

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 A

Phase B

○ Nickel atom

● Copper atom

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1

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 $C_0 < 65$ wt% sugar: syrup

If $C_0 > 65$ wt% sugar: syrup + sugar

Sucrose/Water Phase Diagram

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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

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

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Effect of T & Composition (C_0)

- Changing T can change # of phases: path **A** to **B**.
- Changing C_0 can change # of phases: path **B** to **D**.

water-sugar system

Adapted from Fig. 9.1, Callister 7e. Chapter 9 - 4

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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.

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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).)

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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

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).

Cu-Ni phase diagram

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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 $T_A = 1320^\circ\text{C}$:
Only Liquid (L)
 $C_L = C_o (= 35$ wt% Ni)
 - At $T_D = 1190^\circ\text{C}$:
Only Solid (α)
 $C_\alpha = C_o (= 35$ wt% Ni)
 - At $T_B = 1250^\circ\text{C}$:
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.)

Cu-Ni system

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Phase Diagrams: weight fractions of phases

- Rule 3: If we know T and C_0 , then we know:
 - the amount of each phase (given in wt%).
- Examples:
 - $C_0 = 35 \text{ wt\% Ni}$
 - At T_A : Only Liquid (L)
 - $W_L = 100 \text{ wt\%}$, $W_\alpha = 0$
 - At T_D : Only Solid (α)
 - $W_L = 0$, $W_\alpha = 100 \text{ wt\%}$
 - At T_B : Both α and L

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

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

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.)

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The Lever Rule

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

How much of each phase?
Think of it as a lever (teeter-totter)

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

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

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

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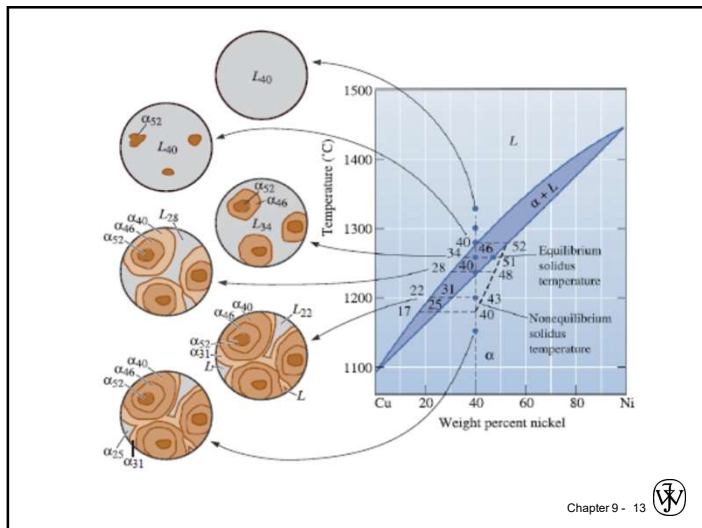
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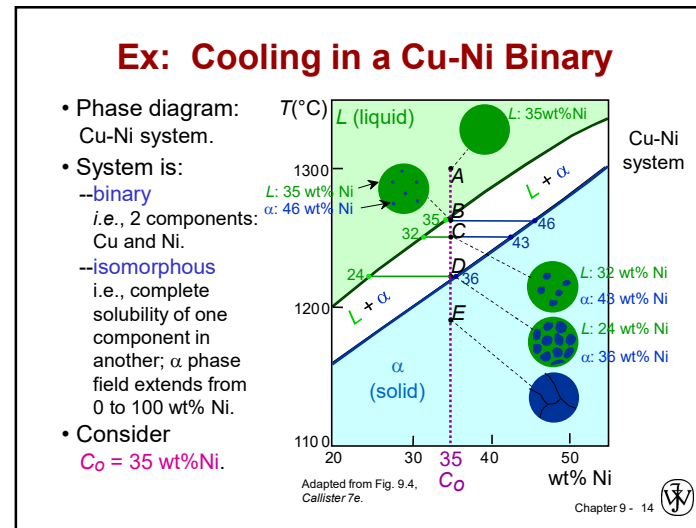
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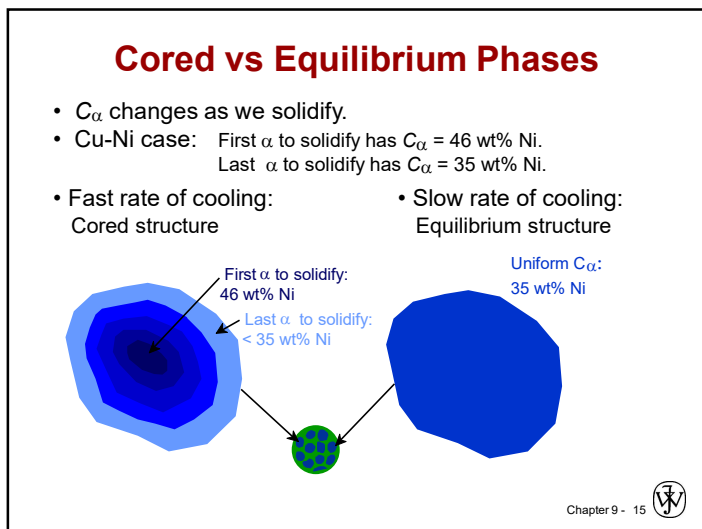
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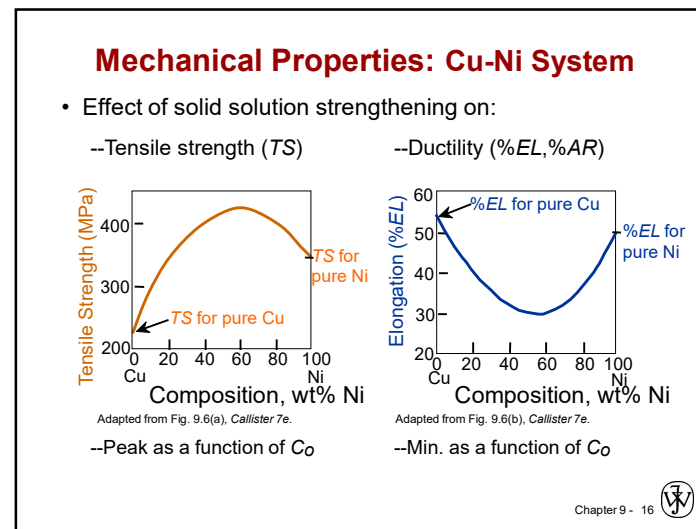
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Binary-Eutectic Systems

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. Chapter 9 - 17

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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
 - $C_\alpha = 11$ wt% Sn
 - $C_\beta = 99$ 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. Chapter 9 - 18

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EX: Pb-Sn Eutectic System (2)

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find...
 - the phases present: $\alpha + L$
 - compositions of phases:
 - $C_o = 40$ wt% Sn
 - $C_\alpha = 17$ 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. Chapter 9 - 19

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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. Chapter 9 - 20

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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. (sol. limit at T_{Room}) (sol. limit at T_E)

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Microstructures in Eutectic Systems: III

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

Micrograph of Pb-Sn eutectic microstructure

Adapted from Fig. 9.13, Callister 7e.

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Lamellar Eutectic Structure

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

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Microstructures in Eutectic Systems: IV

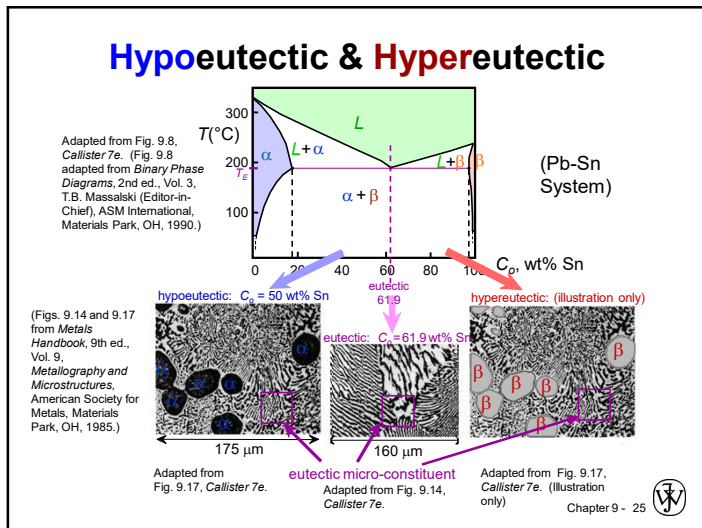
- 18.3 wt% Sn < C_o < 61.9 wt% Sn
- Result: α crystals and a eutectic microstructure

- Just above T_E :
 - $C_\alpha = 18.3$ 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 :
 - $C_\alpha = 18.3$ wt% Sn
 - $C_\beta = 97.8$ wt% Sn
 - $W_\alpha = \frac{S}{R+S} = 73$ wt%
 - $W_\beta = 27$ wt%

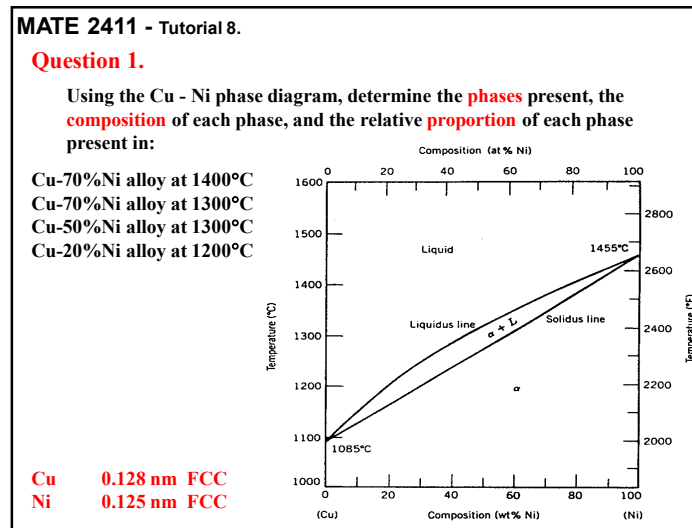
Adapted from Fig. 9.16, Callister 7e.

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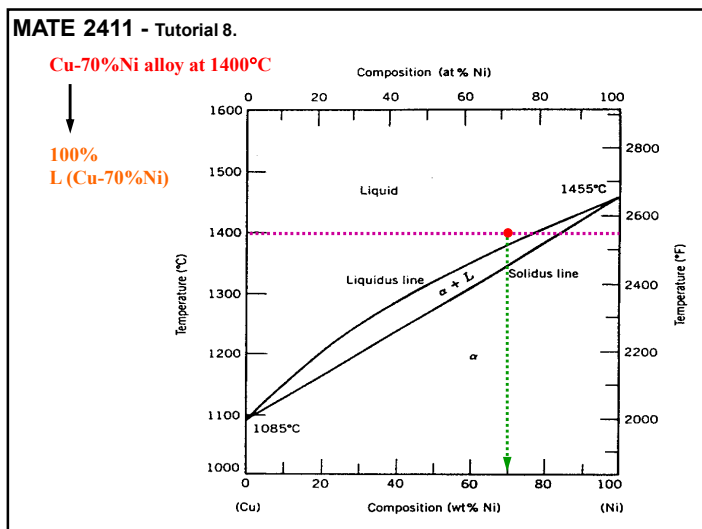
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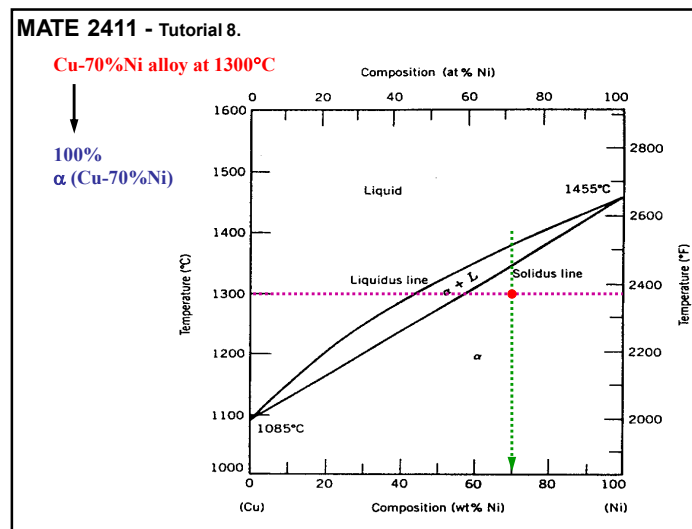
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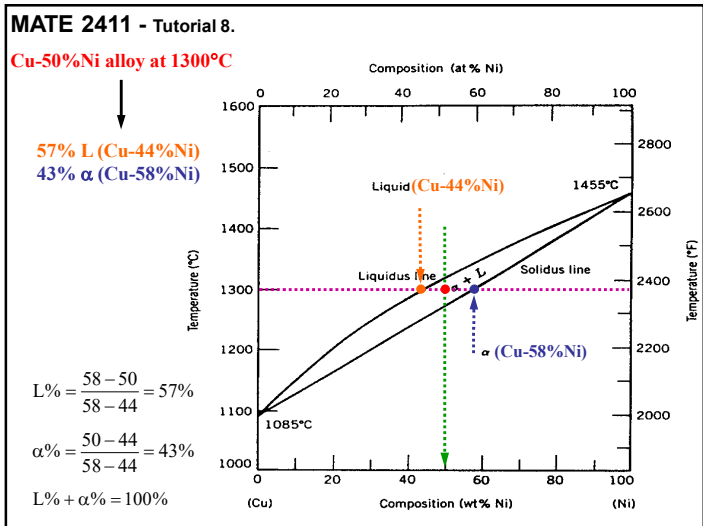
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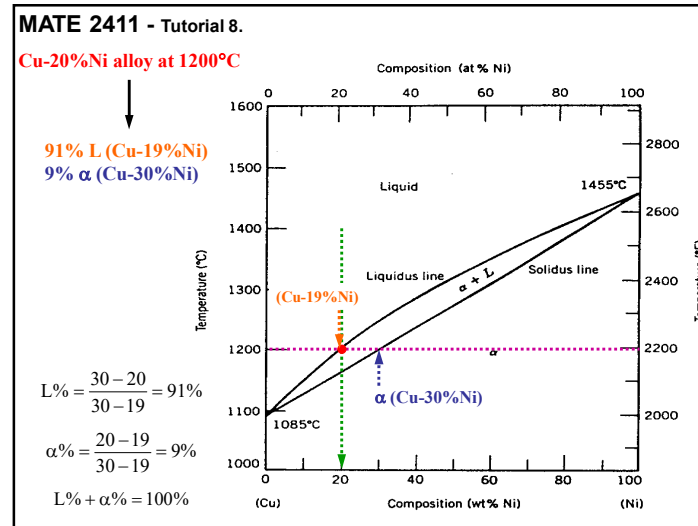
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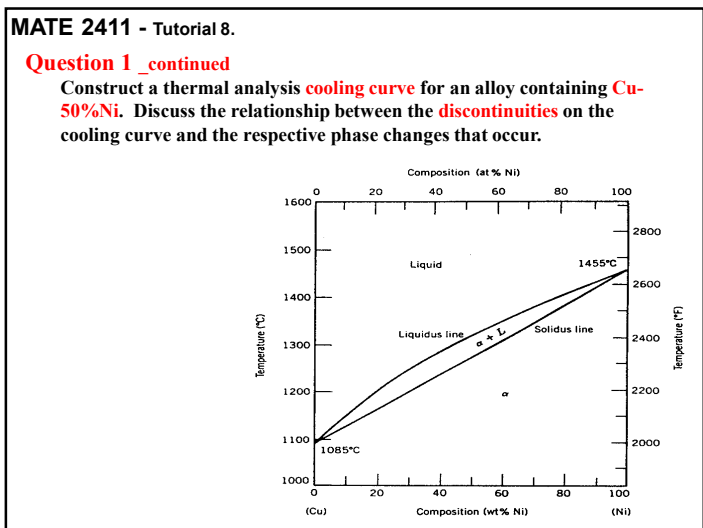
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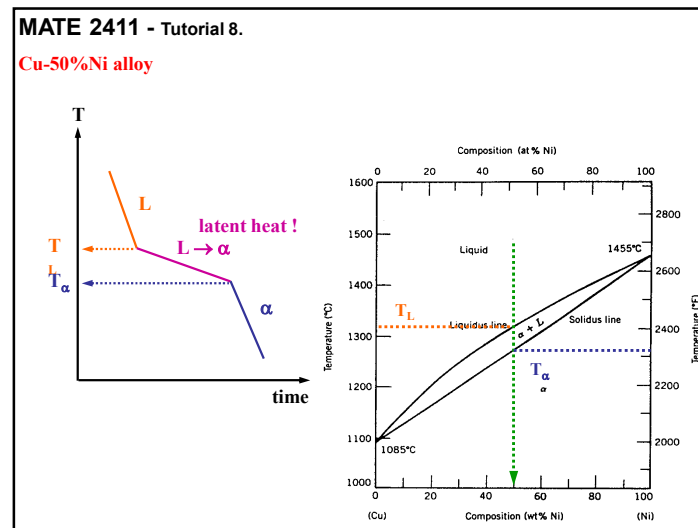
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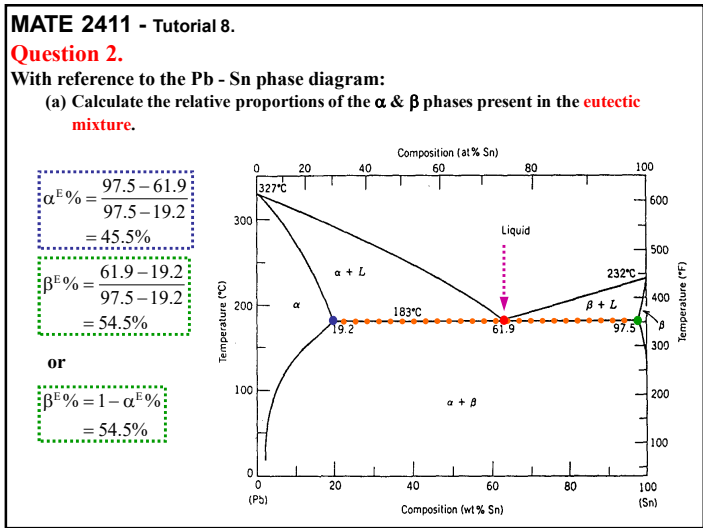
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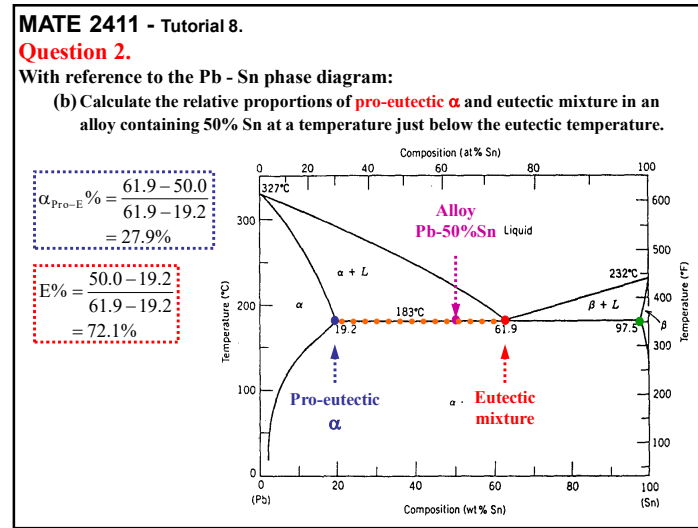
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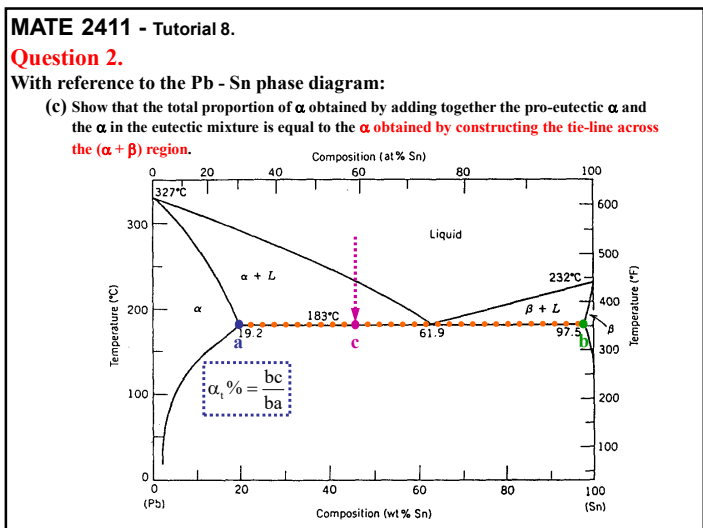
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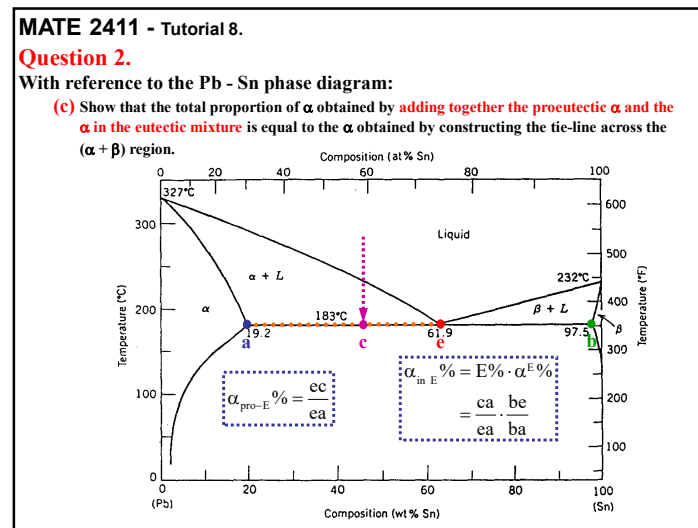
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MATE 2411 - Tutorial 8.
Question 2.
 With reference to the Pb - Sn phase diagram:

(c) Show that the total proportion of α obtained by adding together the proeutectic α and the α in the eutectic mixture is equal to the α obtained by constructing the tie-line across the ($\alpha + \beta$) region.

$$\alpha_1 \% = \frac{bc}{ba}$$

$$\alpha_1 \% = \alpha_{\text{pro-E}} \% + \alpha_{\text{in E}} \%$$

$$= \frac{ec}{ea} + \frac{ca}{ea} \cdot \frac{be}{ba}$$

$$= \frac{ec \cdot ba + ca \cdot be}{ea \cdot ba}$$

$$= \frac{ec \cdot (bc + ca) + ca \cdot be}{ea \cdot ba}$$

$$= \frac{ec \cdot bc + ca \cdot (be + ec)}{ea \cdot ba}$$

$$= \frac{bc \cdot (ec + ca)}{ea \cdot ba} = \frac{bc}{ba}$$

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$$\% \alpha = \frac{97.5 - 61.9}{97.5 - 19.2} = 45.5\%$$

$$\% \beta = \frac{61.9 - 19.2}{97.5 - 19.2} = 54.5\% \text{ (or } 1 - 45.5\% = 54.5\%)$$

(b) $\% \alpha \text{ (proeutectic)} = \frac{61.9 - 50}{61.9 - 19.2} = 27.9\%$

$$\% \text{eutectic phase} = \frac{50 - 19.2}{61.9 - 19.2} = 72.1\%$$

(c) from (a) and (b)

proeutectic α : $\% \alpha_{\text{pro}} = 27.9\%$

α in eutectic mixture: $\% \alpha_{\text{eut}} = 72.1\% \times \frac{45.5}{100}$

total proportion of α phase in Pb-50wt%Sn:
 $\% \alpha_{\text{tot}} = \% \alpha_{\text{pro}} + \% \alpha_{\text{eut}} = 60.7\%$

alternatively use tie-line across the $\alpha + \beta$ region

$$\% \alpha_{\text{tot}} = \frac{97.5 - 50}{97.5 - 19.2} = 60.7\%$$

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MATE 2411 - Tutorial 8.
Question 2.
 With reference to the Pb - Sn phase diagram:

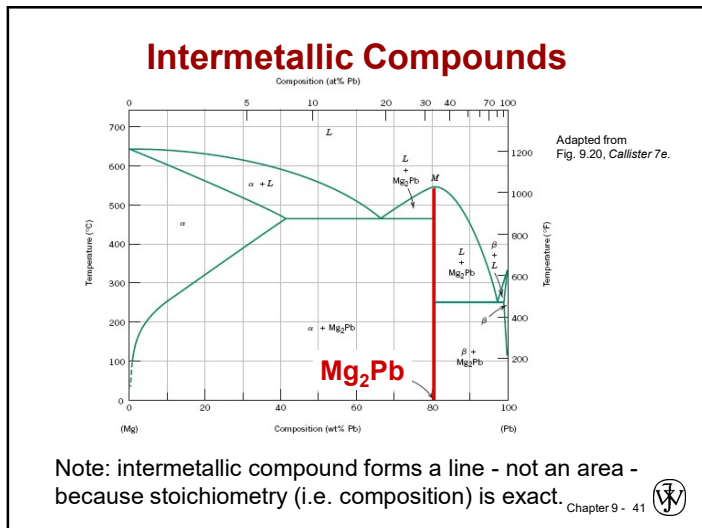
(d) Construct a thermal analysis cooling curve for an alloy containing 30% Sn.
 Discuss the relationship between the discontinuities on the cooling curve and the respective phase changes that occur.

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MATE 2411 - Tutorial 8.
Question 2.
 With reference to the Pb - Sn phase diagram:

(e) Highlight the liquidus and solidus lines. Discuss the significance of the regions above the liquidus, below the solidus and between the two lines. Highlight any solvus line. Discuss the significance of this line, taking example of the cooling process of Pb-10%Sn alloy.

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Eutectoid & Peritectic

- Eutectic** - liquid in equilibrium with two solids

$$L \xrightleftharpoons[\text{heat}]{\text{cool}} \alpha + \beta$$
- Eutectoid** - solid phase in equilibrium with two solid phases

$$S_2 \rightleftharpoons S_1 + S_3$$

intermetallic compound
- cementite

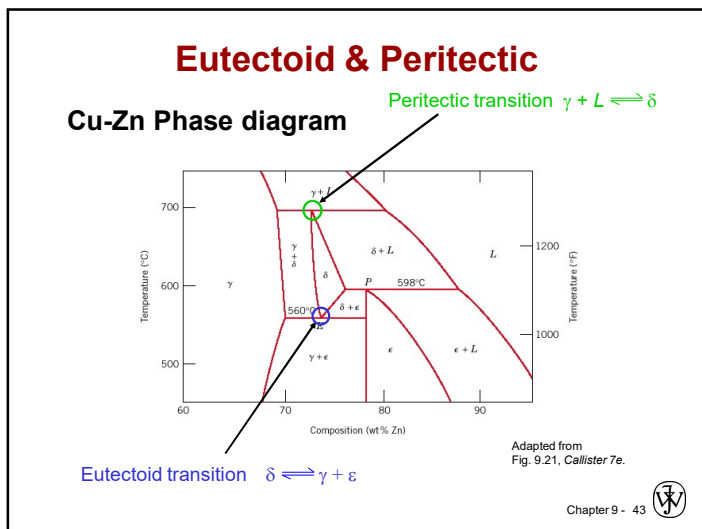
$$\gamma \xrightleftharpoons[\text{heat}]{\text{cool}} \alpha + \text{Fe}_3\text{C} \quad (727^\circ\text{C})$$
- Peritectic** - liquid + solid 1 → solid 2 (Fig 9.21)

$$S_1 + L \rightleftharpoons S_2$$

$$\delta + L \xrightleftharpoons[\text{heat}]{\text{cool}} \gamma \quad (1493^\circ\text{C})$$

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Iron-Carbon (Fe-C) Phase Diagram

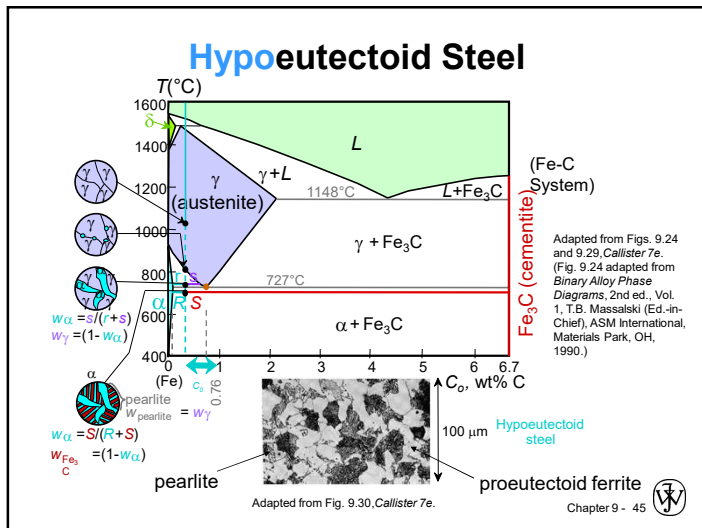
- 2 important points
- Eutectic (A):**
 $L \Rightarrow \gamma + \text{Fe}_3\text{C}$
- Eutectoid (B):**
 $\gamma \Rightarrow \alpha + \text{Fe}_3\text{C}$

Result: Pearlite = alternating layers of α and Fe_3C phases

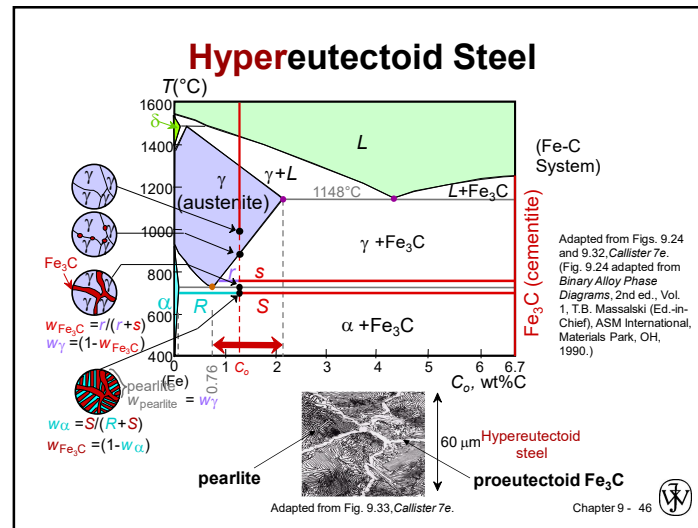
Adapted from Fig. 9.24, Callister 7e.

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Example: Phase Equilibria

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following

- composition of Fe₃C and ferrite (α)
- the amount of carbide (cementite) in grams that forms per 100 g of steel
- the amount of pearlite and proeutectoid ferrite (α)

Fe₃C = 5.7 g
 α = 94.3 g

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Chapter 9 – Phase Equilibria

Solution: a) composition of Fe₃C and ferrite (α)

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

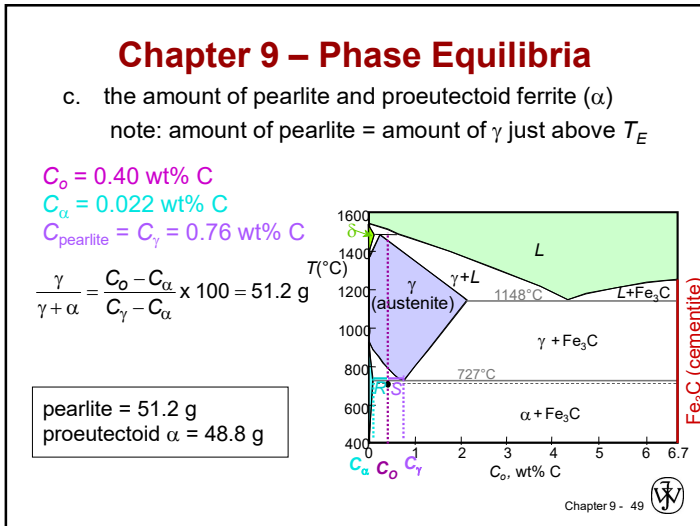
C₀ = 0.40 wt% C
 C _{α} = 0.022 wt% C
 C_{Fe₃C} = 6.70 wt% C

$$\frac{\text{Fe}_3\text{C}}{\text{Fe}_3\text{C} + \alpha} = \frac{C_0 - C_\alpha}{C_{\text{Fe}_3\text{C}} - C_\alpha} \times 100$$

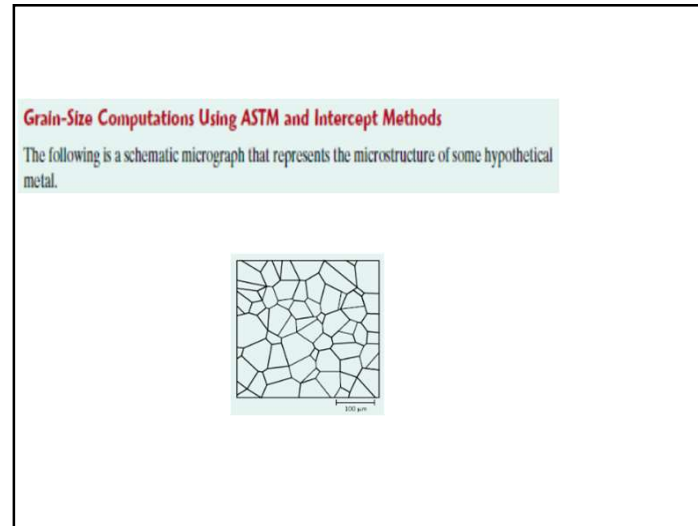
$$= \frac{0.4 - 0.022}{6.7 - 0.022} \times 100 = 5.7\text{g}$$

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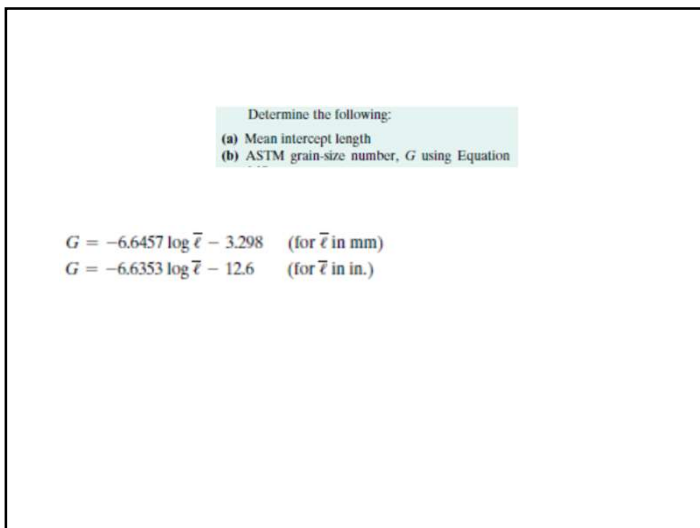
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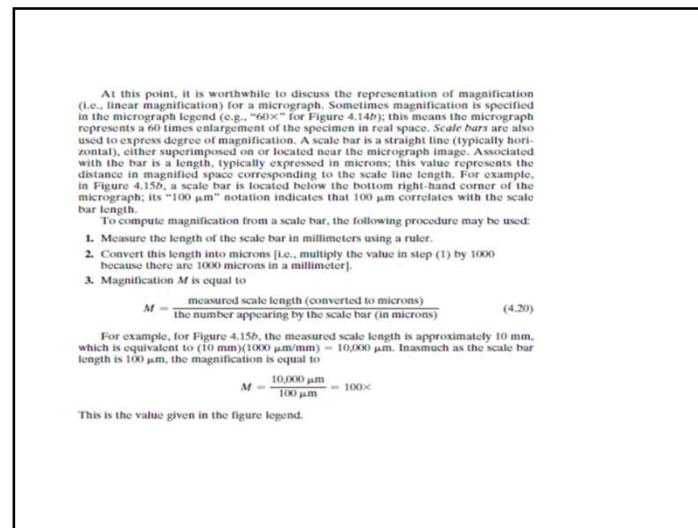
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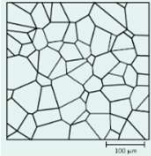
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Solution

(a) We first determine the magnification of the micrograph using Equation 4.20. The scale bar length is measured and found to be 16 mm, which is equal to 16,000 μm ; and because the scale bar number is 100 μm , the magnification is

$$M = \frac{16,000 \mu\text{m}}{100 \mu\text{m}} = 160\times$$


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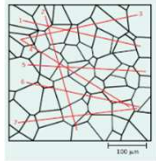
The following sketch is the same micrograph on which have been drawn seven straight lines (in red), which have been numbered.

The length of each line is 50 mm, and thus the total line length (L_T in Equation 4.16) is

$$(7 \text{ lines})(50 \text{ mm/line}) = 350 \text{ mm}$$

Tabulated next is the number of grain-boundary intersections for each line:

Line Number	Number of Grain-Boundary Intersections
1	8
2	8
3	8
4	9
5	9
6	9
7	7
Total	58



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Thus, inasmuch as $L_T = 350 \text{ mm}$, $P = 58$ grain-boundary intersections, and the magnification $M = 160\times$, the mean intercept length $\bar{\tau}$ (in millimeters in real space), Equation 4.16, is equal to

$$\bar{\tau} = \frac{L_T}{PM} = \frac{350 \text{ mm}}{(58 \text{ grain boundary intersections})(160\times)} = 0.0377 \text{ mm}$$

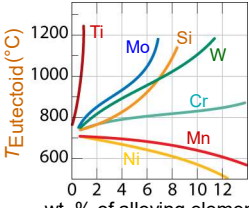
(b) The value of G is determined by substitution of this value for $\bar{\tau}$ into Equation 4.19a; therefore,

$$G = -6.6457 \log \bar{\tau} - 3.298 = (-6.6457) \log(0.0377) - 3.298 = 6.16$$

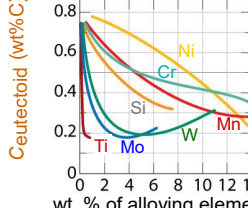
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Alloying Steel with More Elements

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




- Ceutectoid 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.)

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.)

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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: