Phase Diagrams

- 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

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

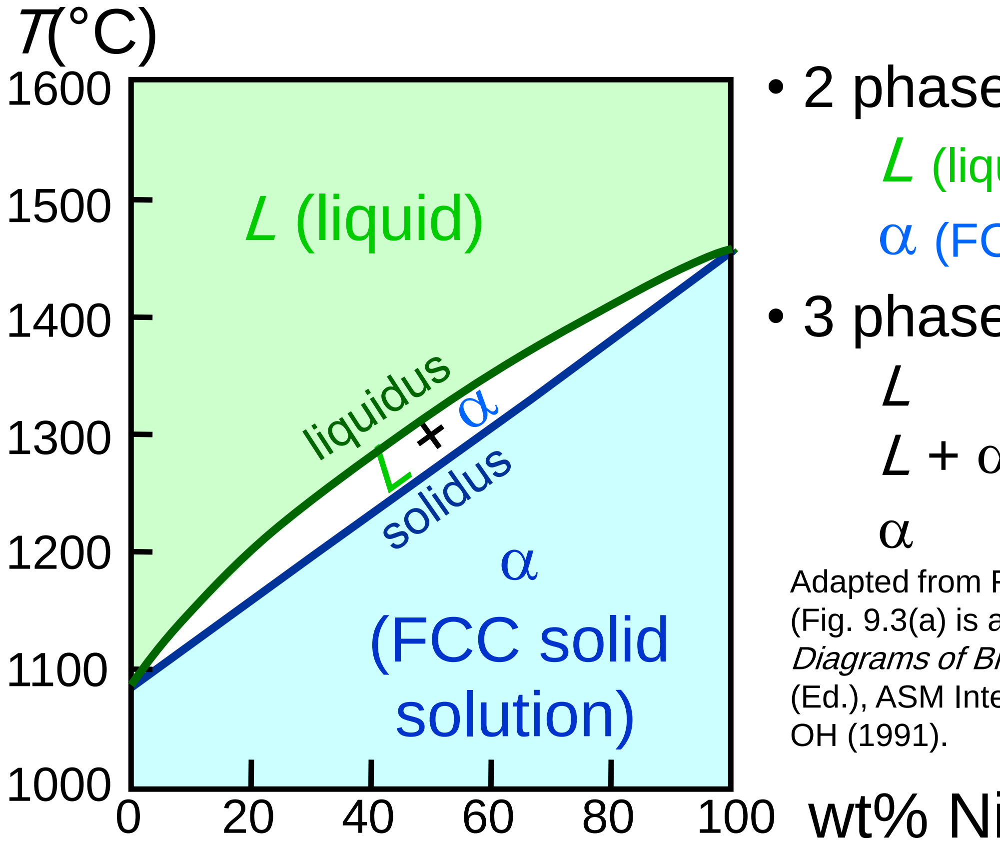
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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).

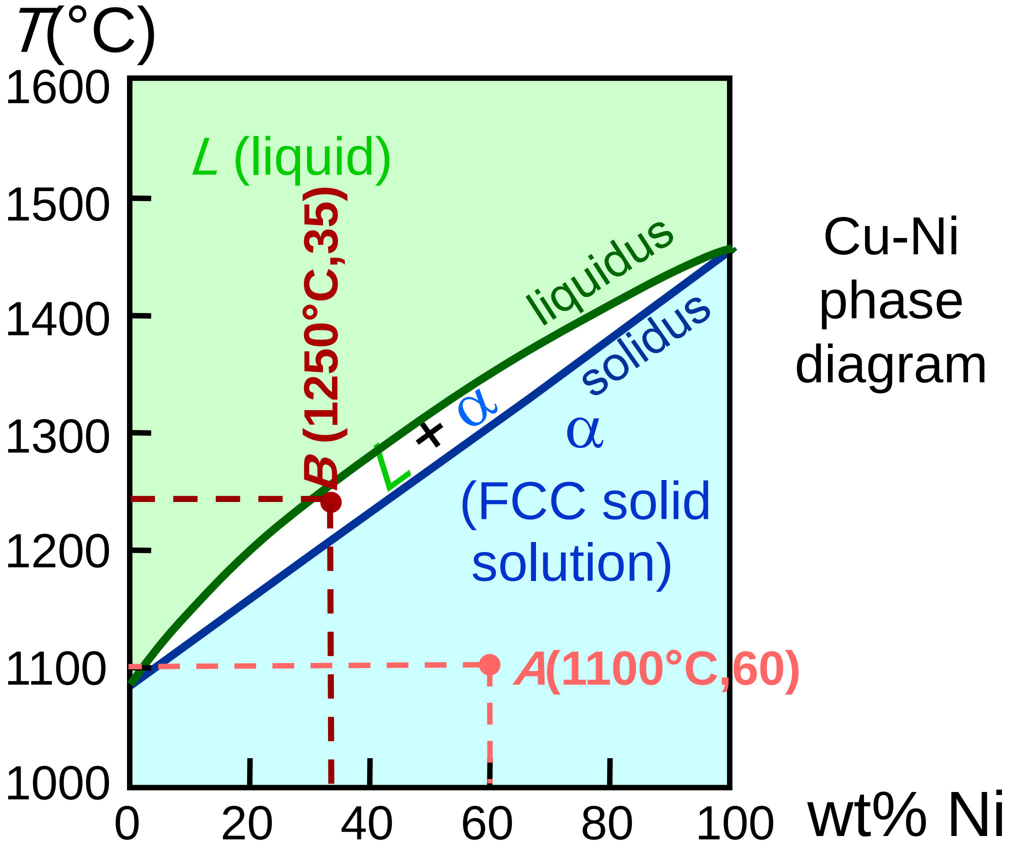
Phase Diagrams:
and types of phases

- 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* + α



Cu-Ni phase diagram

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

Phase Diagrams:
composition of phases

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

- Examples:

  C_o = 35 wt% Ni

  At T_A = 1320°C:

  Only Liquid (L)

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

  At T_D = 1190°C:

  Only Solid (α)

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

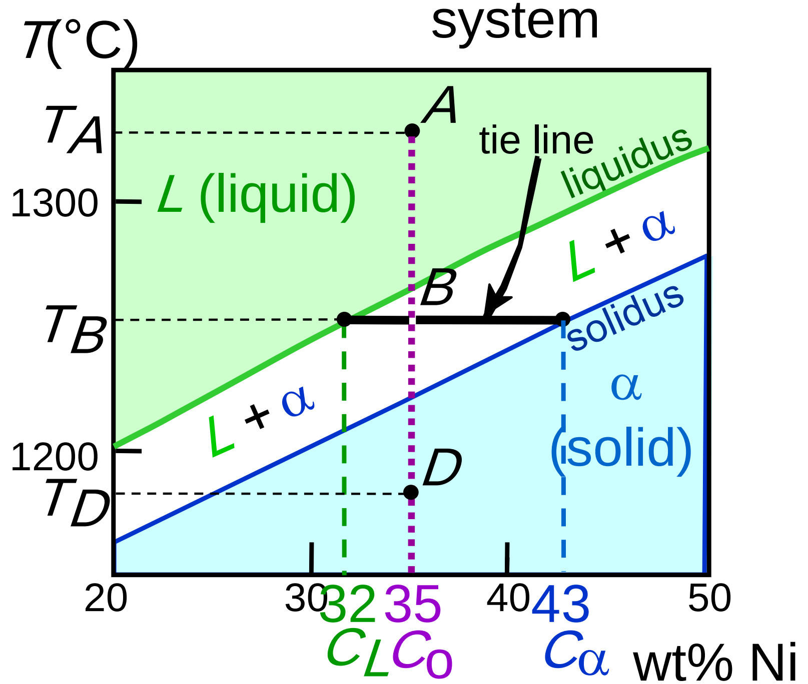
  At T_B = 1250°C:

  Both α and L

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

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

Cu-Ni system



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

Phase Diagrams:
weight fractions of phases

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

$C_o = 35$ wt% Ni

At T_A: Only Liquid (L)

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

At T_D: Only Solid (α)

