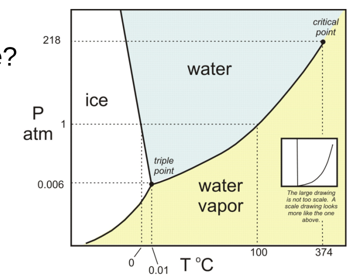
Chapter 9: Phase Diagrams

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*)

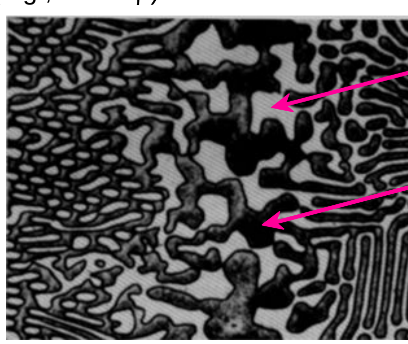
  then...
  How many phases form?
  What is the composition of each phase?
  What is the amount of each phase?



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

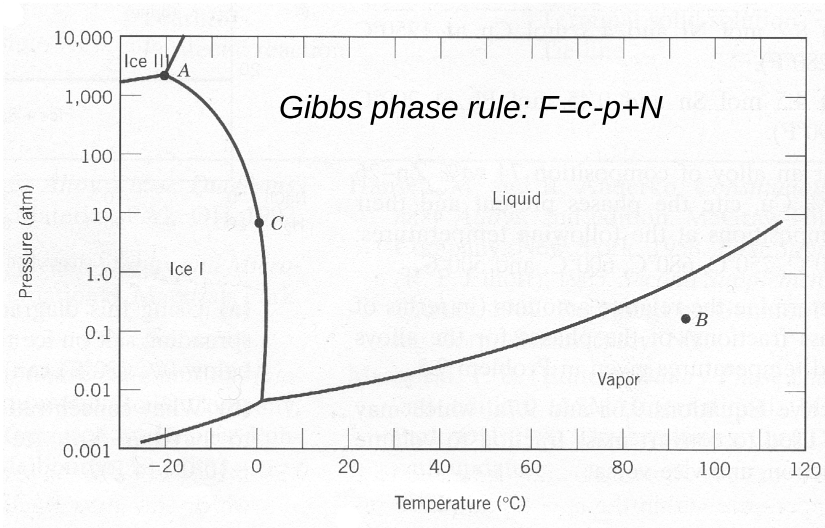


β (lighter phase)

α (darker phase)

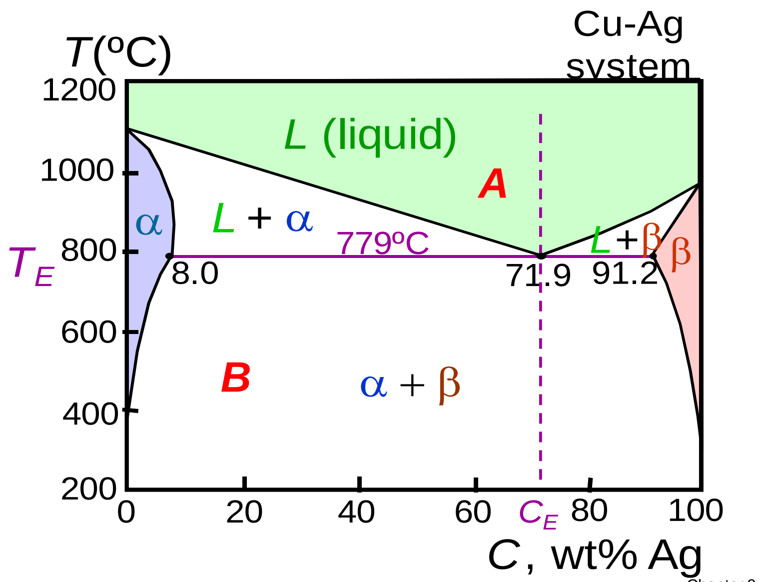
Adapted from chapter-opening photograph, Chapter 9, *Callister, Materials Science & Engineering: An Introduction, 3e.*

In the following Figure is shown the pressure–temperature phase diagram for H_2O. Apply the Gibbs phase rule at points A, B, and C; that is, specify the number of degrees of freedom at each of the points—that is, the number of externally controllable variables that need be specified to completely define the system.

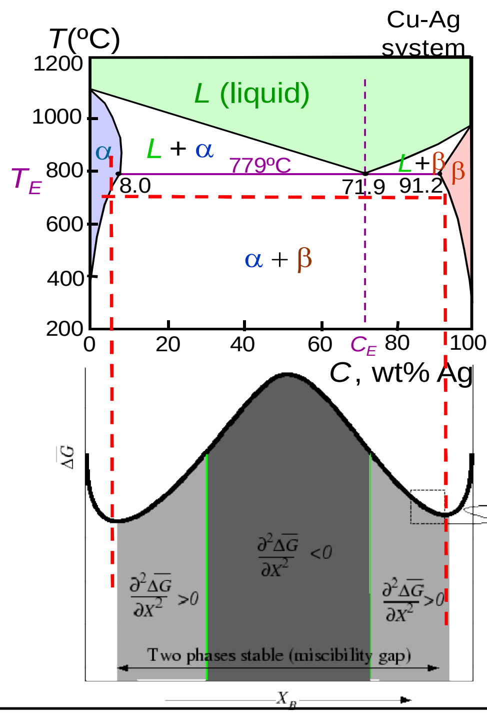


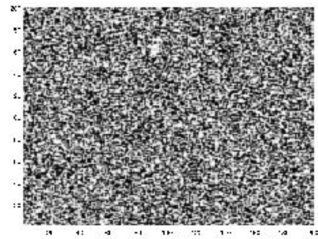
Chapter 9 - 3

Apply the Gibbs phase rule at points A and B, and specify the number of degrees of freedom.

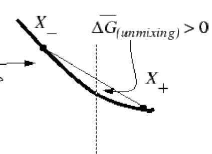


Chapter 9 -





Spinodal Decomposition



Phase Equilibria: Solubility Limit

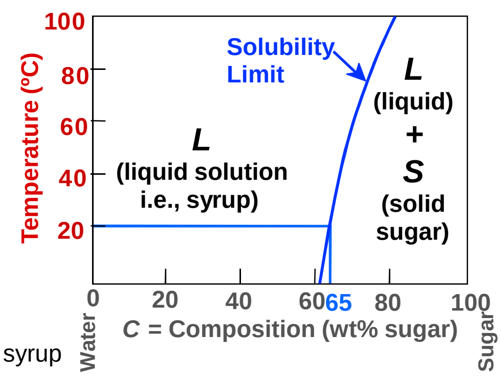
- Solubility Limit:
  Maximum concentration for which only a single phase solution exists.

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

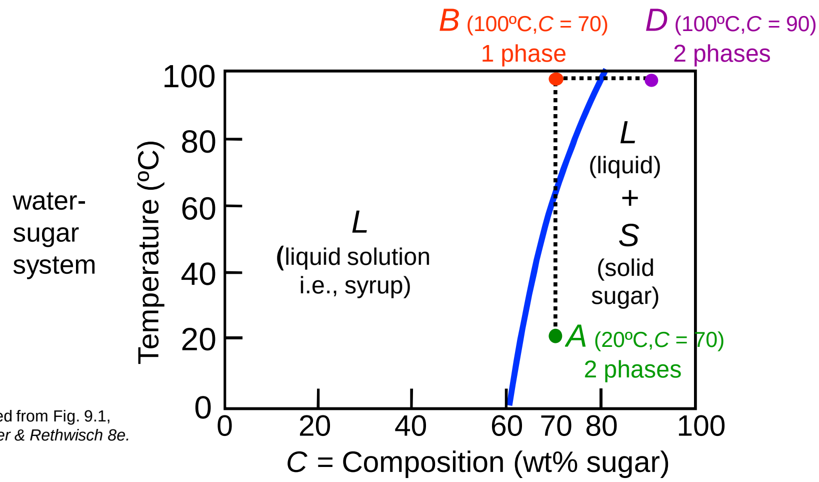
Adapted from Fig. 9.1, *Callister & Rethwisch 8e.*

Sugar/Water Phase Diagram



Effect of Temperature & Composition

- Altering *T* can change # of phases: path *A* to *B*.
- Altering *C* can change # of phases: path *B* to *D*.



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

Criteria for Solid Solubility

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

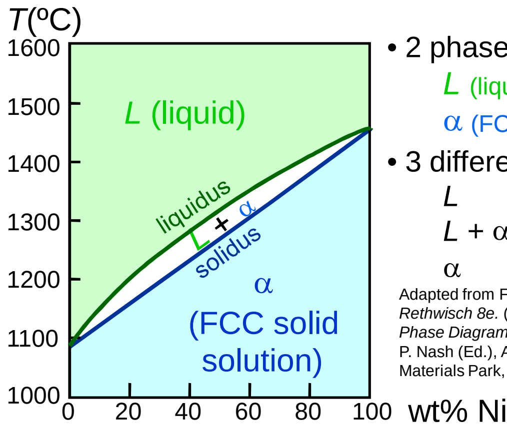
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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



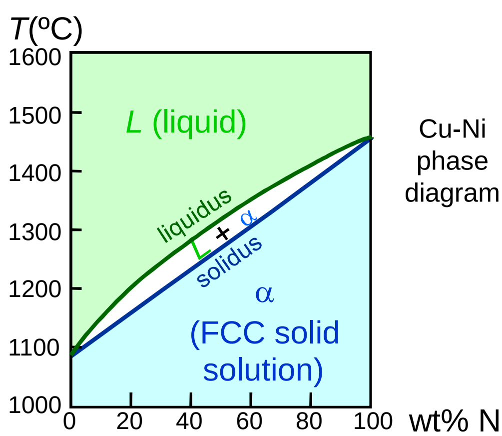
- 2 phases:
  - *L* (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + α
  - α

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).

Chapter 9 - 9

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).

