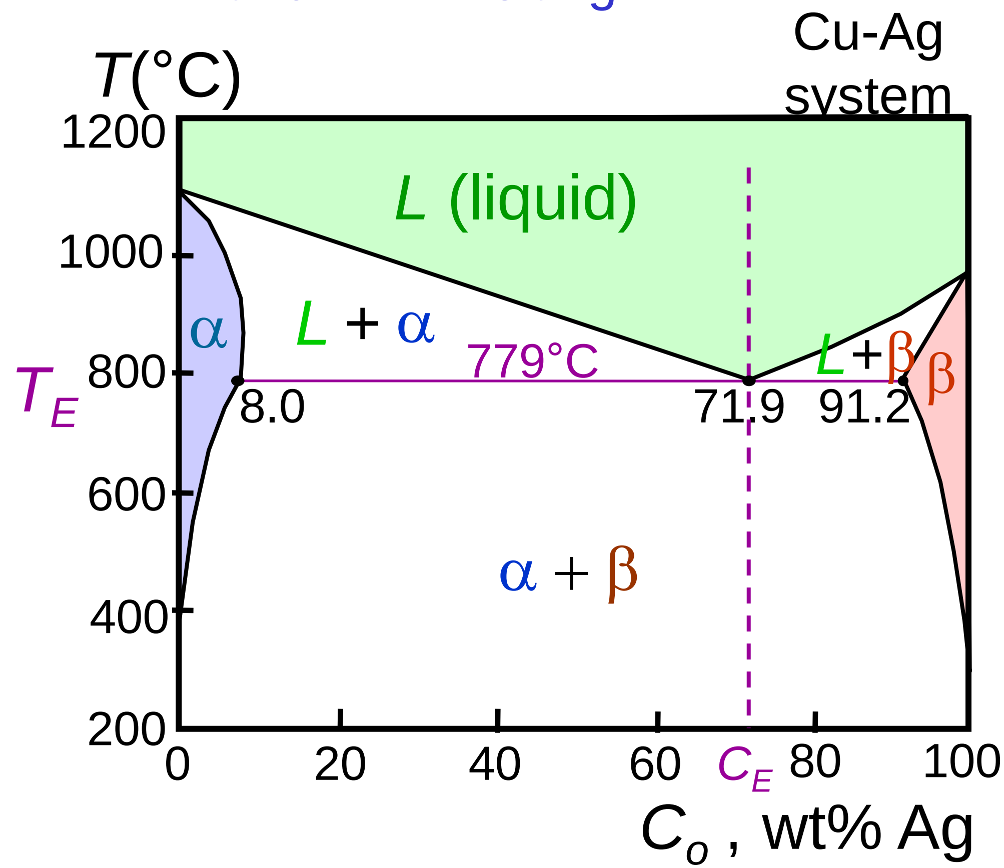
Binary-Eutectic Systems

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



- **Eutectic transition**

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

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

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

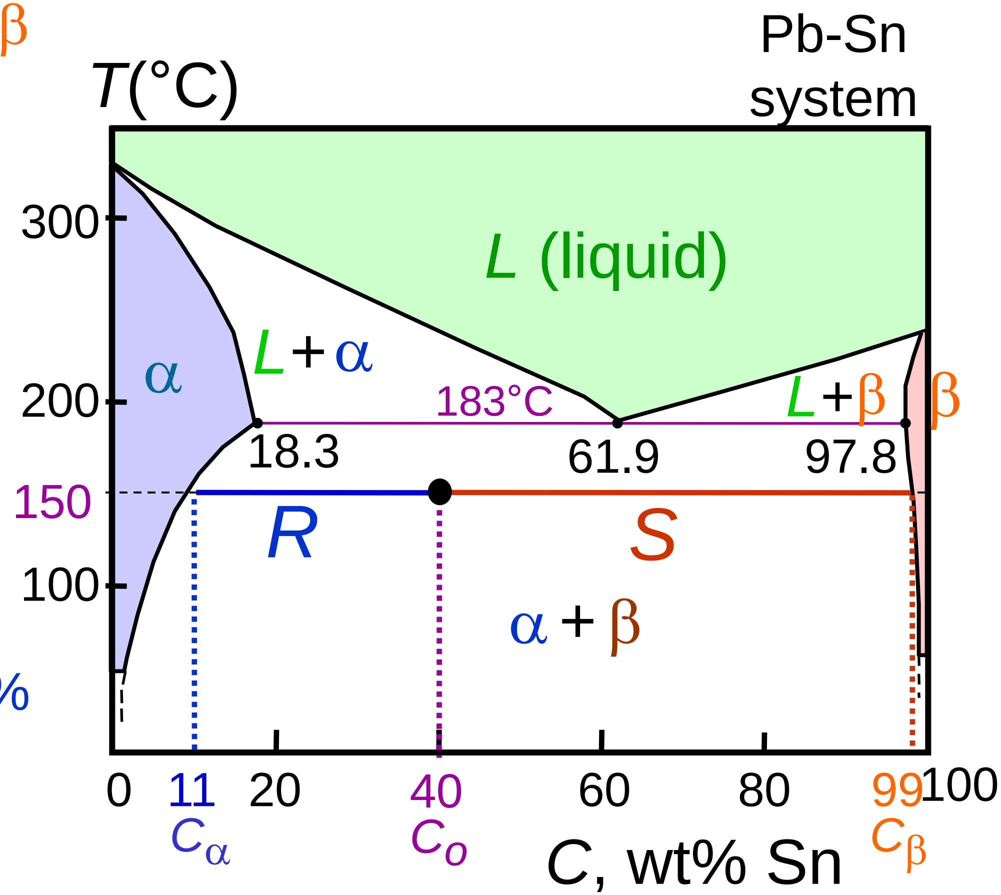
  C_α = 11 wt% Sn

  C_β = 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 200°C, find...
  - --the phases present: α + L
  - --compositions of phases:

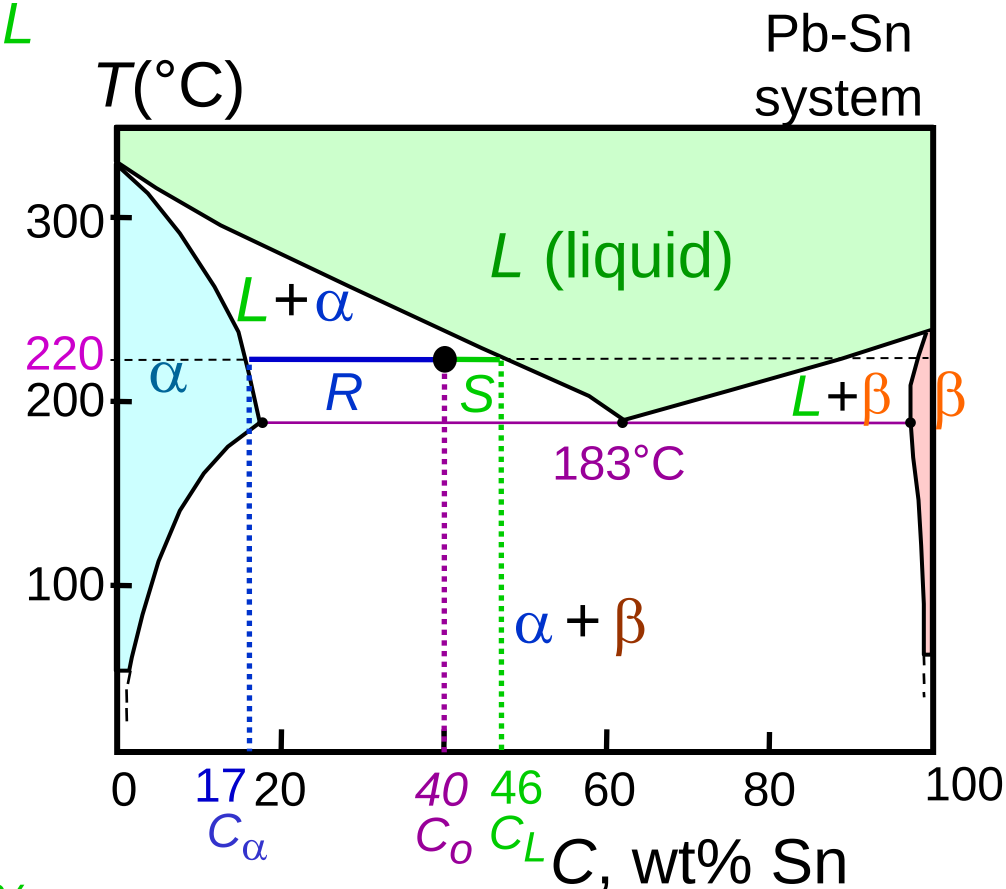
    C_O = 40 wt% Sn
    C_α = 17 wt% Sn
    C_L = 46 wt% Sn

  - --the relative amount of each phase:

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

$$= \frac{6}{29} = 21 \text{ wt\%}$$

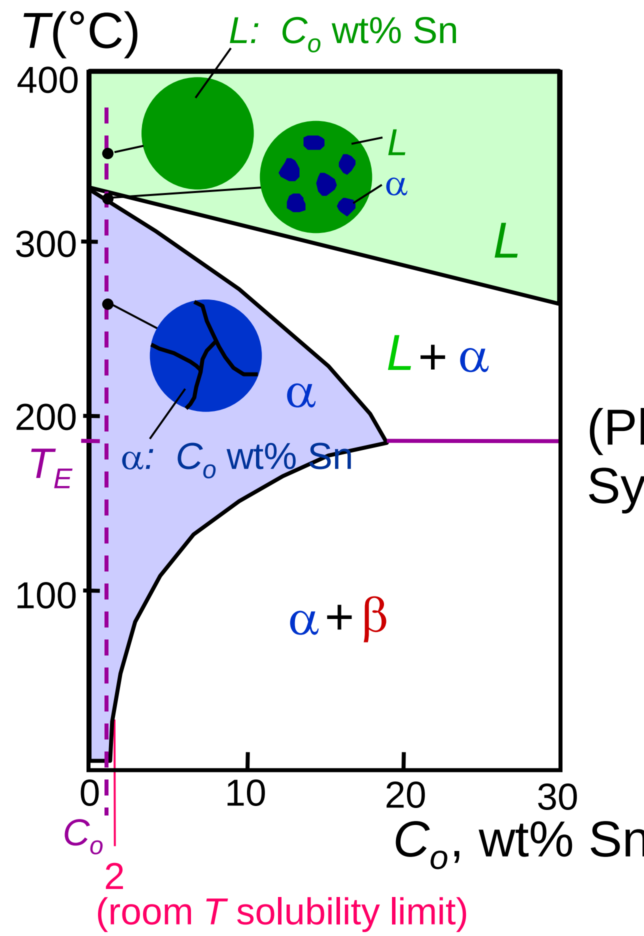
$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$



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.

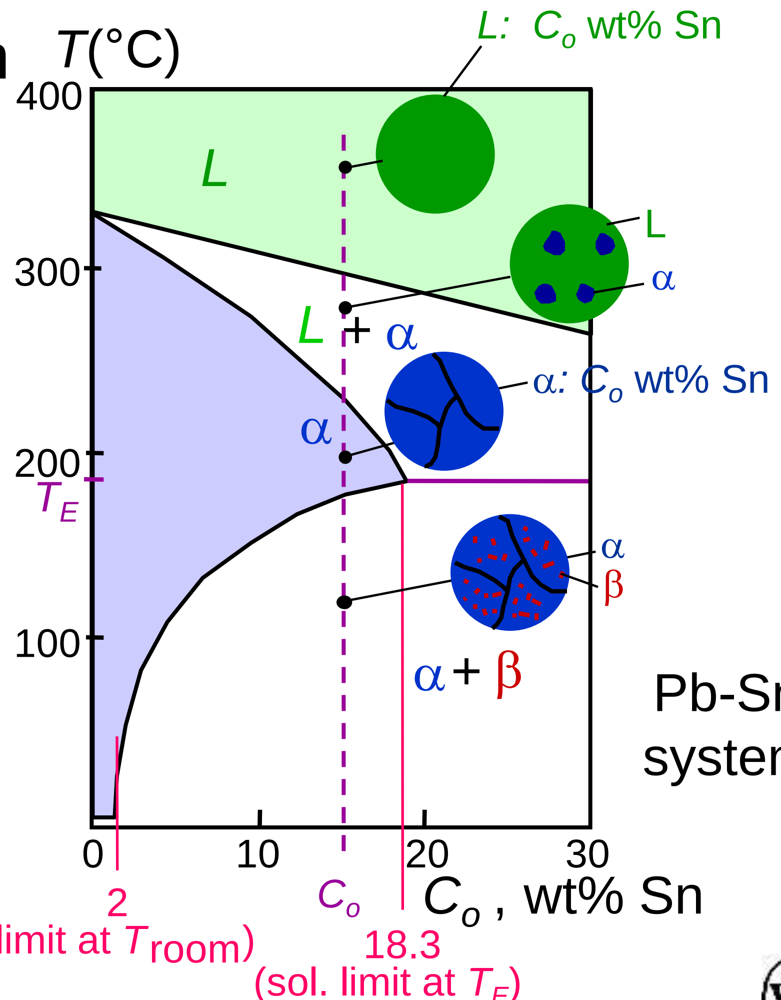


(Pb-Sn System)