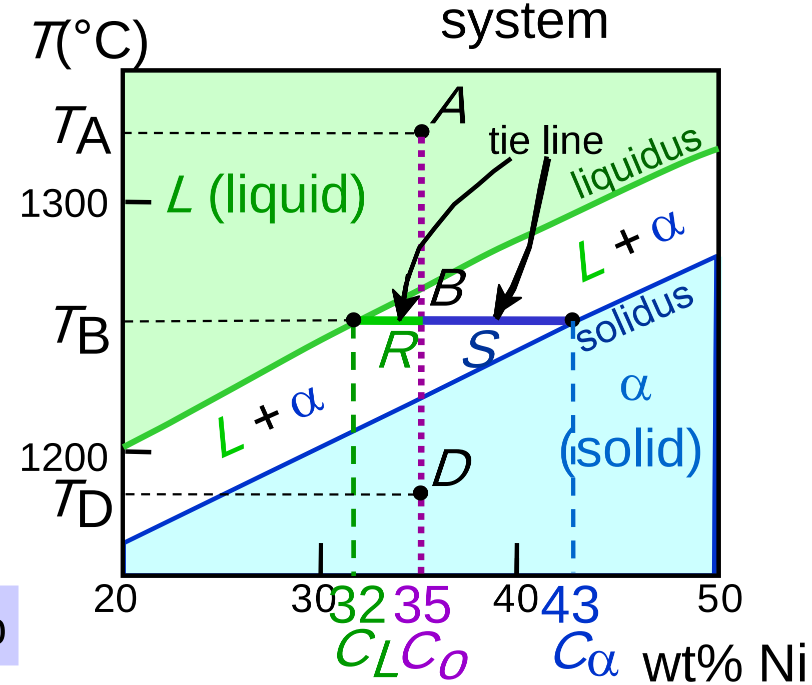
$W_L = 0$, $W_\alpha = 100$ wt%

At T_B: Both α and L

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

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

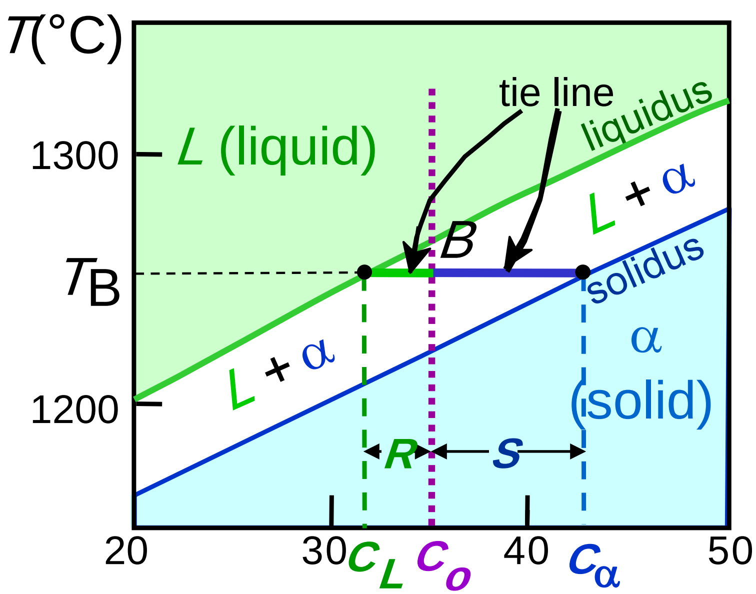
Cu-Ni system



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

The Lever Rule

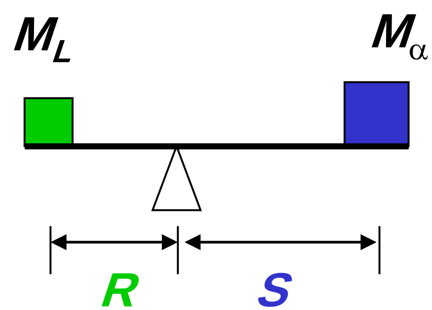
- Tie line – connects the phases in equilibrium with each other - essentially an isotherm



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

How much of each phase?

Think of it as a lever (teeter-totter)



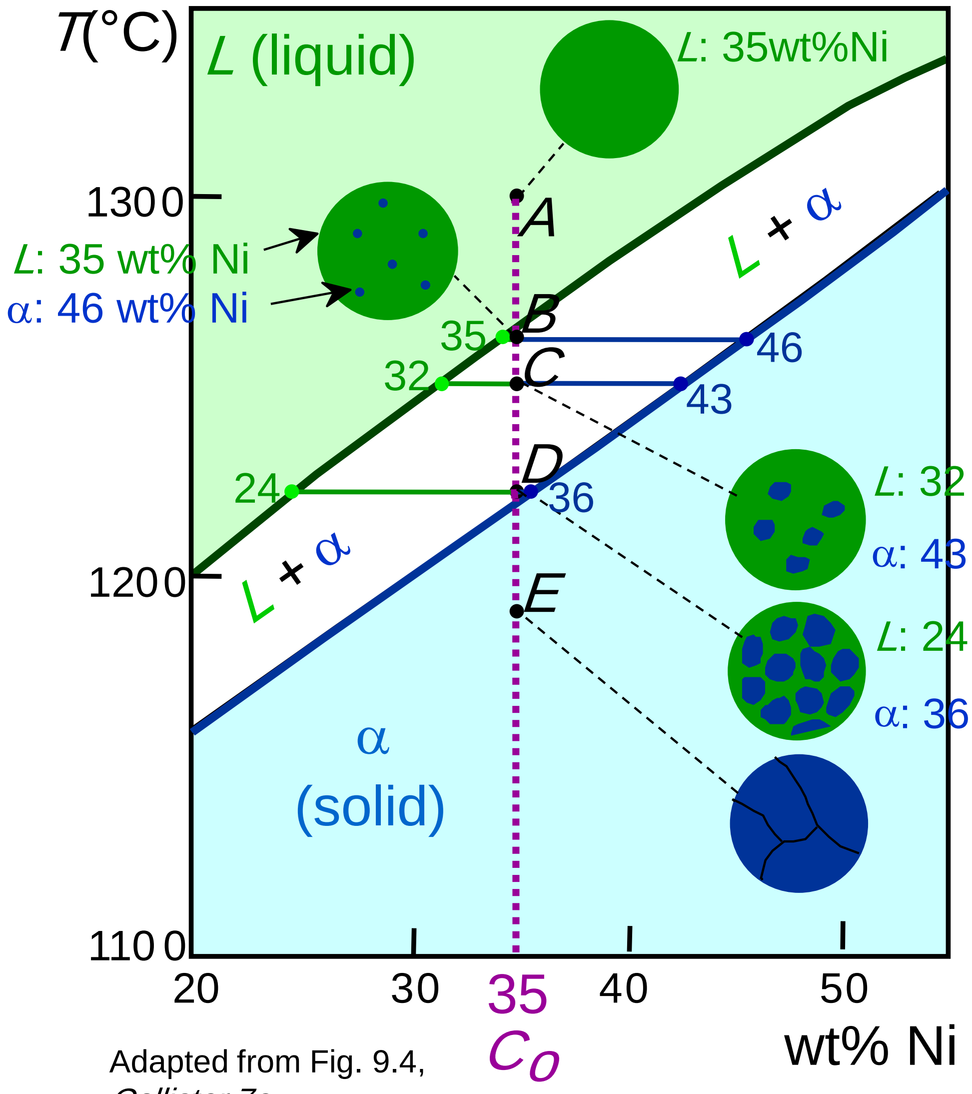
$$M_\alpha \cdot S = M_L \cdot R$$

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

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

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.



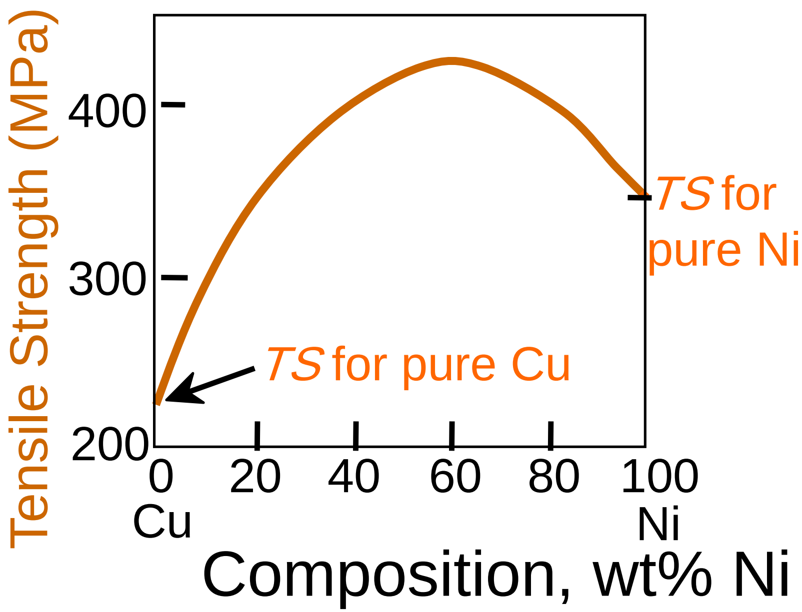
Cu-Ni system

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

Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

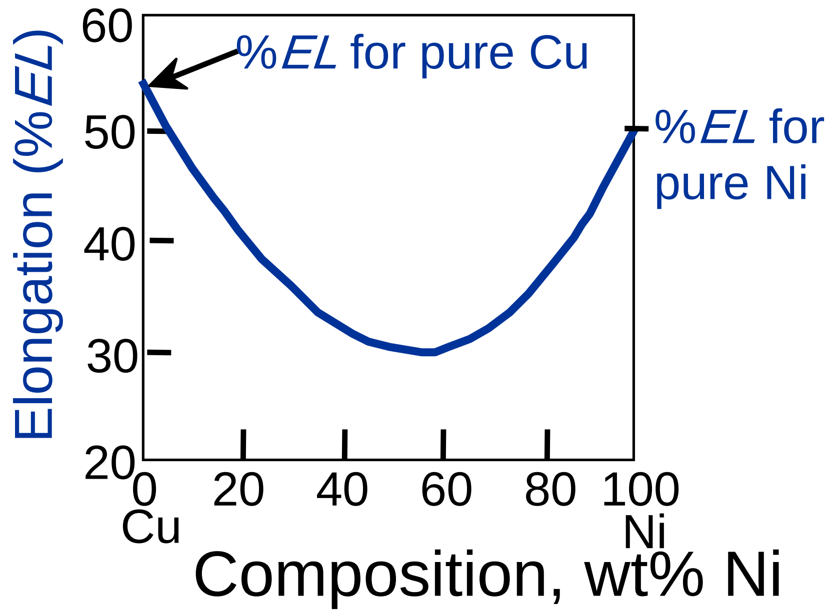
--Tensile strength (*TS*)