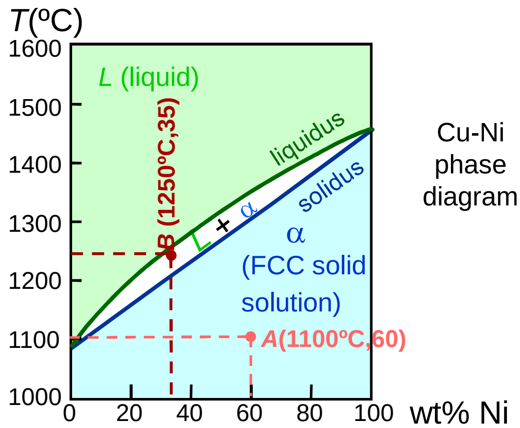
Chapter 9 - 10

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

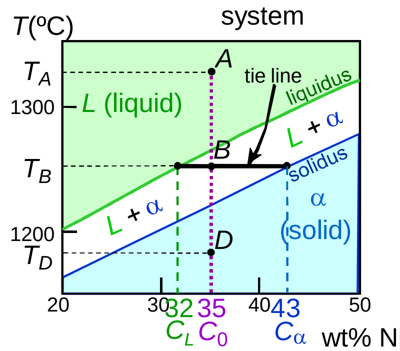
Adapted from Fig. 9.3(a), *Callister & Rethwisch 8e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

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
  $C_L = C_{liquidus}$ (= 32 wt% Ni)
  $C_\alpha = C_{solidus}$ (= 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_α = 0

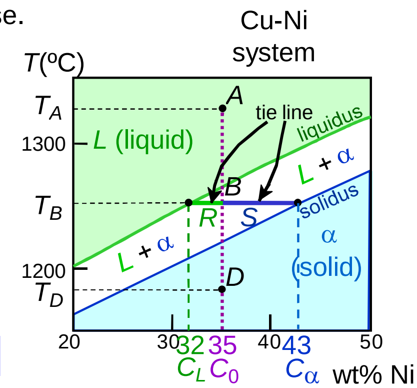
At T_D : Only Solid (α) present

W_L = 0, W_α = 1.00

At T_B : Both α and L present

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

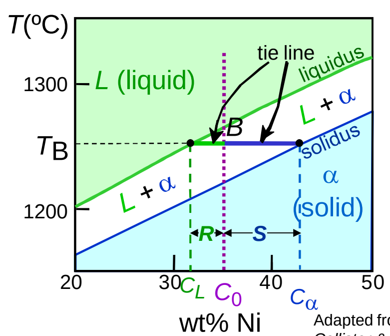
$$W_\alpha = \frac{R}{R+S} = 0.27$$



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).

The Lever Rule

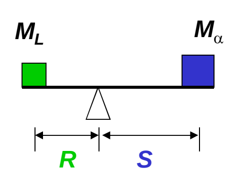
- Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm



Adapted from Fig. 9.3(b), *Callister & Rethwisch 8e.*

What fraction of each phase?

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



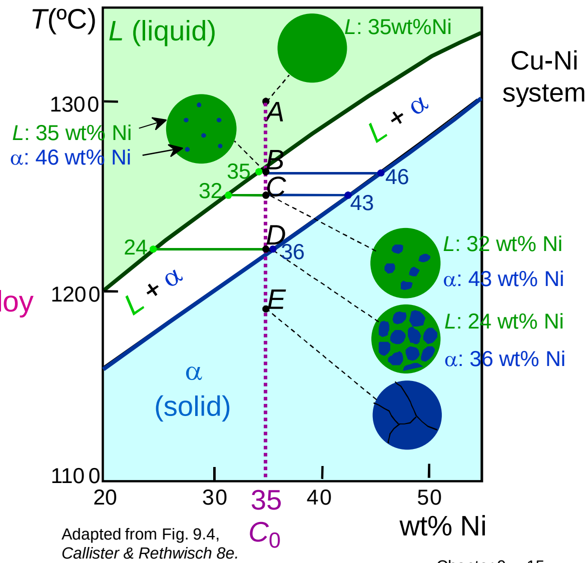
$$M_L \times R = M_\alpha \times S$$

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

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

Ex: Cooling of a Cu-Ni Alloy

- Phase diagram: Cu-Ni system.
- Consider microstructural changes that accompany the cooling of a C_0 = 35 wt% Ni alloy

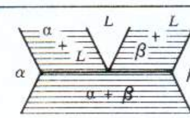
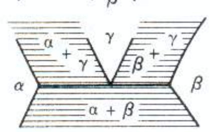
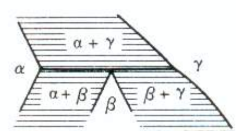