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

Microstructures in Eutectic Systems: II

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

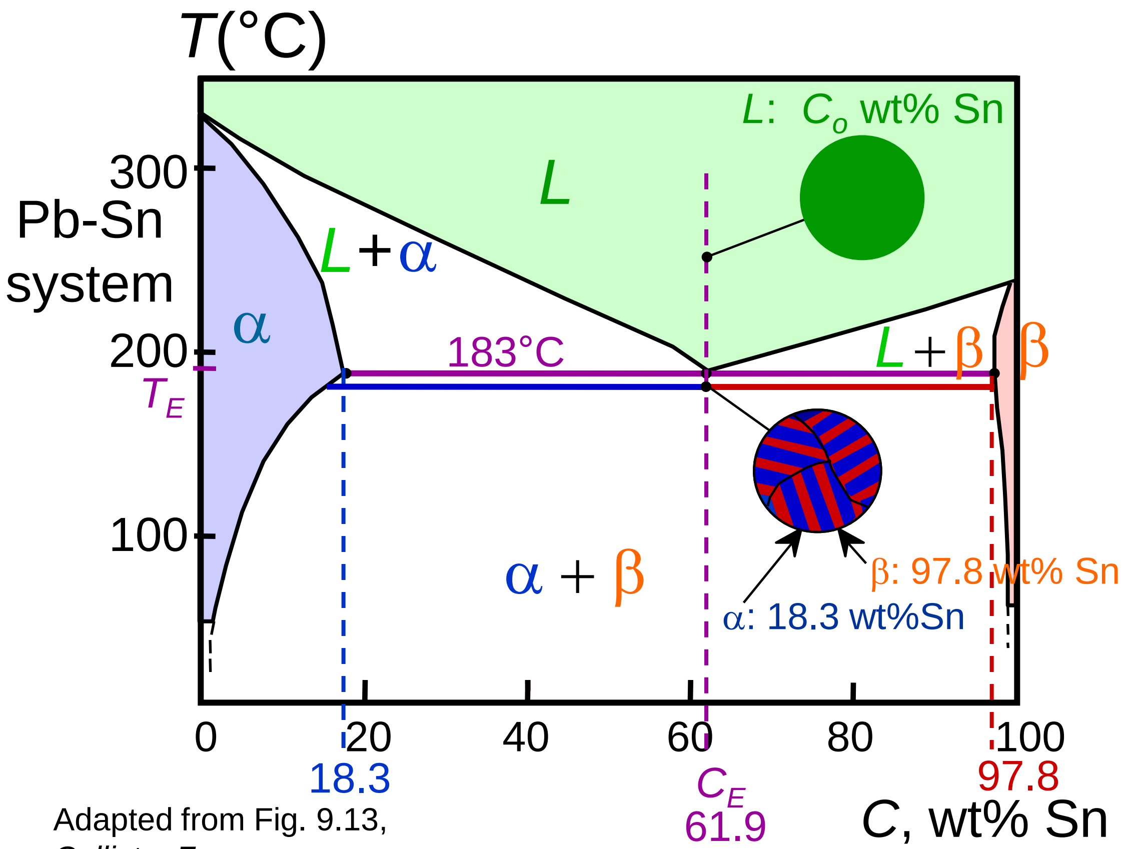


Pb-Sn system

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

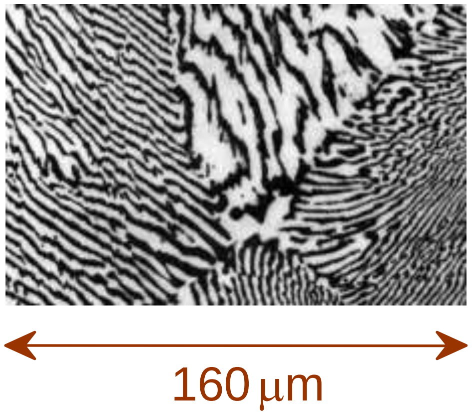
Microstructures in Eutectic Systems: III