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

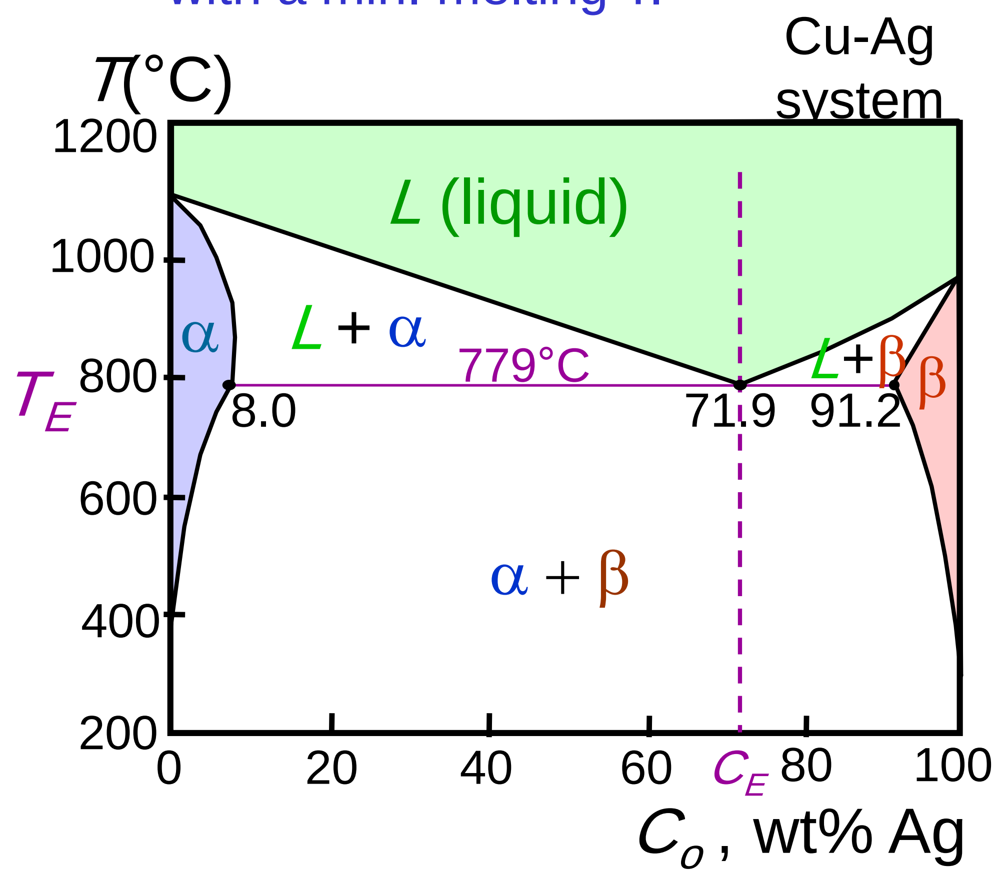
Binary-Eutectic Systems

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



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

- **Eutectic transition**

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

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

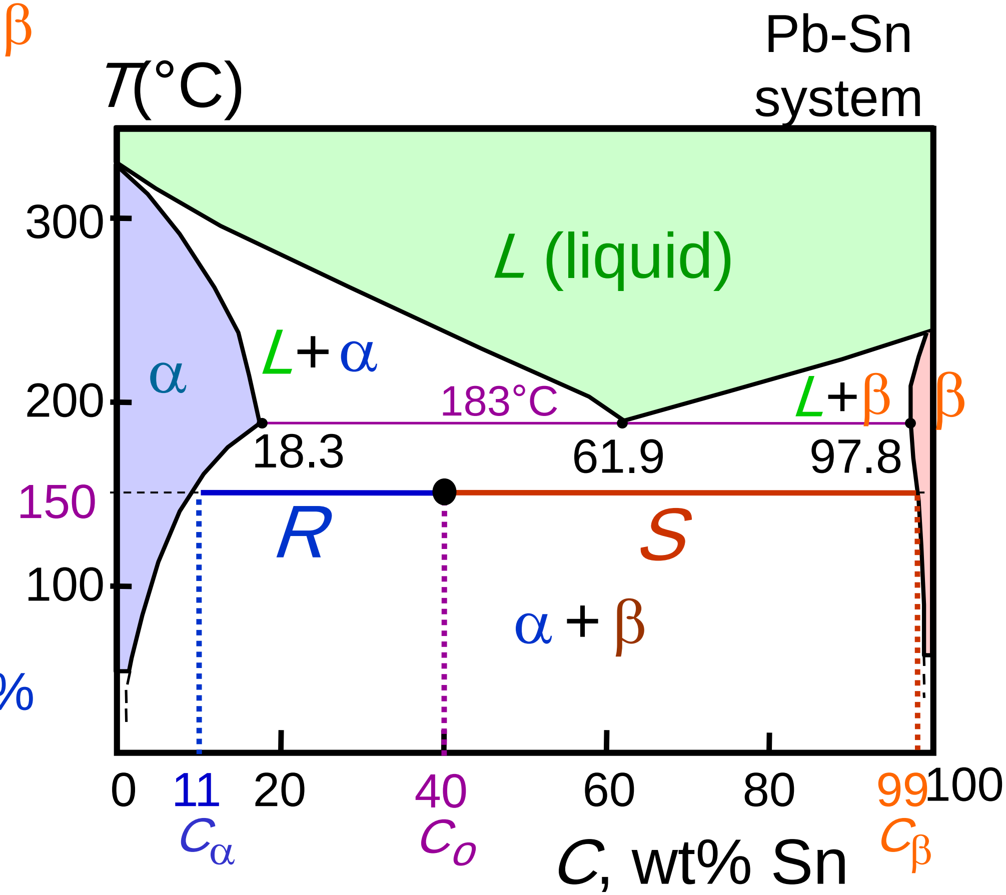
    C_β = 99 wt% Sn
  - --the relative amount of each phase:

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

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

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

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



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

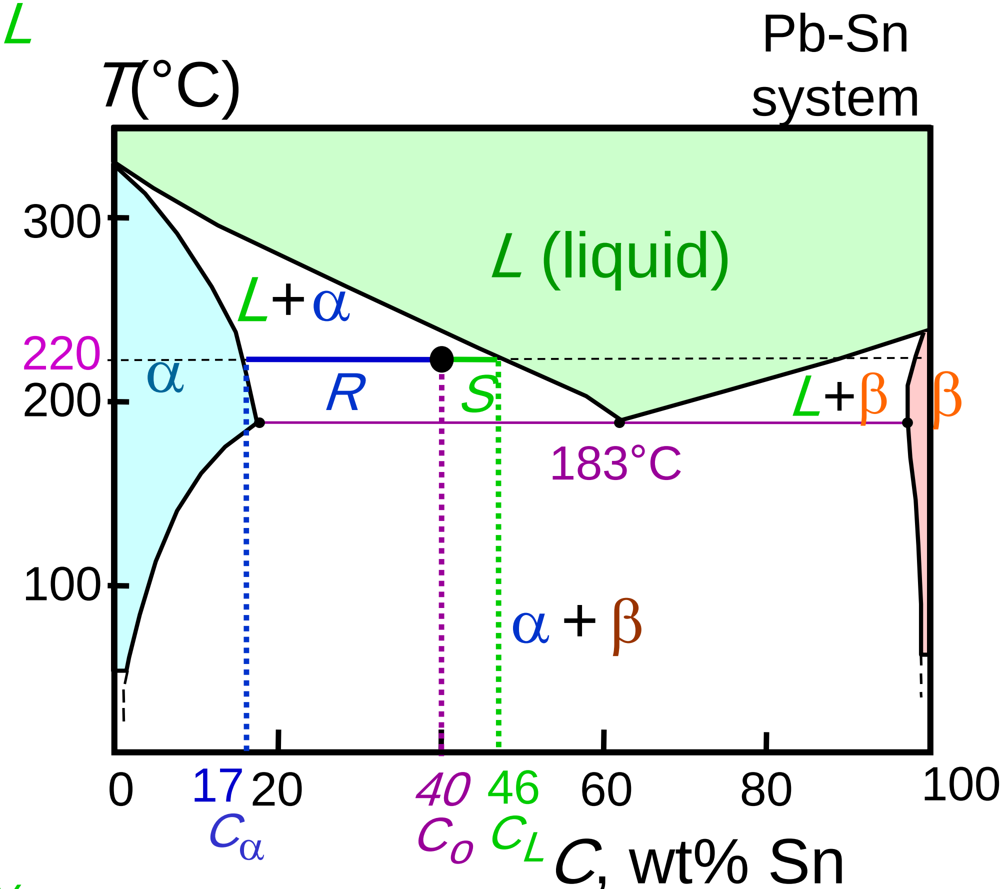
  C_α = 17 wt% Sn

  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.*

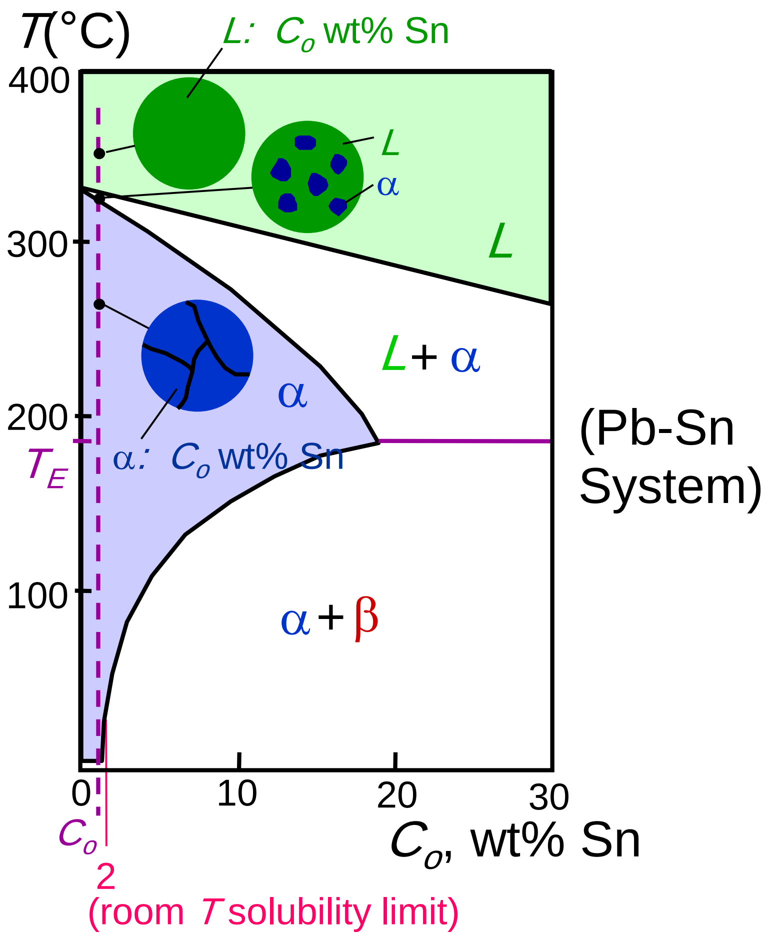
Microstructures in Eutectic Systems: I

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

  --at extreme ends

  --polycrystal of α grains

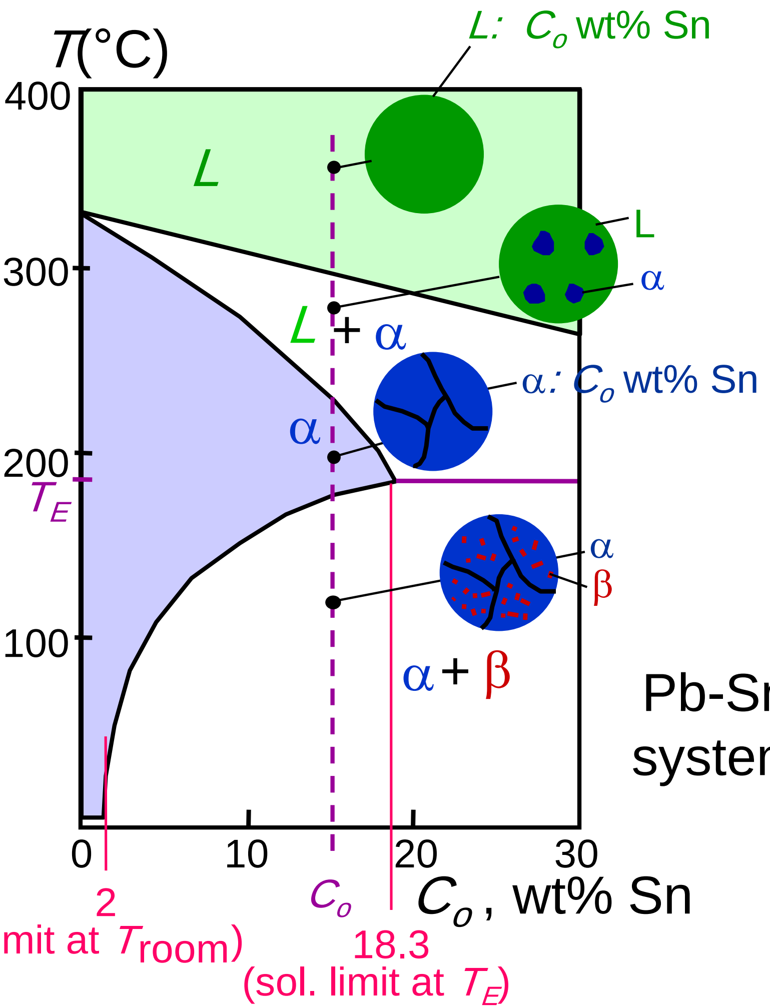
  i.e., only one solid phase.



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

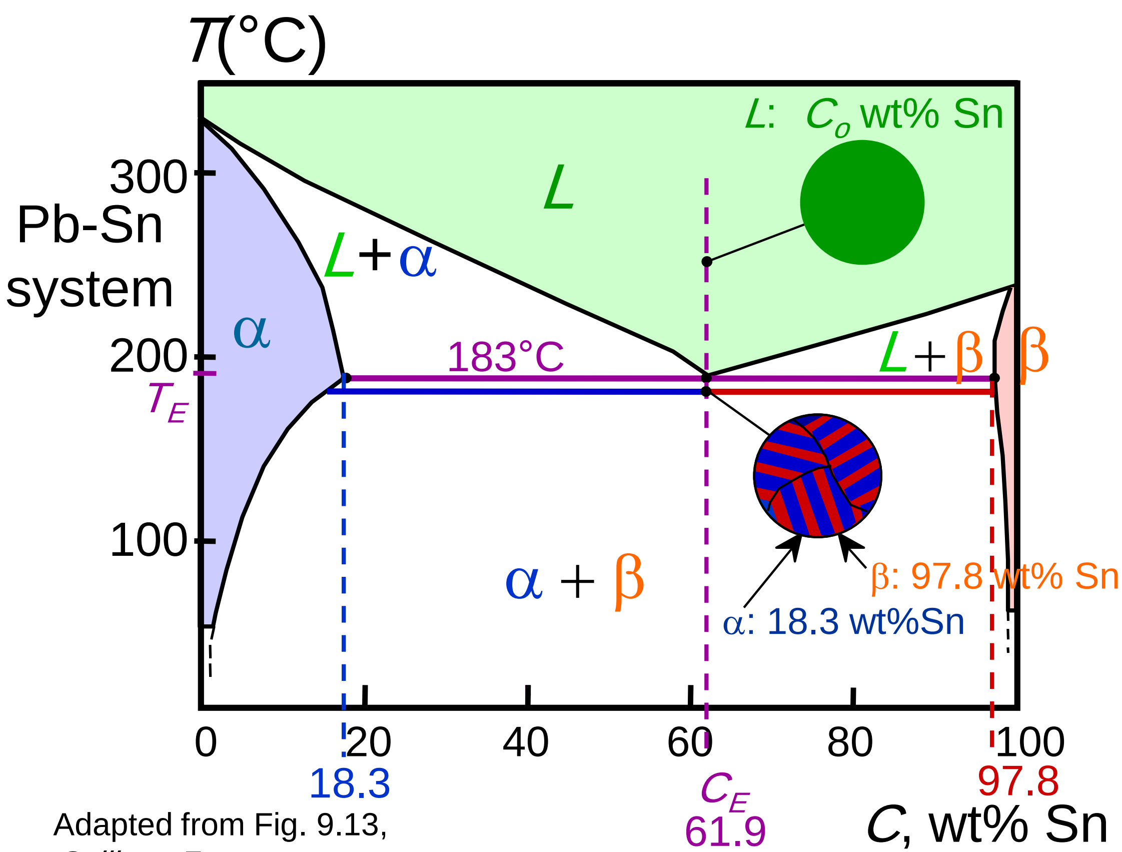


Pb-Sn system

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

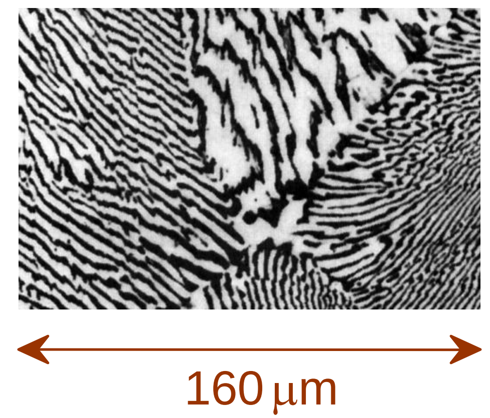
Microstructures in Eutectic Systems: III

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



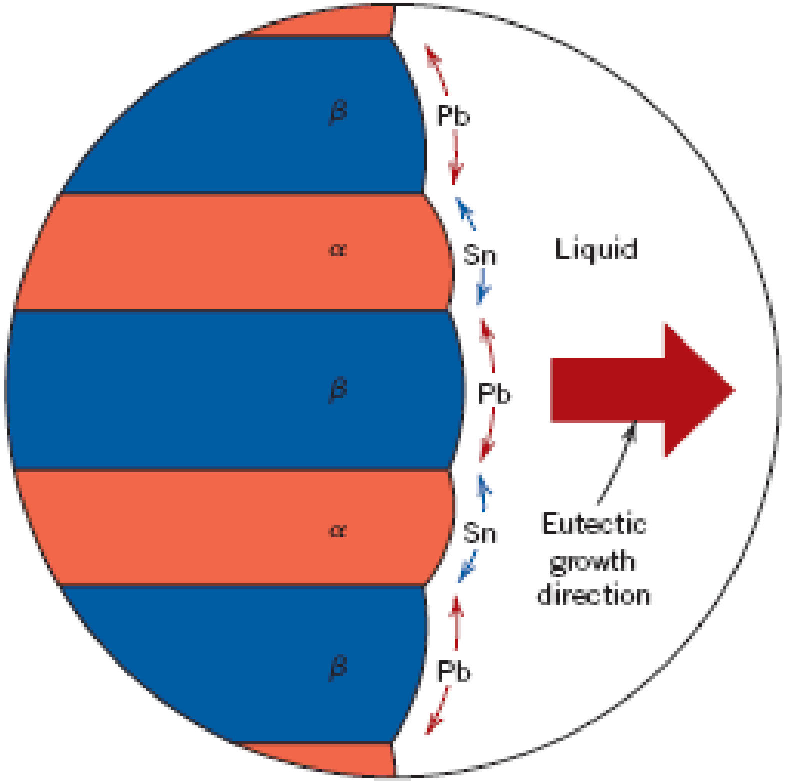
Adapted from Fig. 9.13, *Callister 7e.*

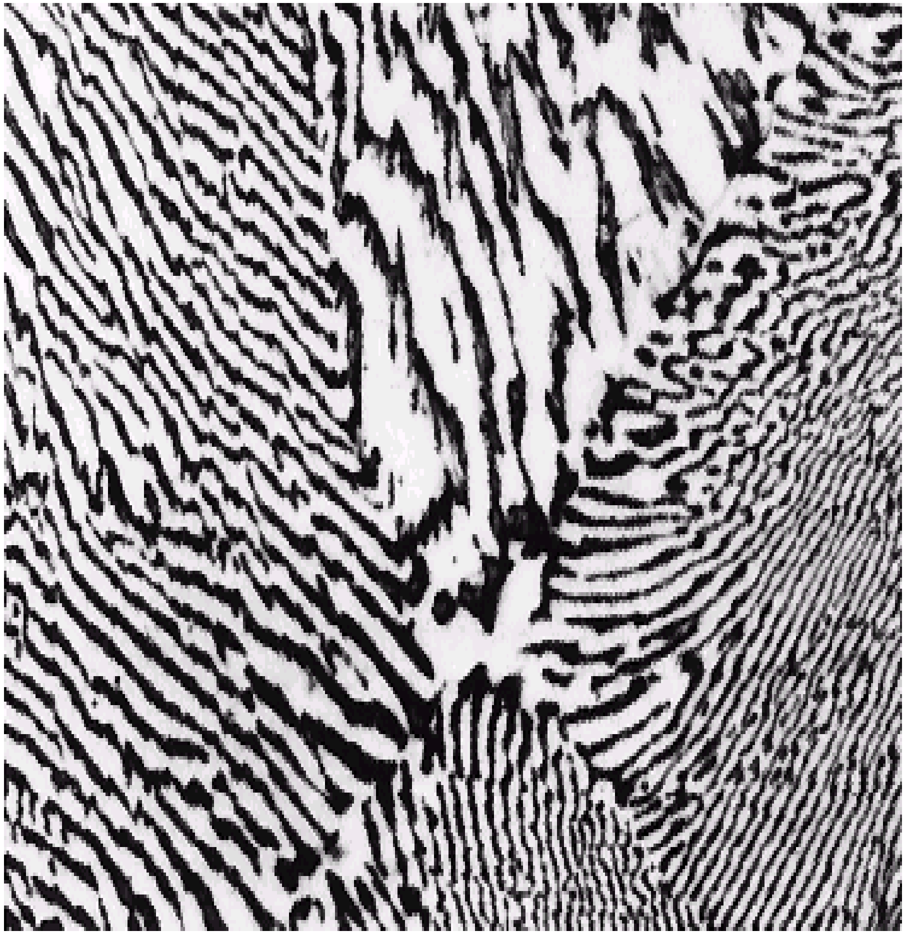
Micrograph of Pb-Sn eutectic microstructure



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

Lamellar Eutectic Structure

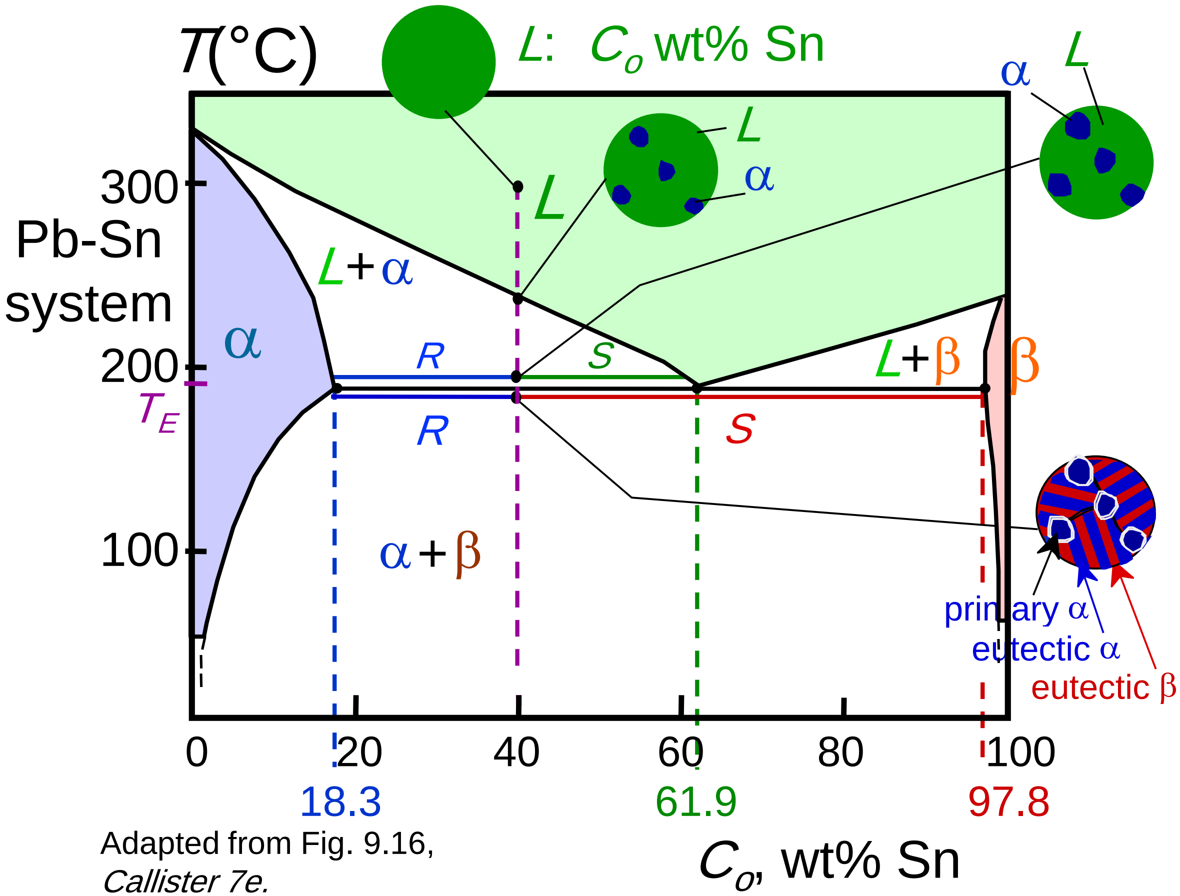




Adapted from Figs. 9.14 & 9.15, *Callister 7e.*

Microstructures in Eutectic Systems: IV

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



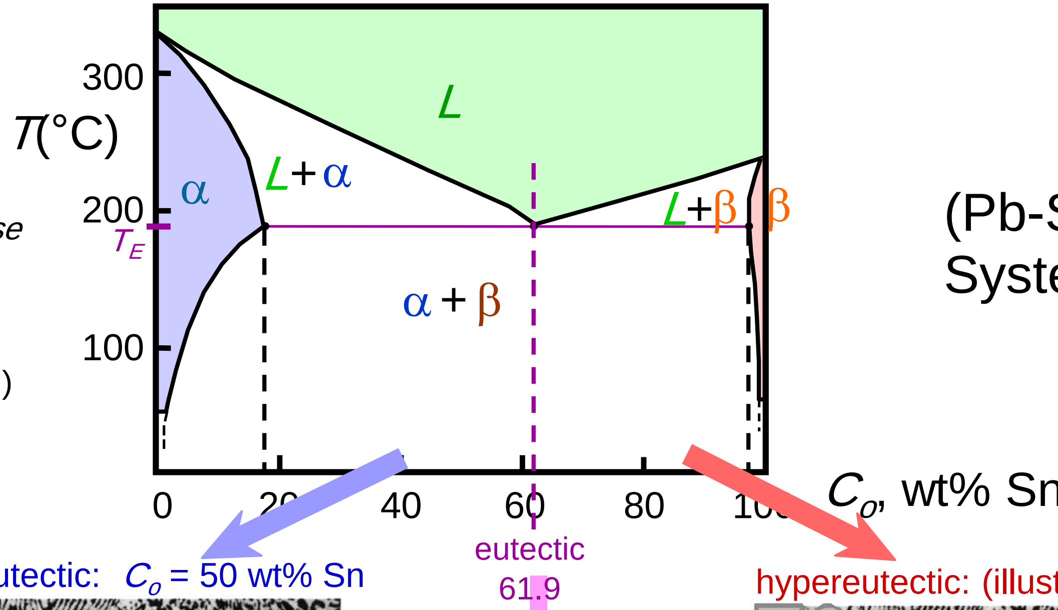
Adapted from Fig. 9.16, *Callister 7e.*

- 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%

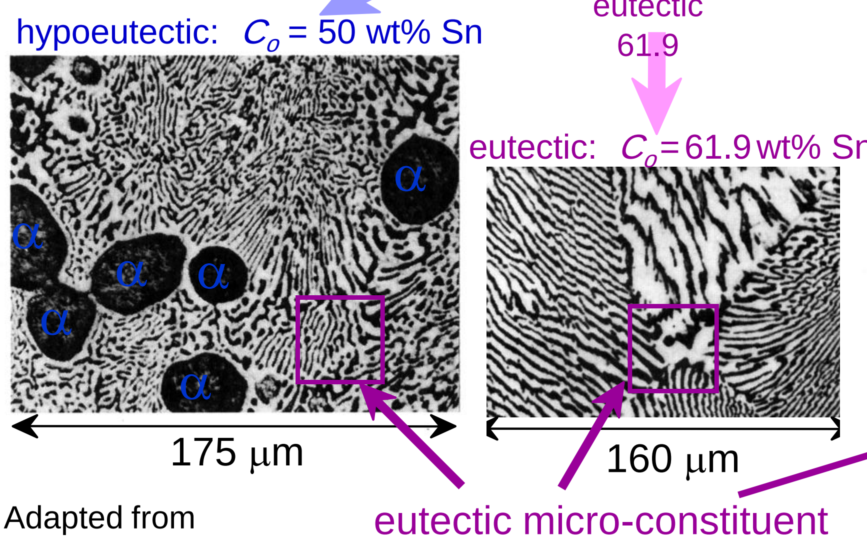
Hypoeutectic & Hypereutectic

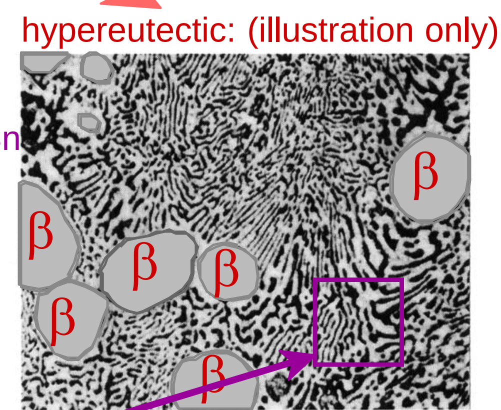
Adapted from Fig. 9.8, *Callister 7e.* (Fig. 9.8 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)



(Pb-Sn System)

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





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

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

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

Eutectoid

- 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

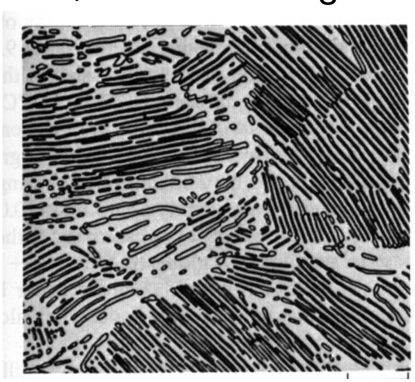
$$S_2 \rightleftharpoons S_1 + S_3$$

intermetallic compound
- cementite

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

Iron-Carbon (Fe-C) Phase Diagram

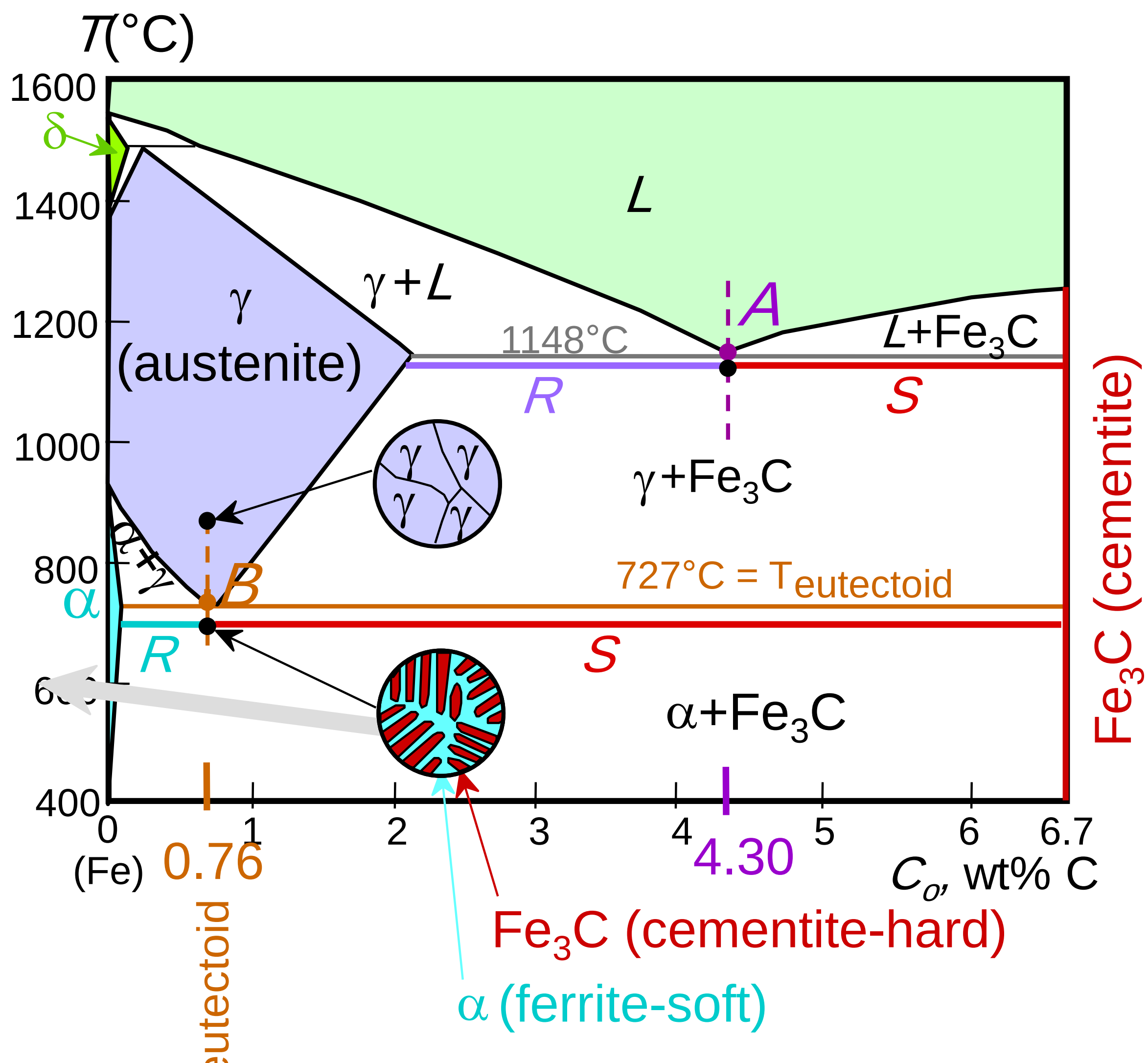
- 2 important points
  - -Eutectic (*A*): $L \Rightarrow \gamma + Fe_3C$
  - -Eutectoid (*B*): $\gamma \Rightarrow \alpha + Fe_3C$



120 μm

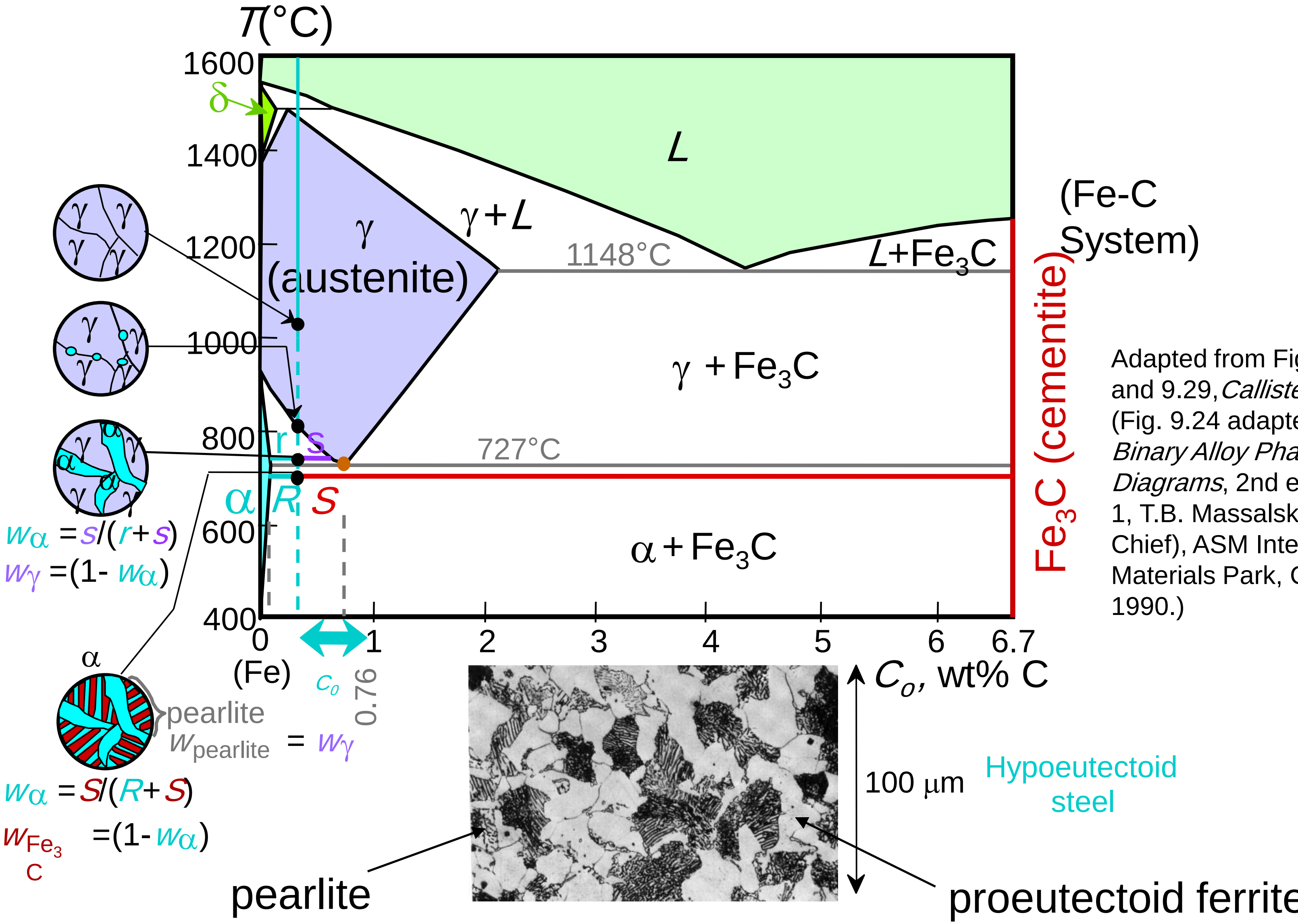
Result: Pearlite = alternating layers of α and Fe_3C phases

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



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

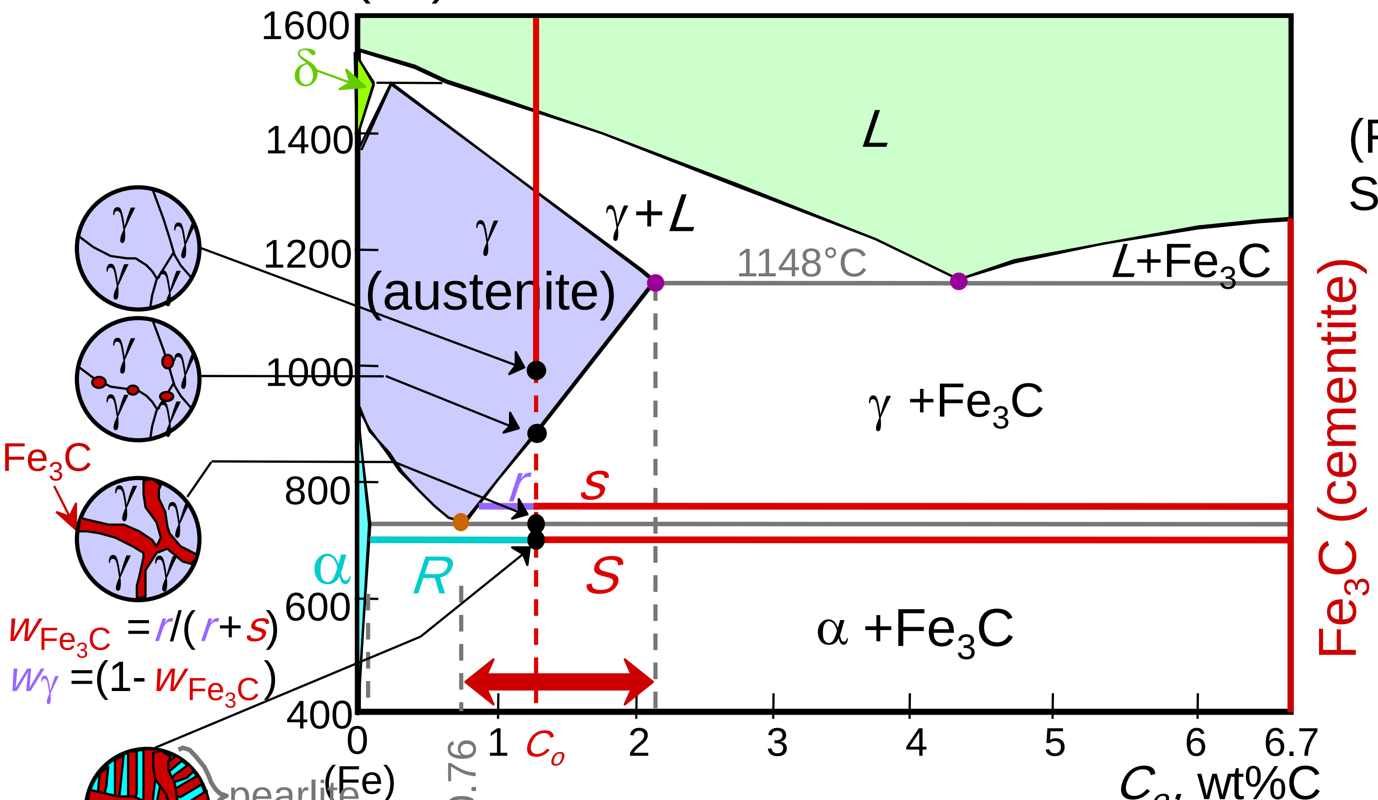
Hypoeutectoid Steel



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.)

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

Hypereutectoid Steel



(Fe-C System)

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)

Phase Equilibria

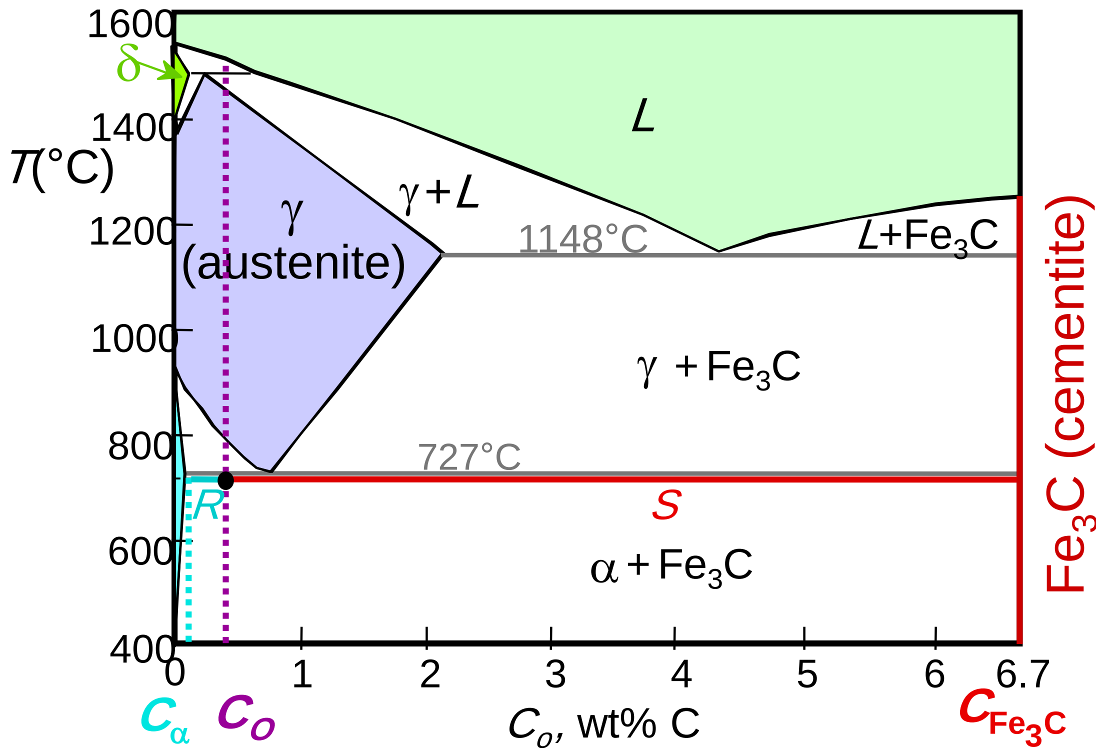
Solution: a) composition of Fe_3C and ferrite (α)

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

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

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



$Fe_3C = 5.7$ g
$\alpha = 94.3$ g

Chapter 9 – Phase Equilibria

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

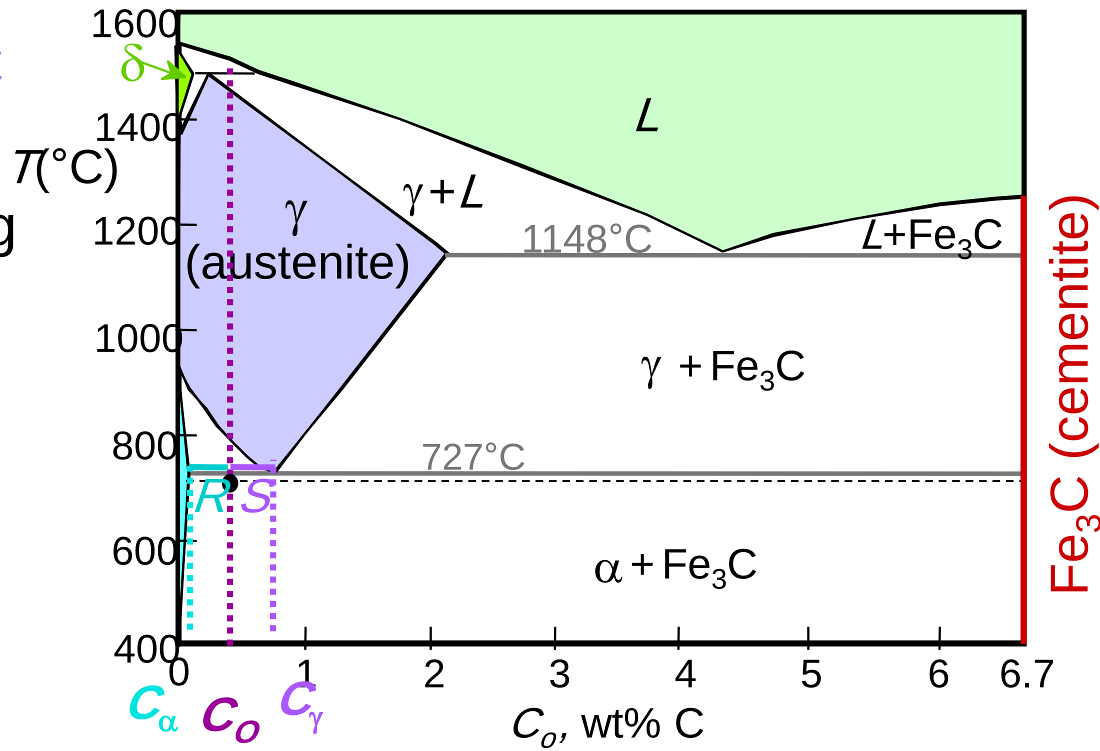
note: amount of pearlite = amount of γ just above T_E

C_o = 0.40 wt% C

C_α = 0.022 wt% C

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

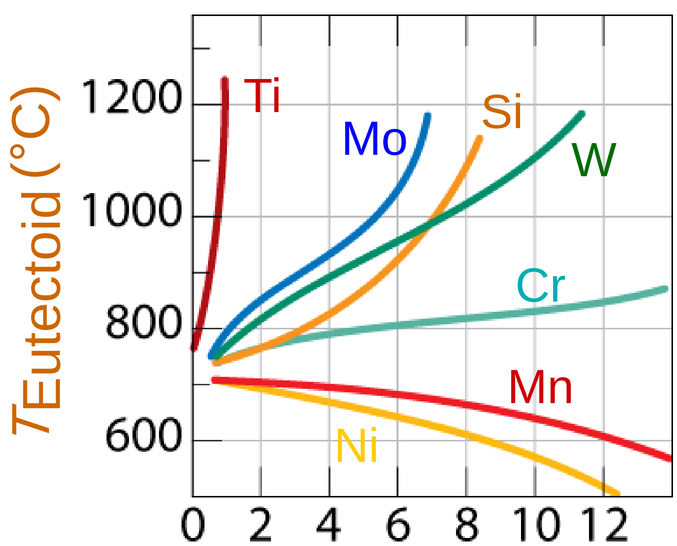
$$\frac{\gamma}{\gamma+\alpha} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha} \times 100 = 51.2 \text{ g}$$



pearlite = 51.2 g
proeutectoid α = 48.8 g

Alloying Steel with More Elements

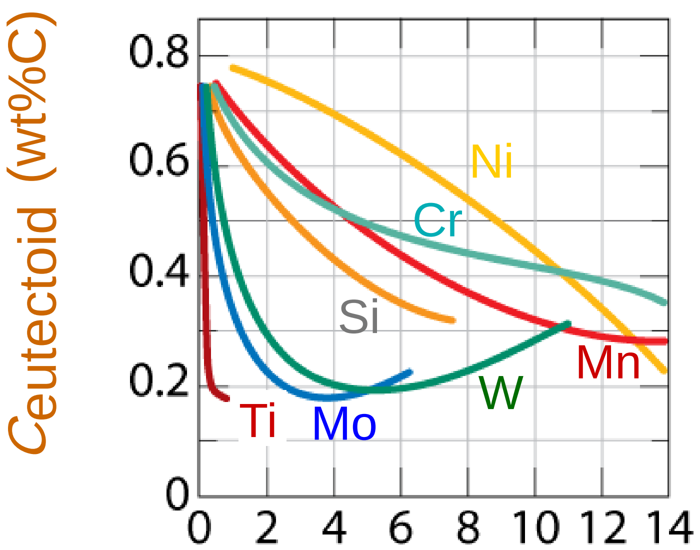
- $T_{eutectoid}$ changes:



wt. % of alloying elements

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:



wt. % of alloying elements

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.