Adapted from Fig. 9.4, *Callister & Rethwisch 8e.*

Chapter 9 - 15

2 Component System – no or limited solubility

Invariant Reactions in Binary Alloys

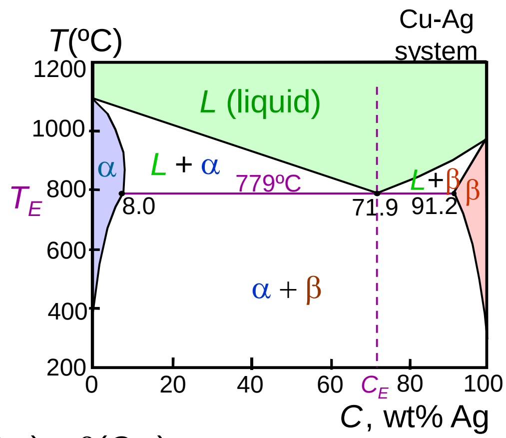
Invariant reaction	Phase reaction	Phase diagram
Eutectic	$L \longrightarrow \alpha(s) + \beta(s)$ cooling	
Peritectic	$\alpha(s) + L \longrightarrow \beta(s)$ cooling	
Eutectoid	$\gamma(s) \longrightarrow \alpha(s) + \beta(s)$ cooling	
Peritectoid	$\alpha(s) + \gamma(s) \longrightarrow \beta(s)$ cooling	

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
- **Eutectic reaction**



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

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

$$L(71.9 \text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(8.0 \text{ wt\% Ag}) + \beta(91.2 \text{ wt\% Ag})$$

9 - 17

EX 1: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 150ºC, 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

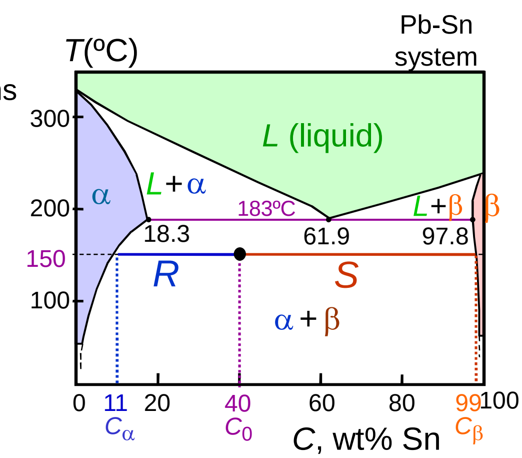
Answer:

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

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

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

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



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

Chapter 9 - 18

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

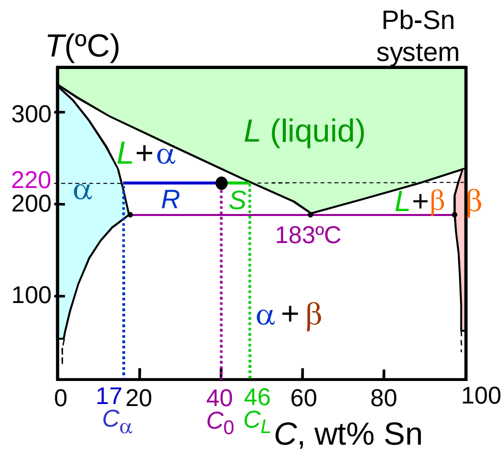
Answer: C_α = 17 wt% Sn
C_L = 46 wt% Sn

-- the relative amount of each phase

Answer:

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

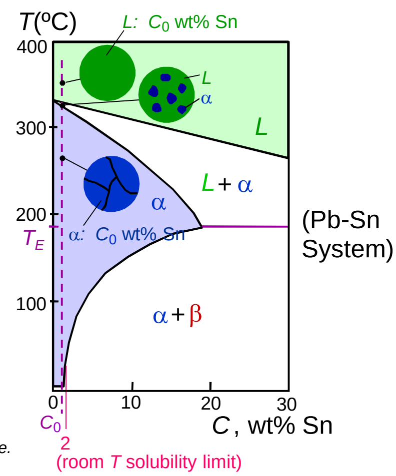
$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$



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

Microstructural Developments in Eutectic Systems I

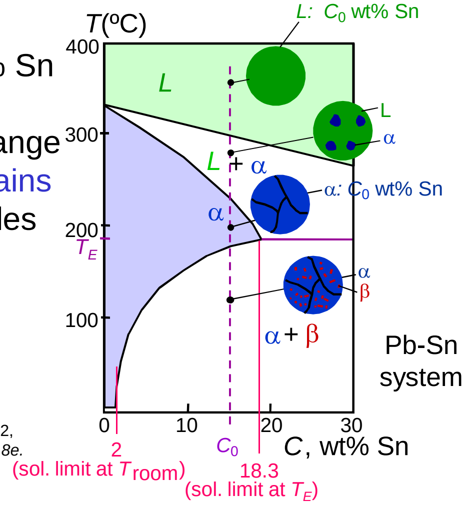
- For alloys for which C_0 < 2 wt% Sn
- Result: at room temperature
  - -- polycrystalline with grains of α phase having composition C_0



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

Microstructural Developments in Eutectic Systems II

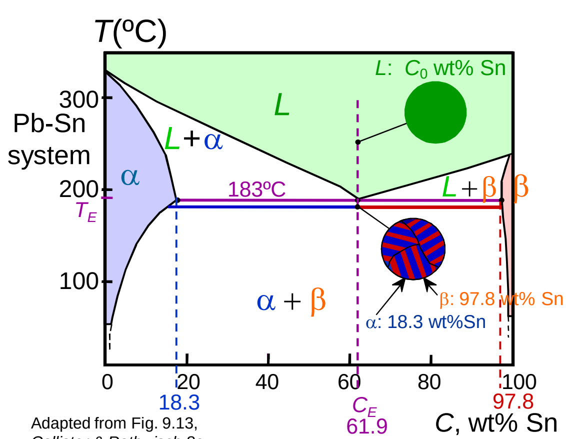
- For alloys for which
  2 wt% Sn < C_0 < 18.3 wt% Sn
- Result:
  at temperatures in $\alpha + \beta$ range
  -- polycrystalline with α grains
  and small β-phase particles



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

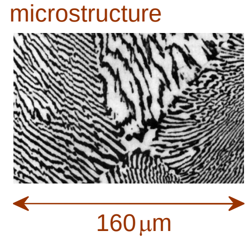
Microstructural Developments in Eutectic Systems III

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



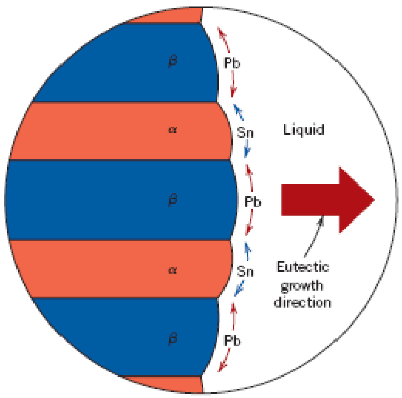
Adapted from Fig. 9.13, *Callister & Rethwisch 8e.*

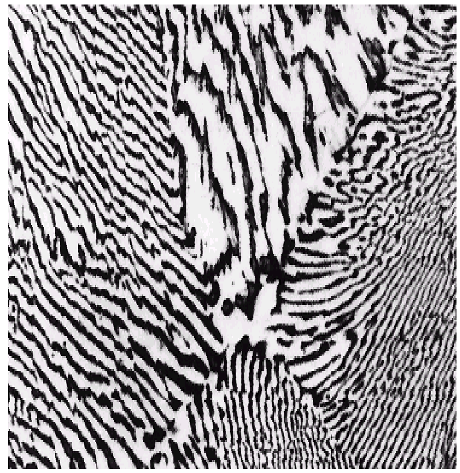
Micrograph of Pb-Sn eutectic microstructure



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

Lamellar Eutectic Structure

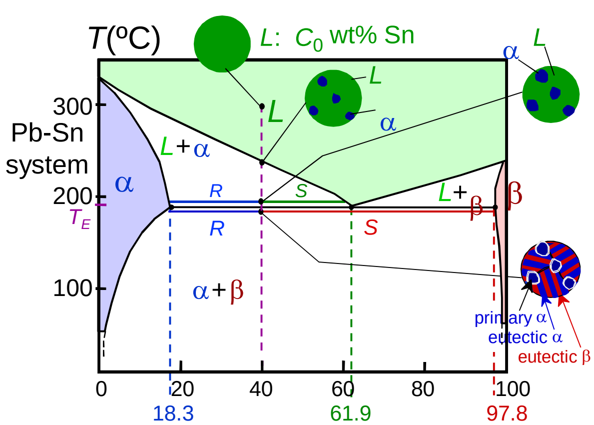




Redistribution of Pb and Sn occurs by short-distance diffusion of both elements.

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 an eutectic microconstituent



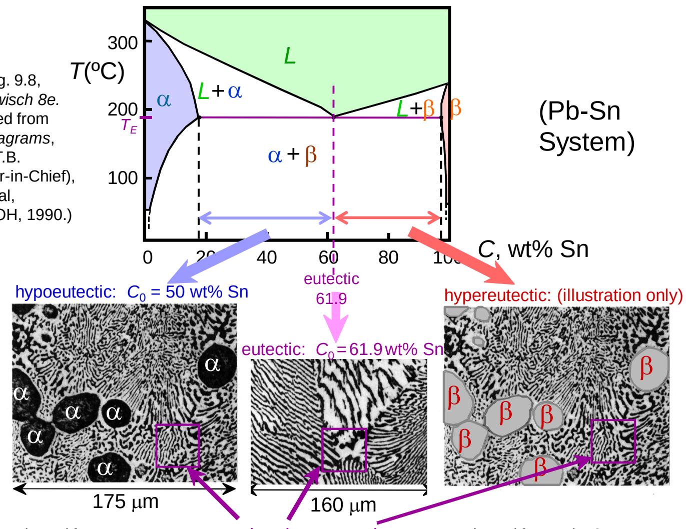
Adapted from Fig. 9.16, *Callister & Rethwisch 8e.*

- 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)



(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

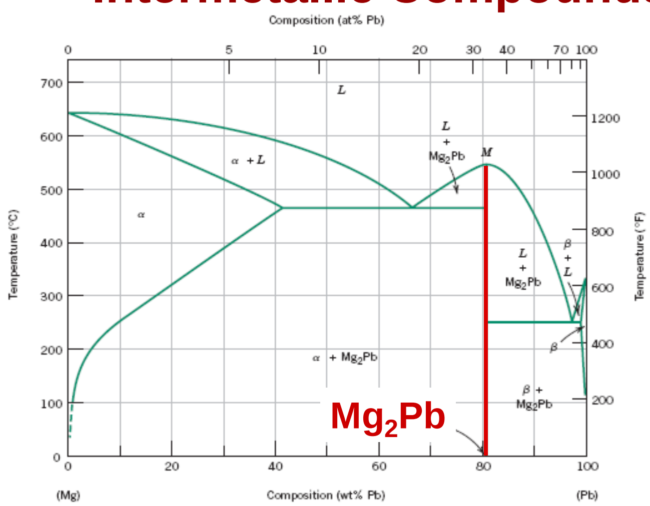
Adapted from Fig. 9.17, *Callister & Rethwisch 8e.*

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

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

Chapter 9 - 25

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).

Chapter 9 - 26

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

  $S_2 \rightleftharpoons S_1 + S_3$

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

  intermetallic compound - cementite

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

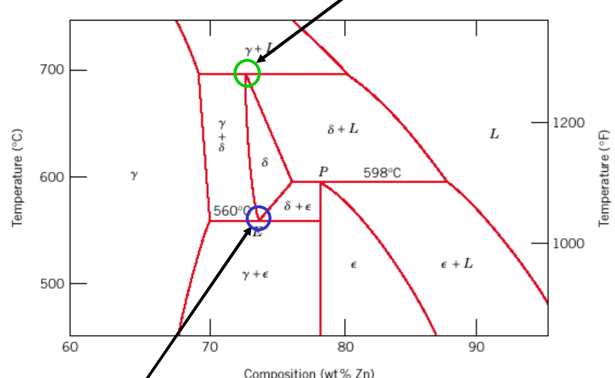
  $S_1 + L \rightleftharpoons S_2$

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

Eutectoid & Peritectic

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

Cu-Zn Phase diagram

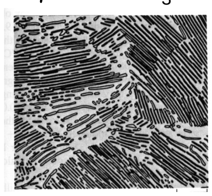


Adapted from Fig. 9.21, *Callister & Rethwisch 8e.*

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

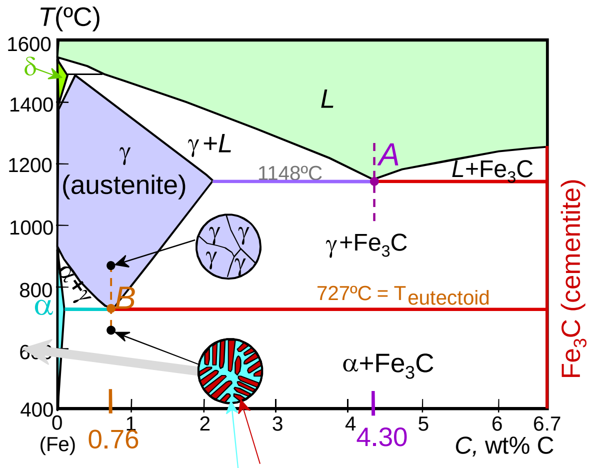
Iron-Carbon (Fe-C) Phase Diagram

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



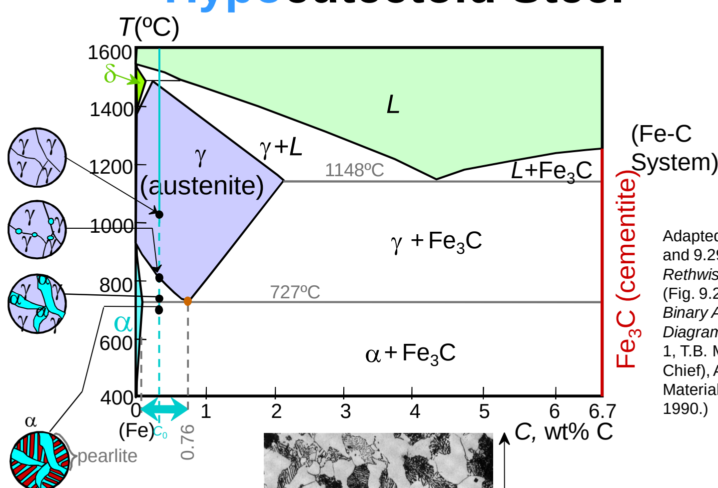
Result: Pearlite = alternating layers of α and Fe_3C phases

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

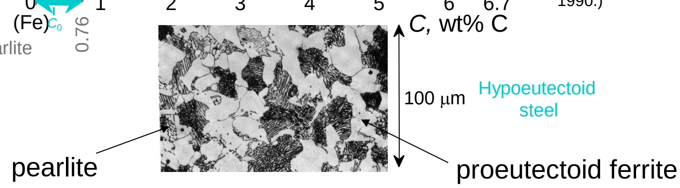


Adapted from Fig. 9.24, *Callister & Rethwisch 8e.*

Hypoeutectoid Steel

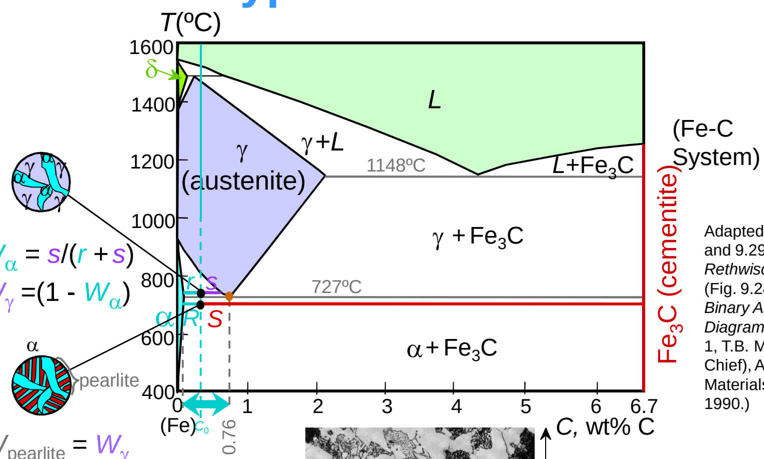


Adapted from Figs. 9.24 and 9.29, *Callister & Rethwisch 8e.* (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



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

Hypoeutectoid Steel



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

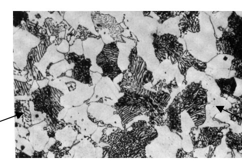
$W_\gamma = (1 - W_\alpha)$

$W_{pearlite} = W_\gamma$

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

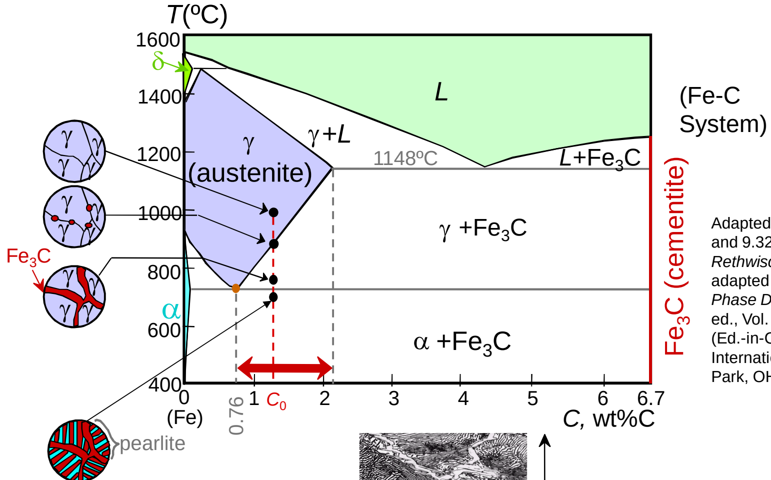
$W_{Fe_3C} = (1 - W_{\alpha'})$

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.)



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

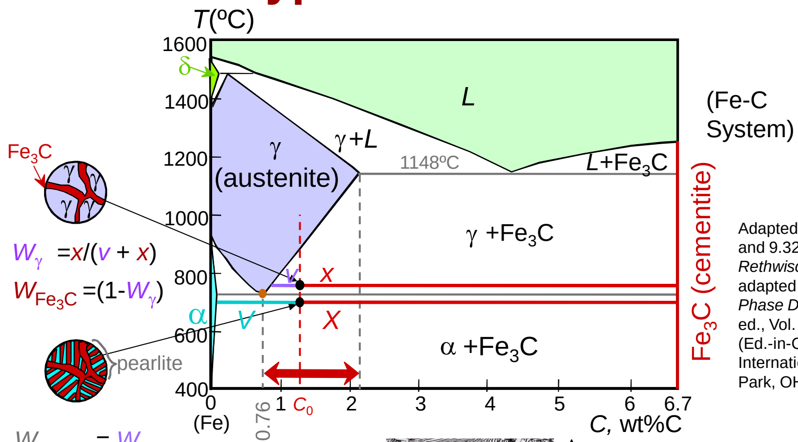
Hypereutectoid Steel



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



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

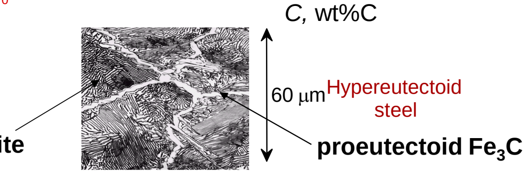
$W_{Fe_3C} = (1 - W_{\gamma})$

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

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

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

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

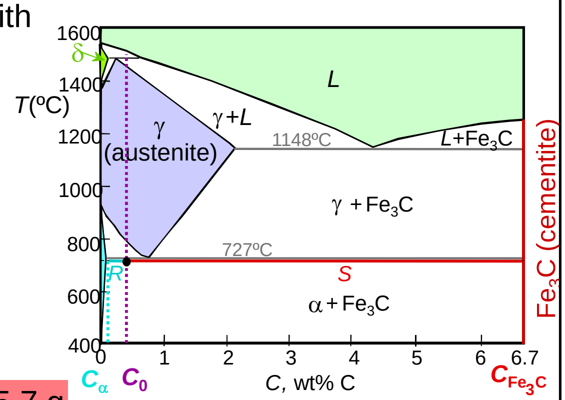
$$W_{Fe_3C} = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha}$$

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

Amount of Fe_3C in 100 g

= (100 g)W_{Fe_3C}

= (100 g)(0.057) = 5.7 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_α = 0.022 wt% C
$C_{pearlite} = C_\gamma$ = 0.76 wt% C

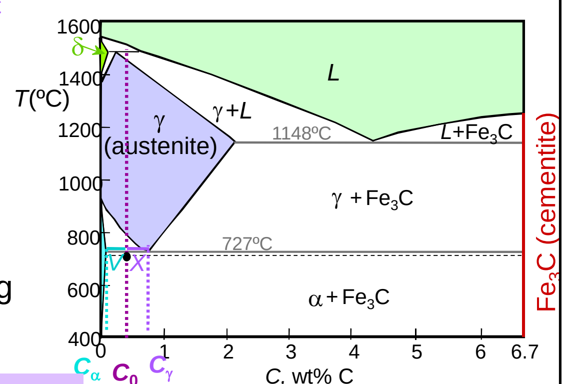
$$W_{pearlite} = \frac{V}{V+X} = \frac{C_0 - C_\alpha}{C_\gamma - C_\alpha}$$

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

Amount of pearlite in 100 g

= (100 g)$W_{pearlite}$

= (100 g)(0.512) = 51.2 g

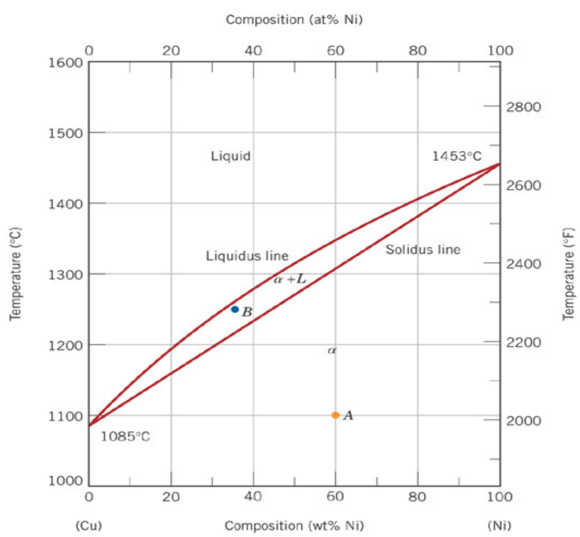


Summary

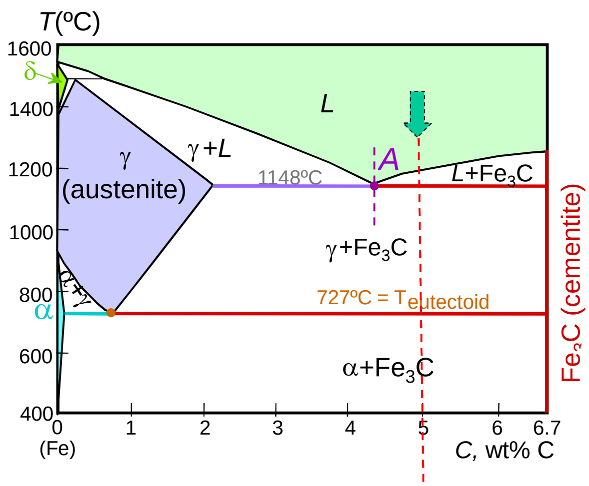
- Phase diagrams are useful tools to determine:
  - -- the number and types of phases present,
  - -- the composition of each phase,
  - -- and the weight fraction of each phase

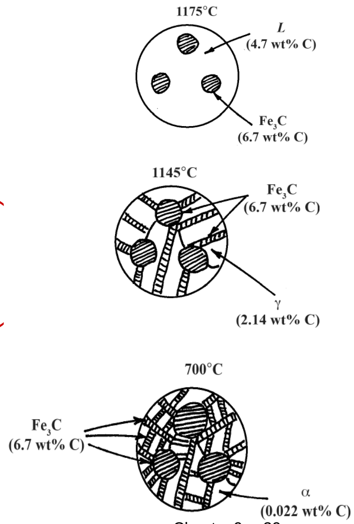
  given the temperature and composition of the system.
- The microstructure of an alloy depends on composition and cooling rate.
- Important phase diagram phase transformations include eutectic, eutectoid, and peritectic.

Is it possible to have a copper–nickel alloy that, at equilibrium, consists of a liquid phase of composition 20 wt% Ni–80 wt% Cu and also an a phase of composition 39 wt% Ni–63 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.



For an iron-carbon alloy of composition 5 wt% C-95 wt% Fe, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1175°C (2150°F), 1145°C (2095°F), and 700°C (1290°F). Label the phases and indicate their compositions (approximate).





Chapter 9 - 39