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



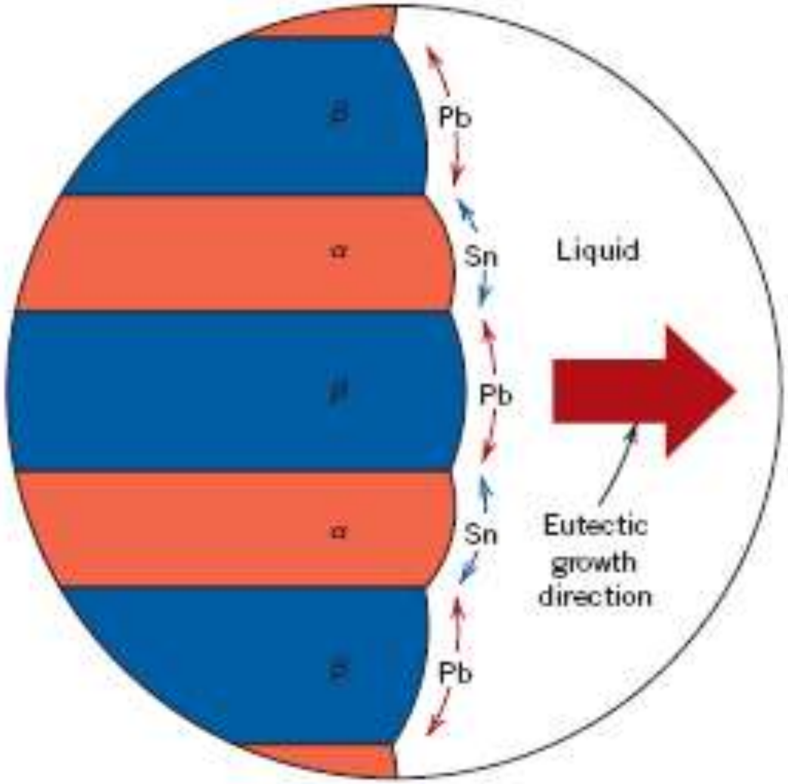
Adapted from Fig. 9.13, *Callister 7e.*

Micrograph of Pb-Sn eutectic microstructure

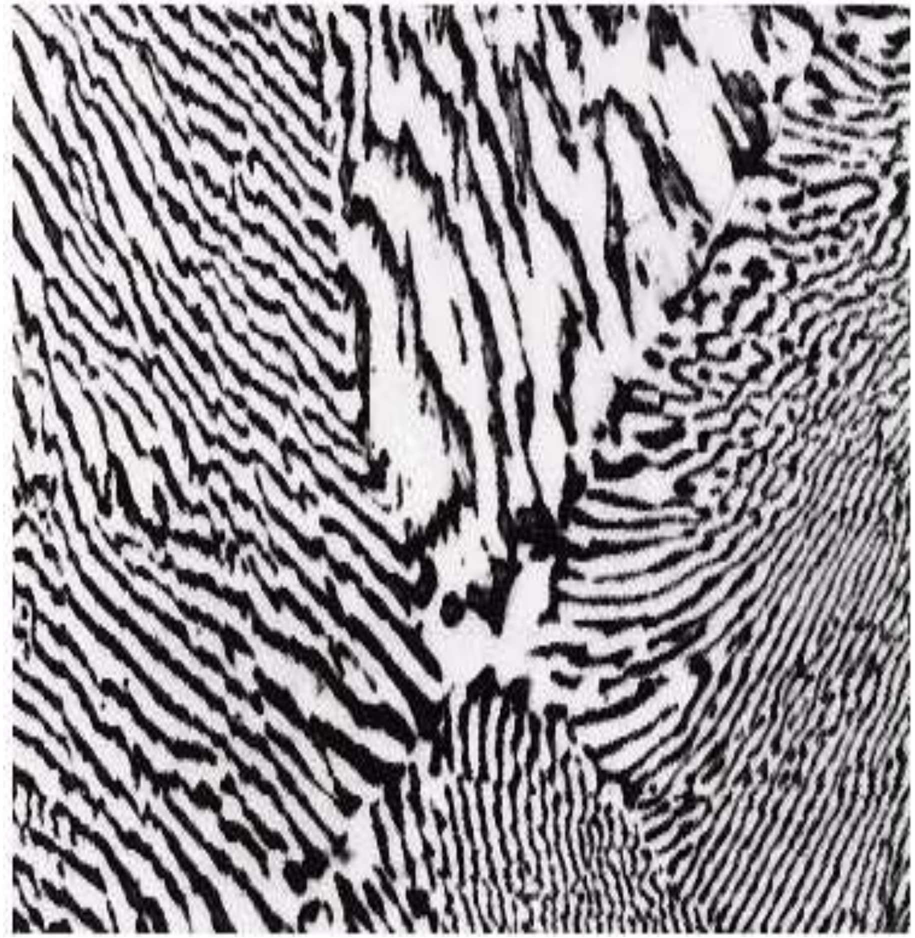


Adapted from Fig. 9.14, *Callister 7e.*

Lamellar Eutectic Structure

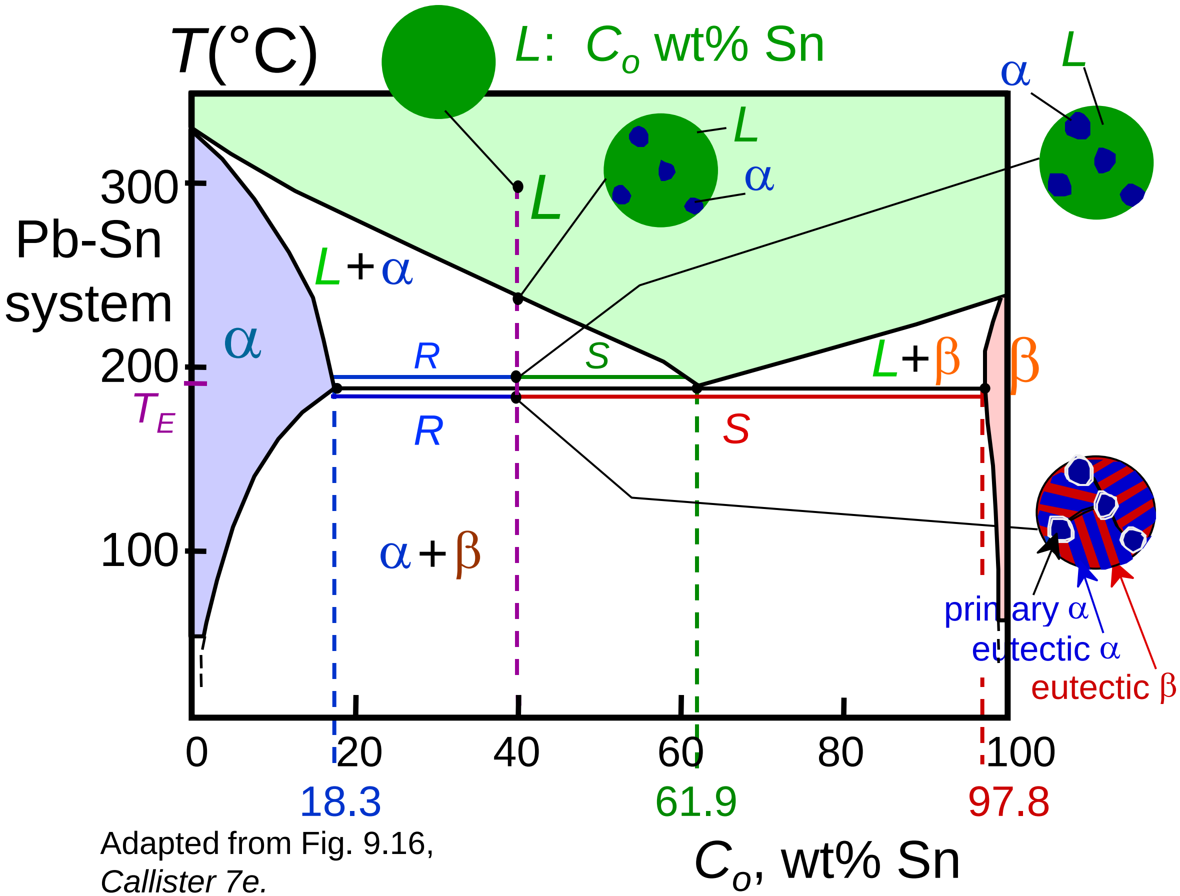


Adapted from Figs. 9.14 & 9.15, *Callister 7e.*



Microstructures in Eutectic Systems: IV

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

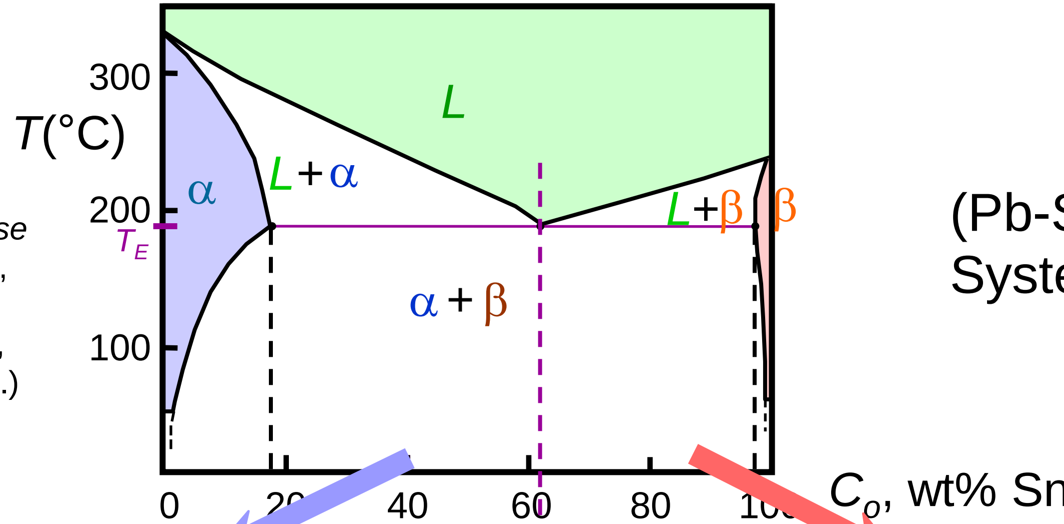


Adapted from Fig. 9.16, *Callister 7e.*

- Just above T_E :
  - C_α = 18.3 wt% Sn
  - C_L = 61.9 wt% Sn
  - $W_\alpha = \frac{S}{R+S}$ = 50 wt%
  - $W_L = (1 - W_\alpha)$ = 50 wt%
- Just below T_E :
  - C_α = 18.3 wt% Sn
  - C_β = 97.8 wt% Sn
  - $W_\alpha = \frac{S}{R+S}$ = 73 wt%
  - W_β = 27 wt%

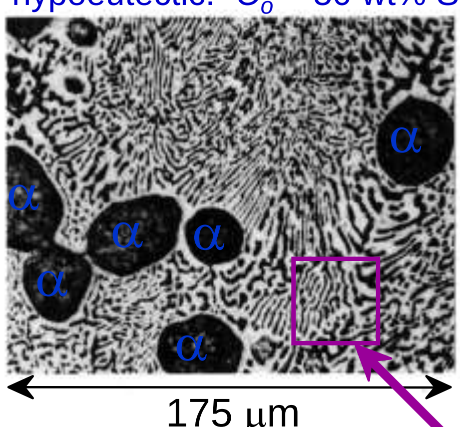
Hypoeutectic & Hypereutectic

Adapted from Fig. 9.8, *Callister 7e.* (Fig. 9.8 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)

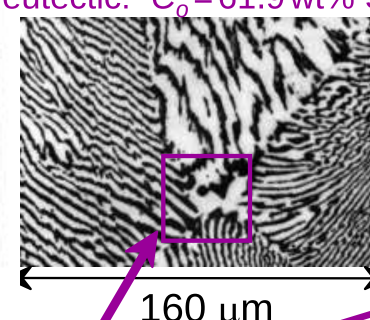


(Pb-Sn System)

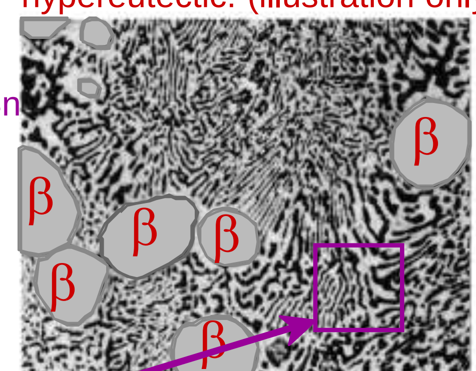
hypoeutectic: C_o = 50 wt% Sn



eutectic: C_o = 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.)

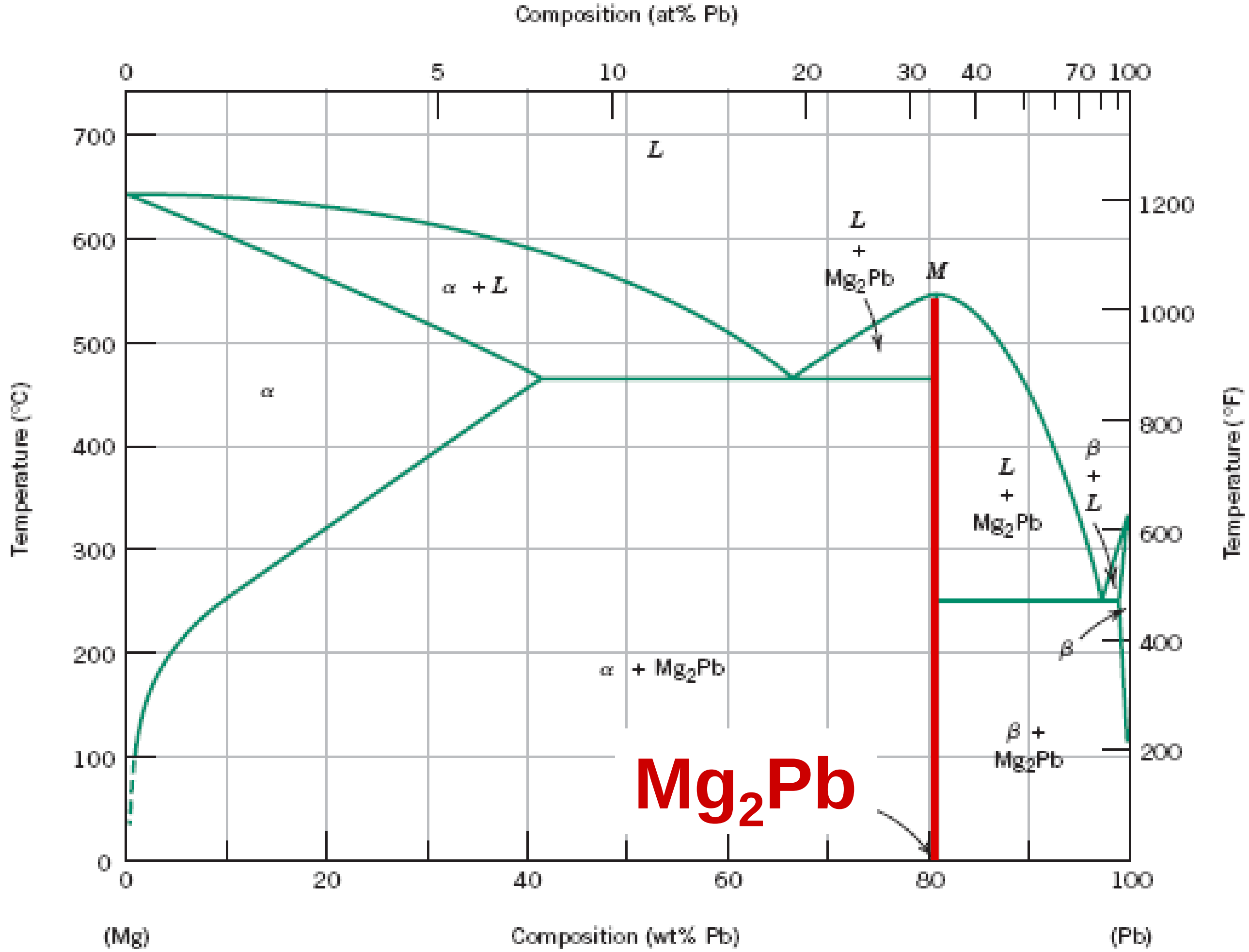
eutectic micro-constituent

Adapted from Fig. 9.17, *Callister 7e.*

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

Adapted from Fig. 9.17, *Callister 7e.* (Illustration only)

Intermetallic Compounds



Adapted from
Fig. 9.20, *Callister 7e.*

Note: intermetallic compound forms a line - not an area - because stoichiometry (i.e. composition) is exact.

Eutectoid & Peritectic

- Eutectic - liquid in equilibrium with two solids

$$L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + \beta$$

- Eutectoid - solid phase in equation with two solid phases

$$S_2 \rightleftharpoons S_1 + S_3$$

intermetallic compound
- cementite

$$\gamma \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + Fe_3C \qquad (727^{\circ}C)$$

- Peritectic - liquid + solid 1 → solid 2 (Fig 9.21)

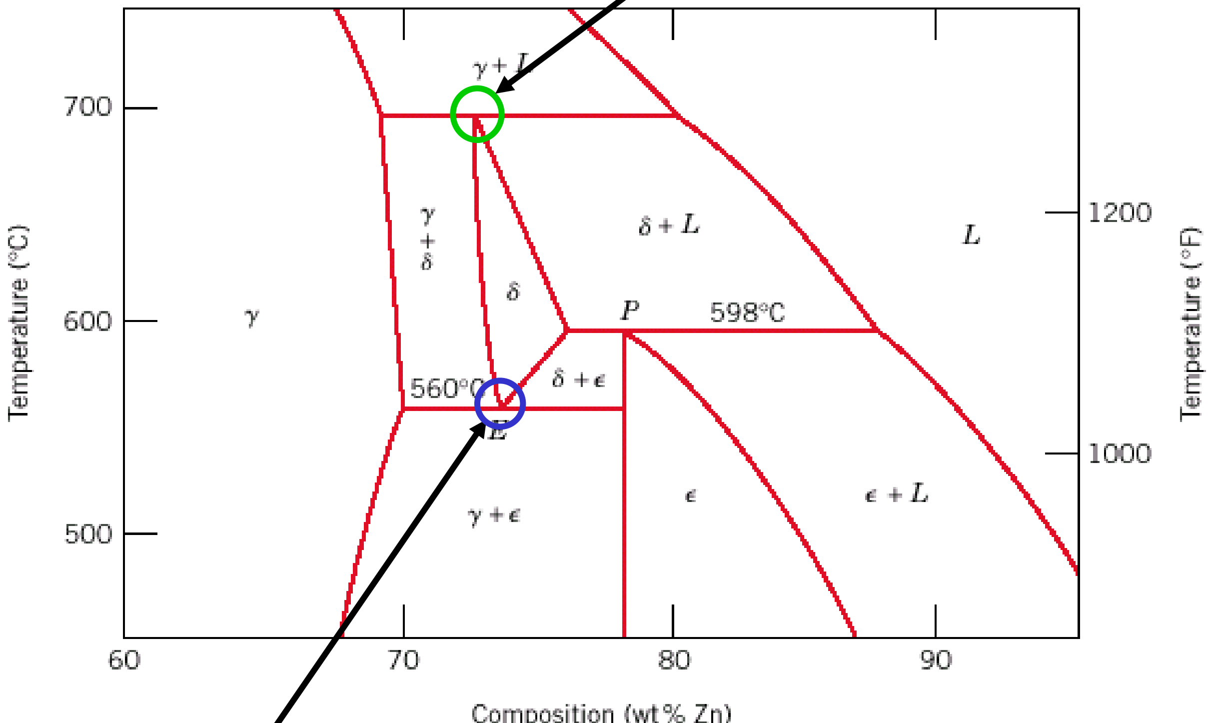
$$S_1 + L \rightleftharpoons S_2$$

$$\delta + L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \gamma \qquad (1493^{\circ}C)$$

Eutectoid & Peritectic

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

Cu-Zn Phase diagram



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

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

Iron-Carbon (Fe-C) Phase Diagram

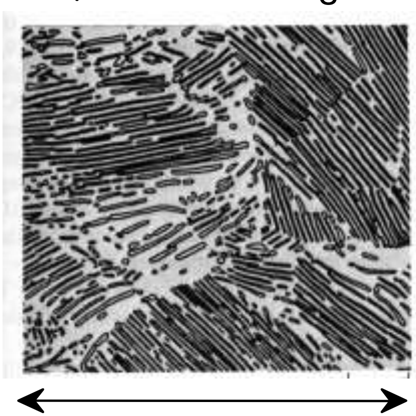
- 2 important points

  -Eutectic (*A*):

  $L \Rightarrow \gamma + Fe_3C$

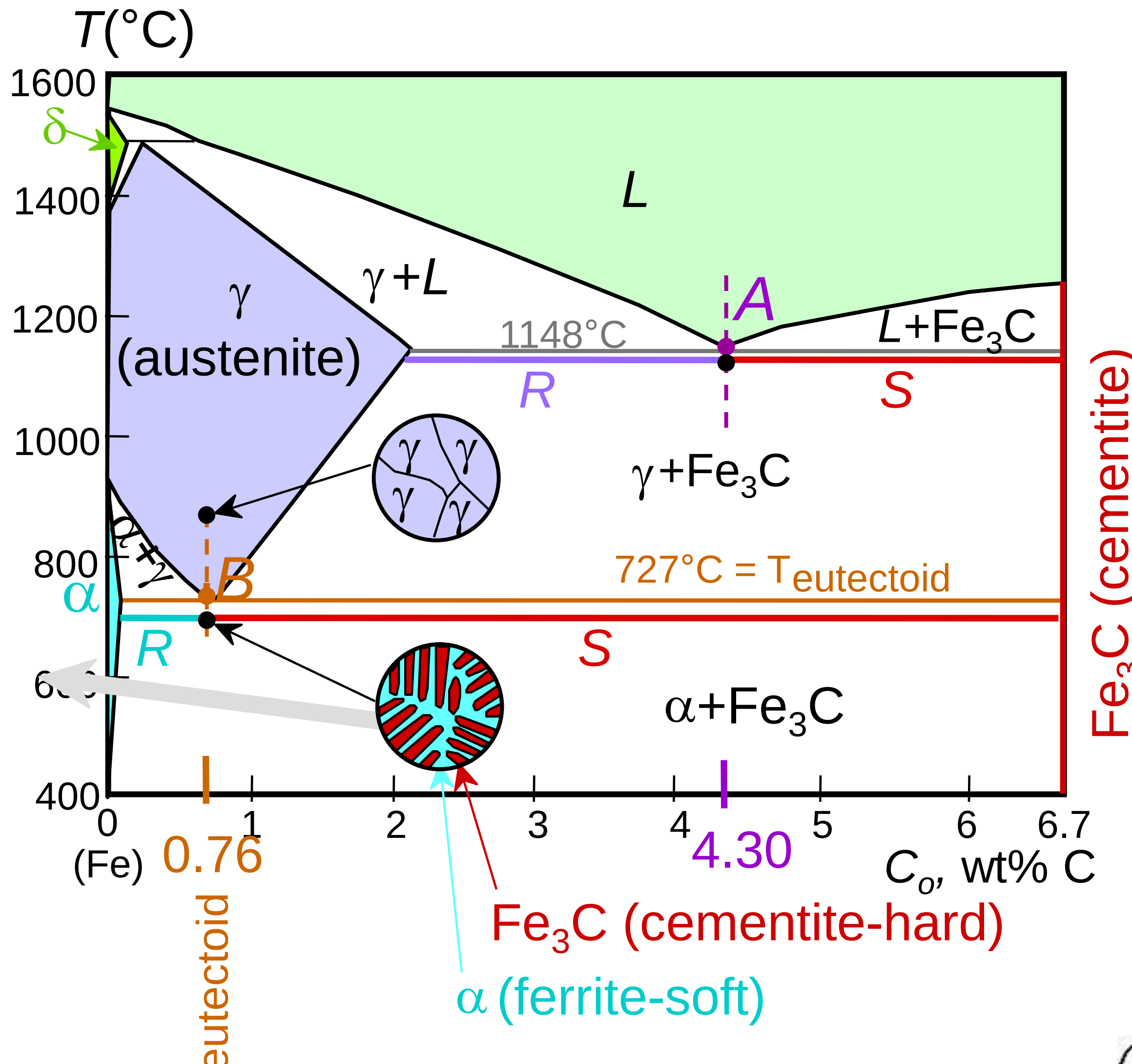
  -Eutectoid (*B*):

  $\gamma \Rightarrow \alpha + Fe_3C$



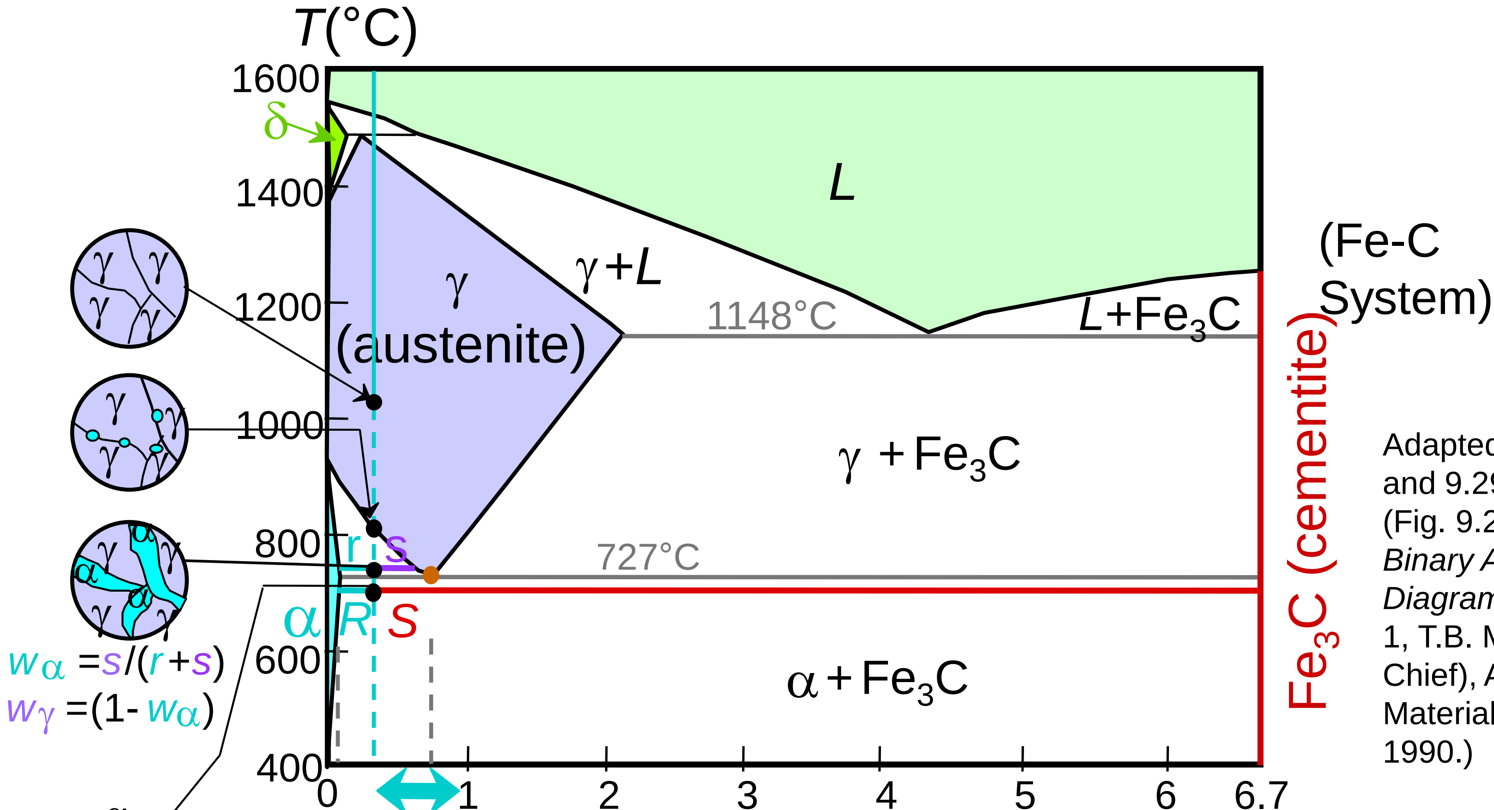
Result: Pearlite = alternating layers of α and Fe_3C phases

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

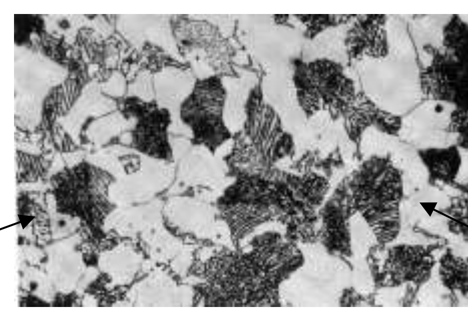


Adapted from Fig. 9.24, *Callister 7e*.

Hypoeutectoid Steel



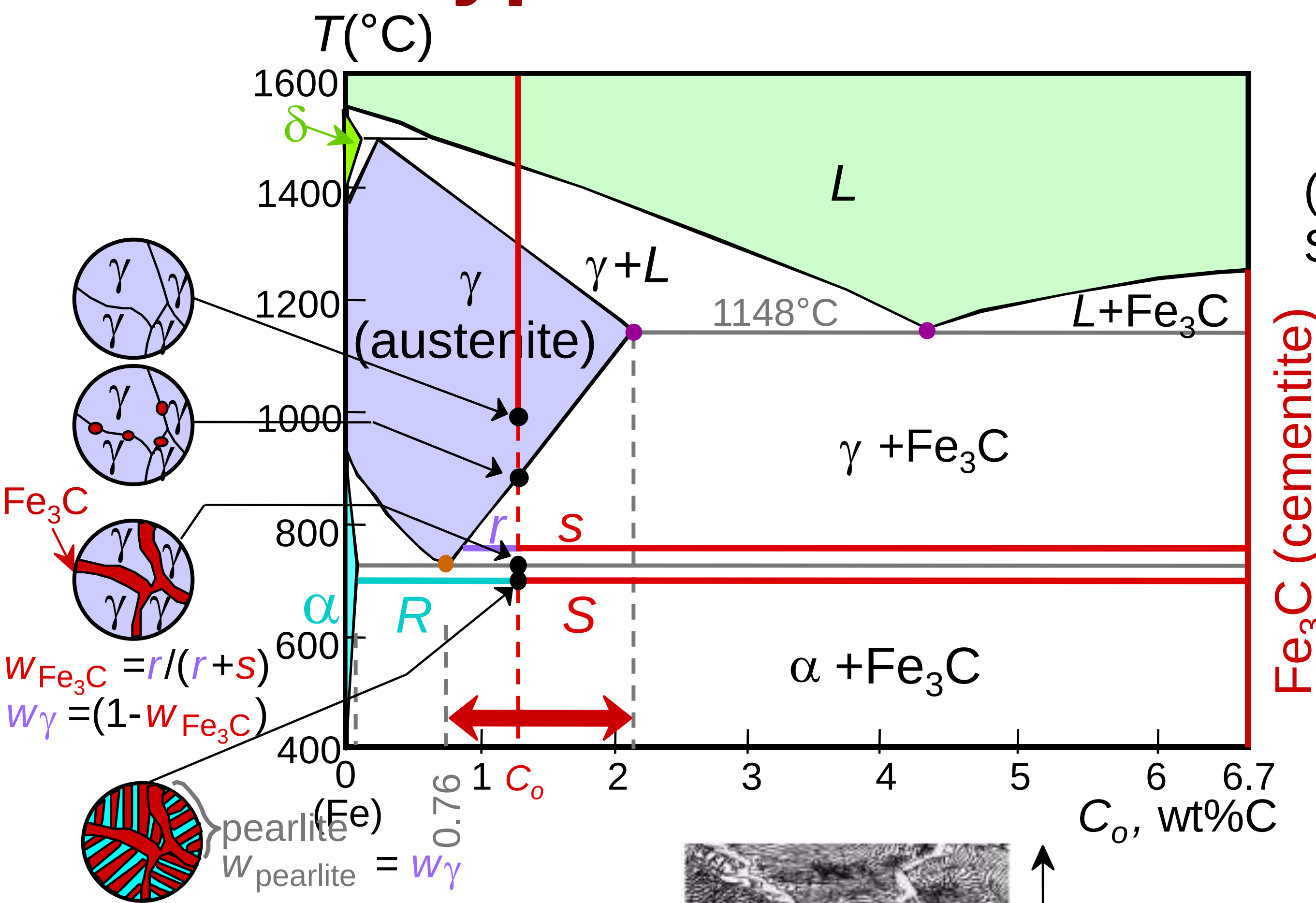
Adapted from Figs. 9.24 and 9.29, *Callister 7e*. (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



Hypoeutectoid steel

Adapted from Fig. 9.30, *Callister 7e*.

Hypereutectoid Steel



(Fe-C System)

$w_{Fe_3C} = r/(r+s)$

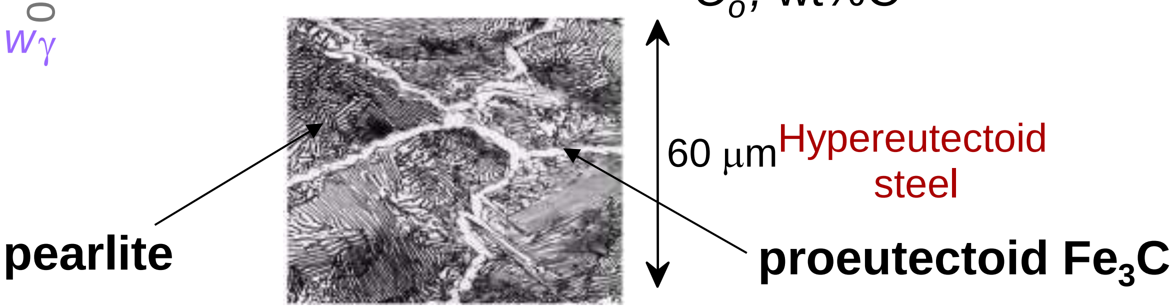
$w_\gamma = (1 - w_{Fe_3C})$

$w_{pearlite} = w_\gamma$

$w_\alpha = S/(R+S)$

$w_{Fe_3C} = (1 - w_\alpha)$

Adapted from Figs. 9.24 and 9.32, *Callister 7e*. (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 7e*.

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 (α)

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

c) the amount of pearlite and proeutectoid ferrite (α)

Chapter 9 – Phase Equilibria

Solution: a) composition of Fe_3C and ferrite (α)

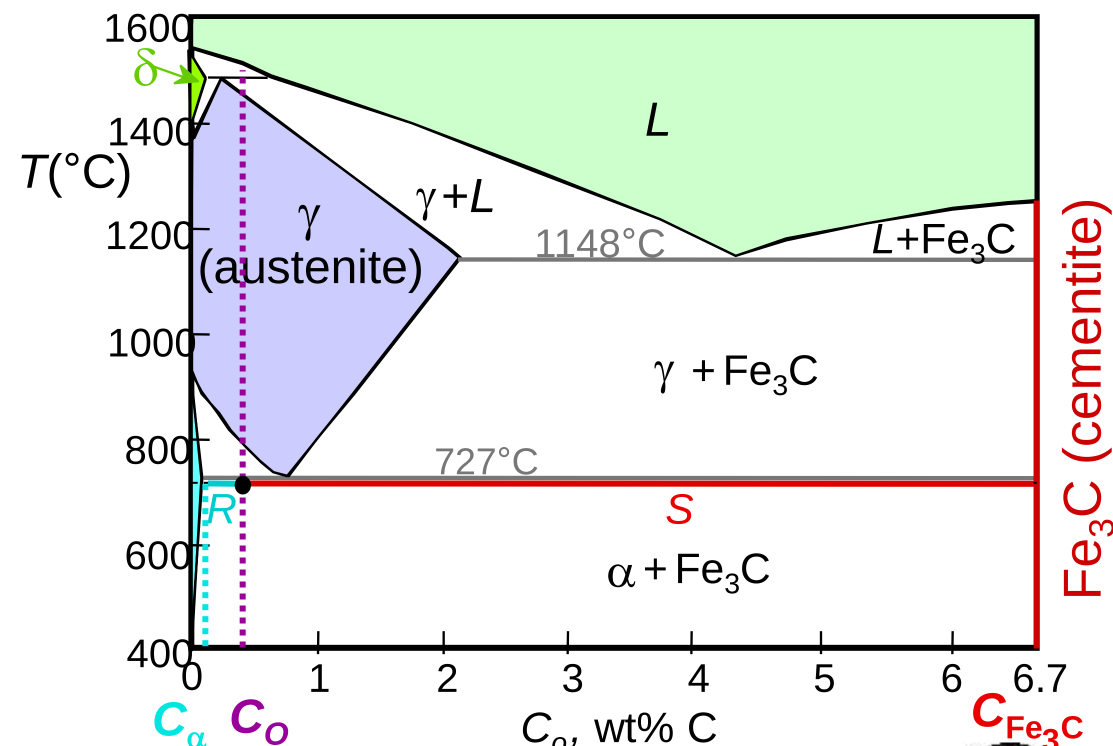
b) the amount of carbide (cementite) in grams that forms per 100 g of steel

C_O = 0.40 wt% C
C_α = 0.022 wt% C
C_{Fe_3C} = 6.70 wt% C

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

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

$$\boxed{\begin{array}{l} Fe_3C = 5.7 \text{ g} \\ \alpha = 94.3 \text{ g} \end{array}}$$



Chapter 9 – Phase Equilibria

c. the amount of pearlite and proeutectoid ferrite (α)

note: amount of pearlite = amount of γ just above T_E

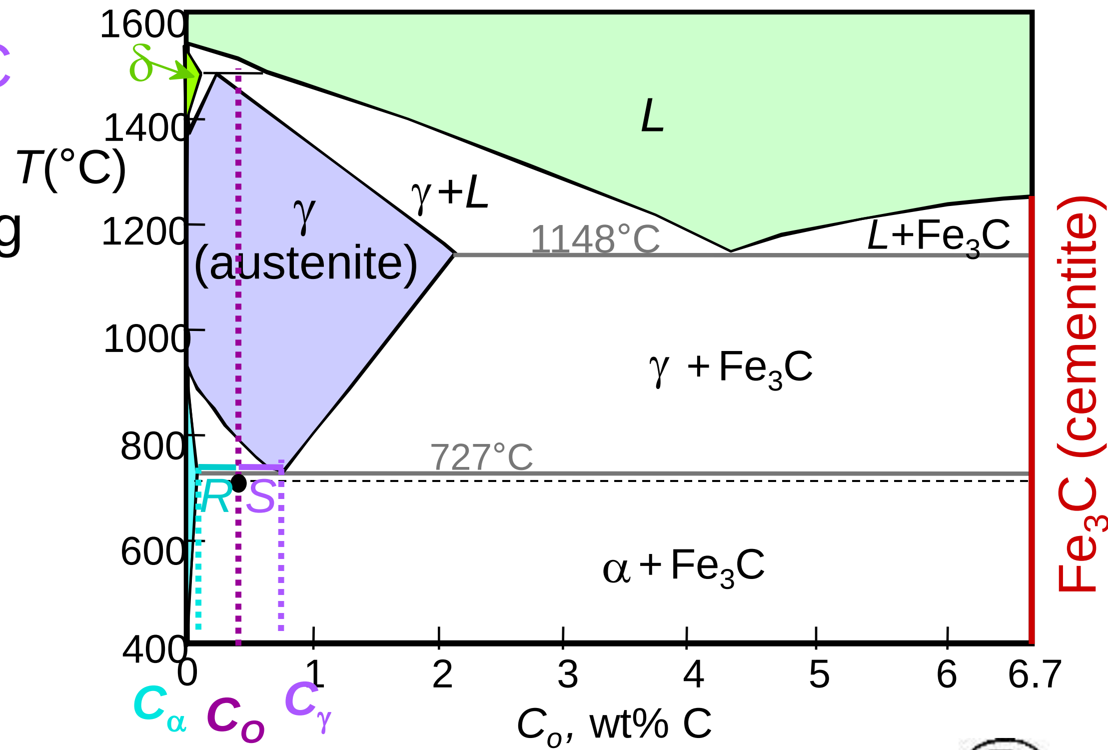
C_o = 0.40 wt% C

C_α = 0.022 wt% C

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

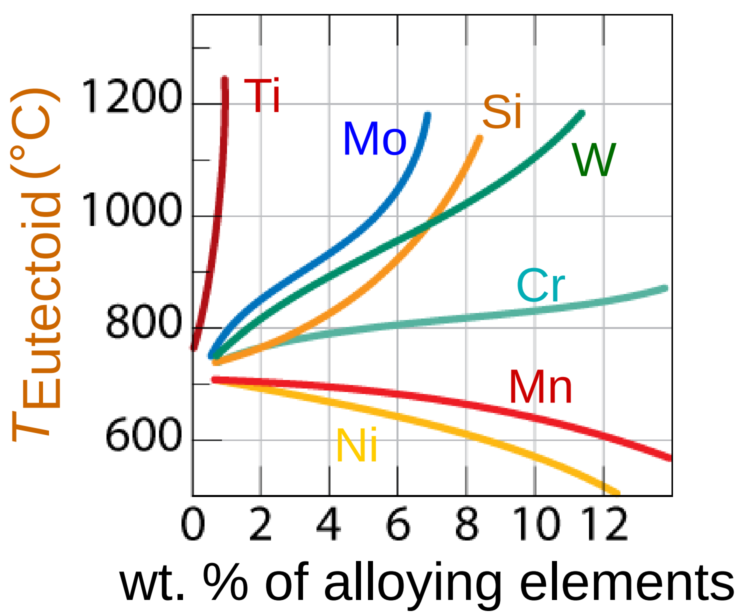
$$\frac{\gamma}{\gamma+\alpha} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha} \text{ x } 100 = 51.2 \text{ g}$$

pearlite = 51.2 g
proeutectoid α = 48.8 g



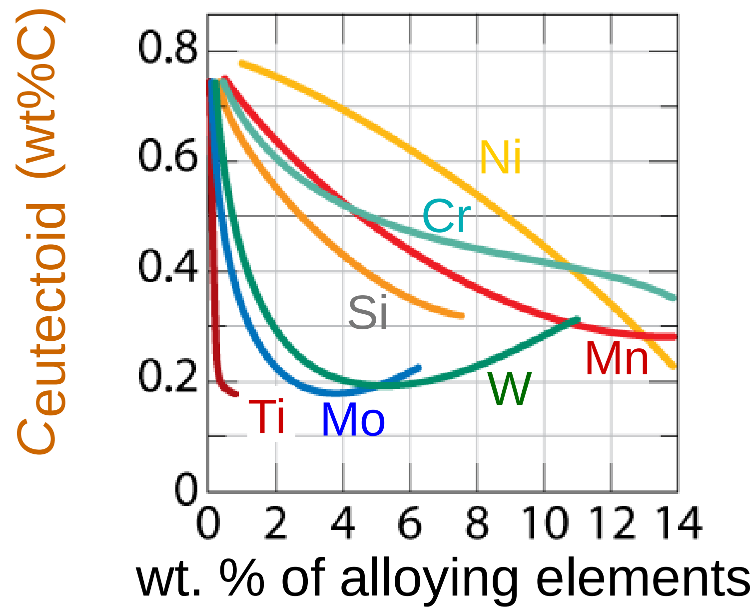
Alloying Steel with More Elements

- $T_{eutectoid}$ 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.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: