# Chapter 10: Phase Diagrams

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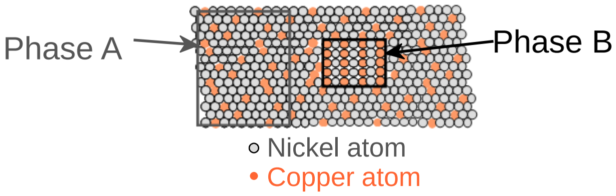
## ISSUES TO ADDRESS...

- 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?

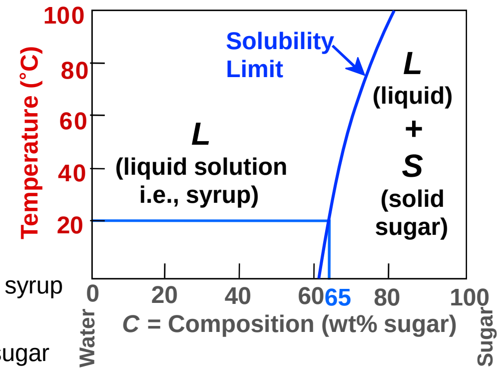


# Phase Equilibria: Solubility Limit

- Solution – solid, liquid, or gas solutions, single phase
- Mixture – more than one phase
- Solubility Limit:
  Maximum concentration for which only a single phase solution exists.

Adapted from Fig. 10.1, *Callister & Rethwisch 3e.*

Sugar/Water Phase Diagram




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

Answer: 65 wt% sugar.

At 20°C, if *C* < 65 wt% sugar: syrup

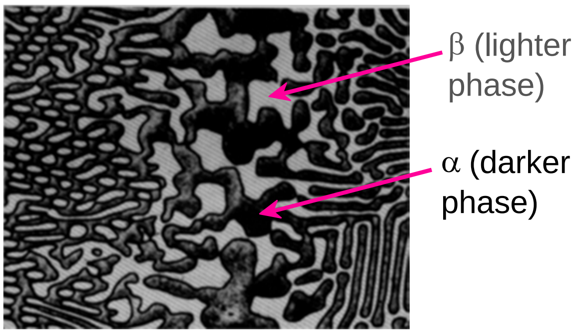
At 20°C, if *C* > 65 wt% sugar: syrup + sugar



# 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

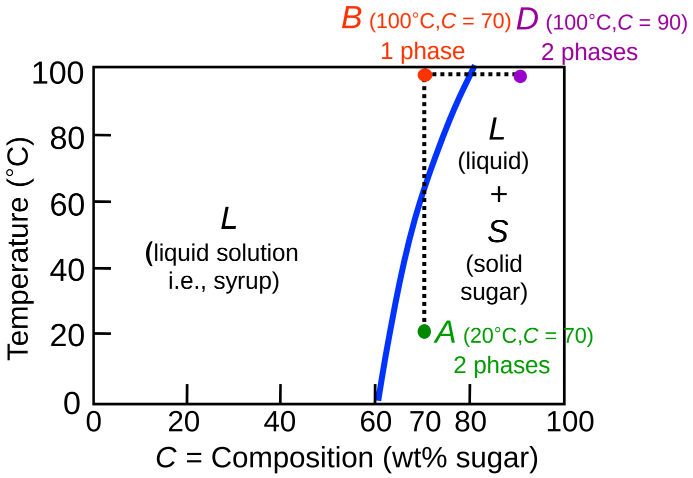



Adapted from chapter-opening photograph, Chapter 9, *Callister, Materials Science & Engineering: An Introduction, 3e.*

# 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. 10.1, *Callister & Rethwisch 3e.*



# Criteria for Solid Solubility

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

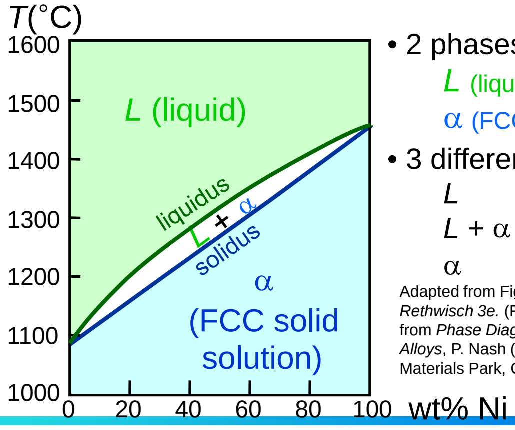
| | Crystal Structure | electroneg | *r* (nm) |
|---|---|---|---|
| Ni | FCC | 1.9 | 0.1246 |
| Cu | FCC | 1.8 | 0.1278 |

- 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



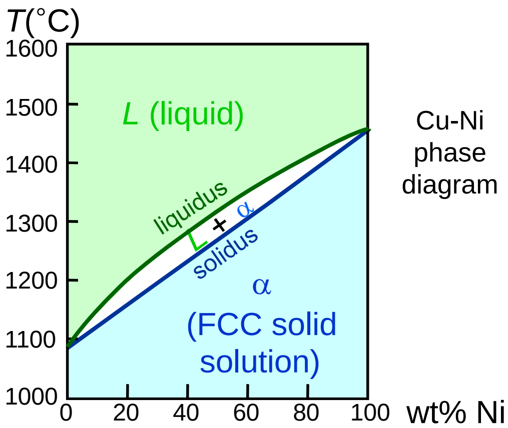

- 2 phases:
  - *L* (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + α
  - α

Adapted from Fig. 10.3(a), *Callister & Rethwisch 3e.* (Fig. 10.3(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.



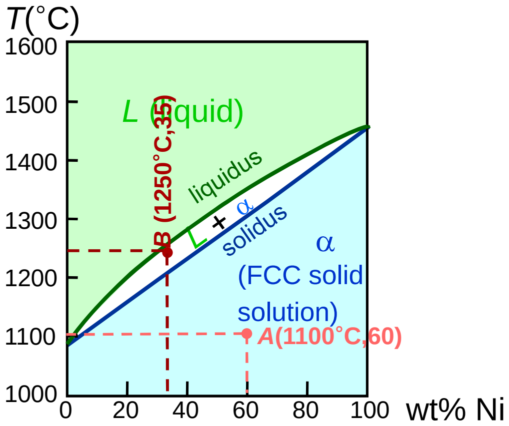

Cu-Ni phase diagram

Adapted from Fig. 10.3(a), *Callister & Rethwisch 3e.* (Fig. 10.3(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*(1100°C, 60 wt% Ni):
  1 phase: α
  *B*(1250°C, 35 wt% Ni):
  2 phases: *L* + α



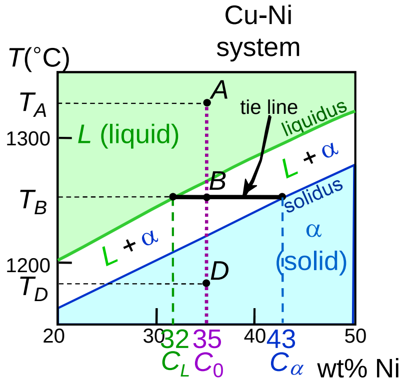

Adapted from Fig. 10.3(a), *Callister & Rethwisch 3e.* (Fig. 10.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).



# 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 $T_A$ = 1320°C:
  Only Liquid (*L*) present
  $C_L = C_0$ ( = 35 wt% Ni)
  At $T_D$ = 1190°C:
  Only Solid (α) present
  $C_\alpha = C_0$ ( = 35 wt% Ni)
  At $T_B$ = 1250°C:
  Both α and *L* present
  $C_L = C_{liquidus}$ ( = 32 wt% Ni)
  $C_\alpha = C_{solidus}$ ( = 43 wt% Ni)




Adapted from Fig. 10.3(a), *Callister & Rethwisch 3e.* (Fig. 10.3(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 ($\alpha$) present

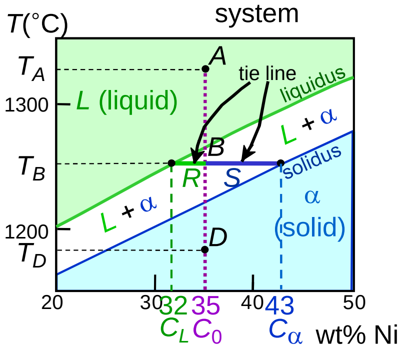
$W_L$ = 0, $W_\alpha$ = 1.00

At $T_B$ : Both $\alpha$ and $L$ present

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

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

Cu-Ni system

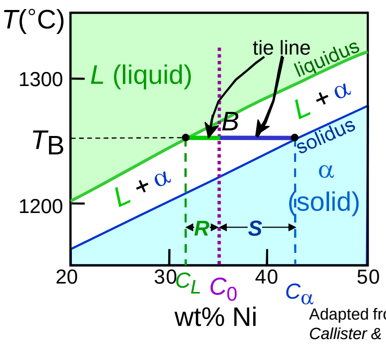



Adapted from Fig. 10.3(a), *Callister & Rethwisch 3e.* (Fig. 10.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).



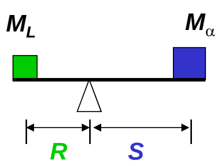
# The Lever Rule

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




Adapted from Fig. 10.3(b), *Callister & Rethwisch 3e.*

What fraction of each phase?
Think of the tie line as a lever (teeter-totter)



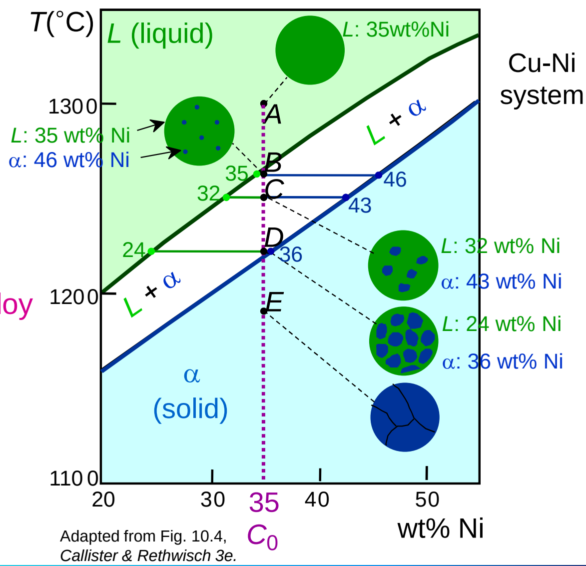

$$M_\alpha \times S = M_L \times R$$

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

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

# Ex: Cooling 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



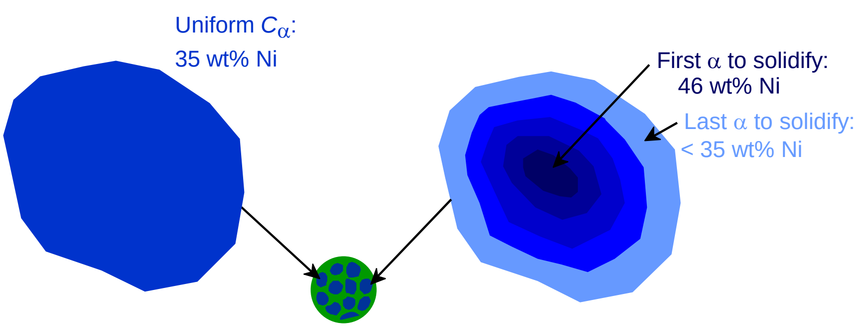

Adapted from Fig. 10.4, *Callister & Rethwisch 3e.*



# Cored vs Equilibrium Structures

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

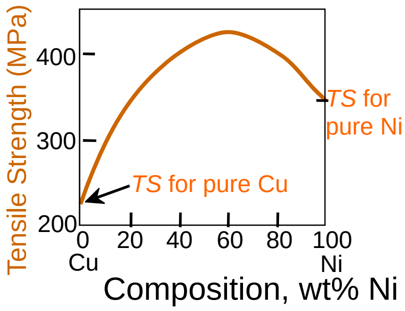
- Slow rate of cooling: Equilibrium structure
- Fast rate of cooling: Cored structure



# Mechanical Properties: Cu-Ni System

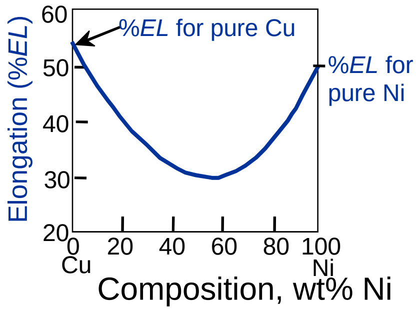
- Effect of solid solution strengthening on:

-- Tensile strength (*TS*)




Adapted from Fig. 10.6(a), *Callister & Rethwisch 3e.*

-- Ductility (%*EL*)




Adapted from Fig. 10.6(b), *Callister & Rethwisch 3e.*



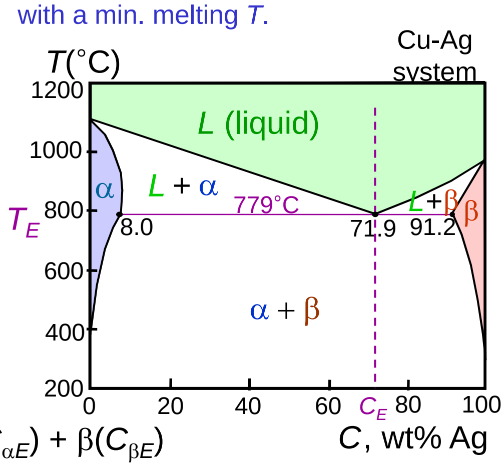
# Binary-Eutectic Systems

2 components

has a special composition with a min. melting *T*.

Ex.: Cu-Ag system

- 3 single phase regions ($L$, $\alpha$, $\beta$)
- Limited solubility:
  $\alpha$: mostly Cu
  $\beta$: mostly Ag
- $T_E$ : No liquid below $T_E$
- $C_E$ : Composition at temperature $T_E$
- **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 150°C, determine:
  - -- the phases present

**Answer:** $\alpha + \beta$

-- the phase compositions

**Answer:** $C_\alpha$ = 11 wt% Sn
$C_\beta$ = 99 wt% Sn

-- the relative amount of each phase

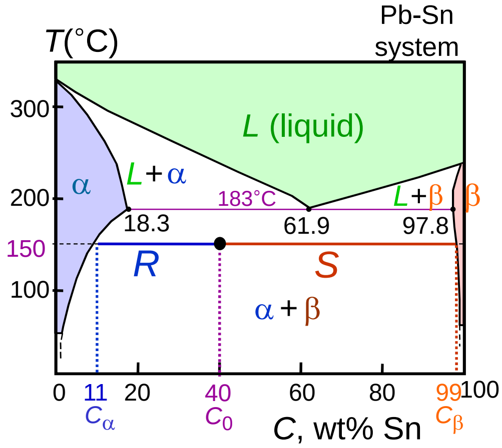
**Answer:**

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

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

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

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




Adapted from Fig. 10.8, *Callister & Rethwisch 3e.*



# EX 2: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, determine:
  - -- the phases present:

**Answer:** $\alpha + L$

-- the phase compositions

**Answer:** $C_\alpha$ = 17 wt% Sn
$C_L$ = 46 wt% Sn

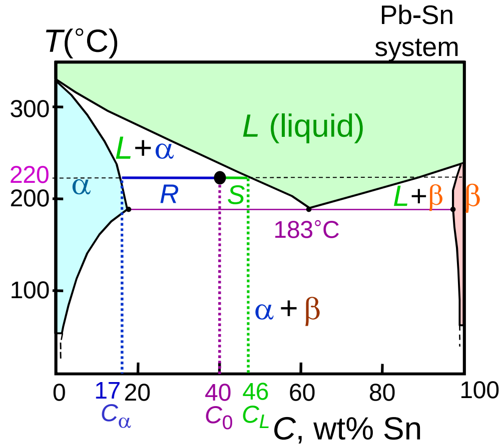
-- the relative amount of each phase

**Answer:**

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

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

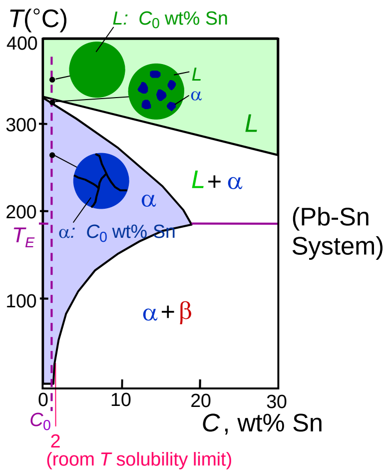
$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$




Adapted from Fig. 10.8, *Callister & Rethwisch 3e.*

# 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 $C_0$

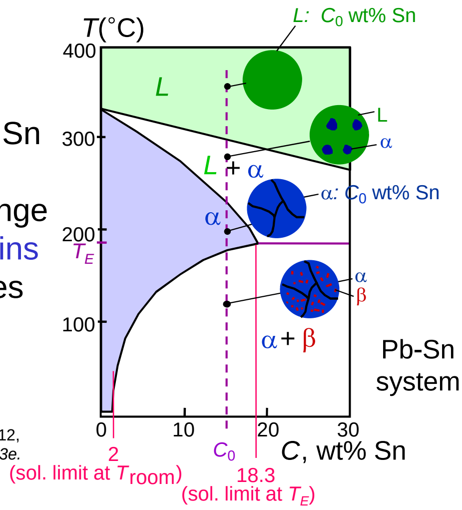



Adapted from Fig. 10.11, *Callister & Rethwisch 3e.*



# Microstructural Developments in Eutectic Systems II

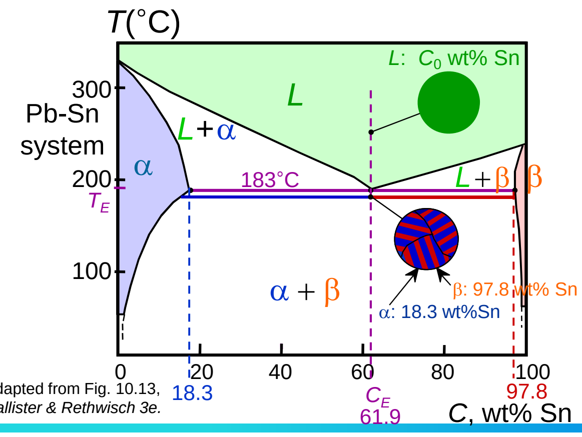
- For alloys for which 2 wt% Sn < $C_0$ < 18.3 wt% Sn
- Result:
  at temperatures in α + β range
  -- polycrystalline with α grains and small β-phase particles




Adapted from Fig. 10.12, *Callister & Rethwisch 3e.*

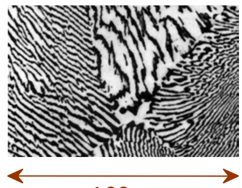
# Microstructural Developments in Eutectic Systems III

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




Adapted from Fig. 10.13, *Callister & Rethwisch 3e.*

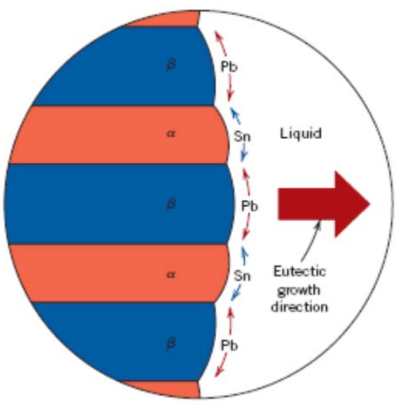
Micrograph of Pb-Sn eutectic microstructure



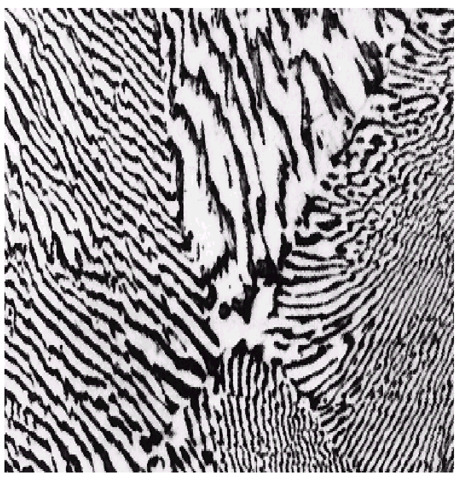

Adapted from Fig. 10.14, *Callister & Rethwisch 3e.*



# Lamellar Eutectic Structure

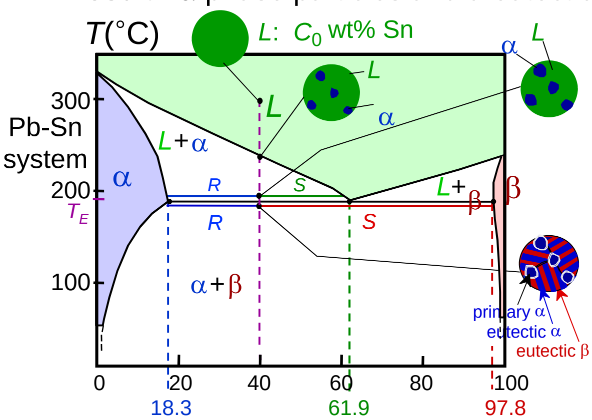



Adapted from Figs. 10.14 & 10.15, *Callister & Rethwisch 3e.*



# 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. 10.16, *Callister & Rethwisch 3e.*

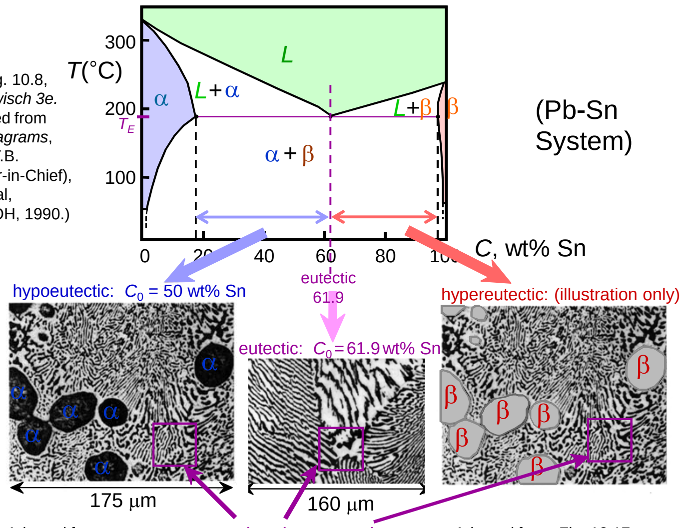
- Just above $T_E$:
  - $C_\alpha$ = 18.3 wt% Sn
  - $C_L$ = 61.9 wt% Sn
  - $W_\alpha = \frac{S}{R+S} = 0.50$
  - $W_L = (1 - W_\alpha) = 0.50$
- Just below $T_E$:
  - $C_\alpha$ = 18.3 wt% Sn
  - $C_\beta$ = 97.8 wt% Sn
  - $W_\alpha = \frac{S}{R+S} = 0.73$
  - $W_\beta = 0.27$



# Hypoeutectic & Hypereutectic

Adapted from Fig. 10.8, *Callister & Rethwisch 3e.* (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)



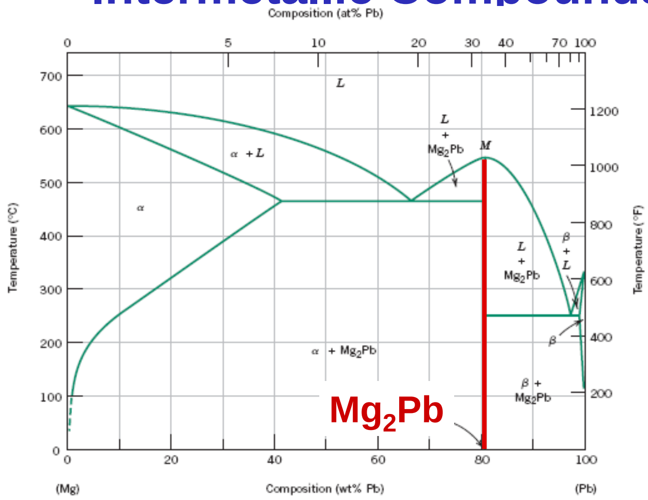

(Figs. 10.14 and 10.17 from *Metals Handbook*, 9th ed., Vol. 9, *Metallography and Microstructures*, American Society for Metals, Materials Park, OH, 1985.)

Adapted from Fig. 10.17, *Callister & Rethwisch 3e.*

Adapted from Fig. 10.14, *Callister & Rethwisch 3e.*

Adapted from Fig. 10.17, *Callister & Rethwisch 3e.* (Illustration only)

# Intermetallic Compounds




Adapted from Fig. 10.20, *Callister & Rethwisch 3e.*

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, 183°C, 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, 727°C, 0.76 wt% C)

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

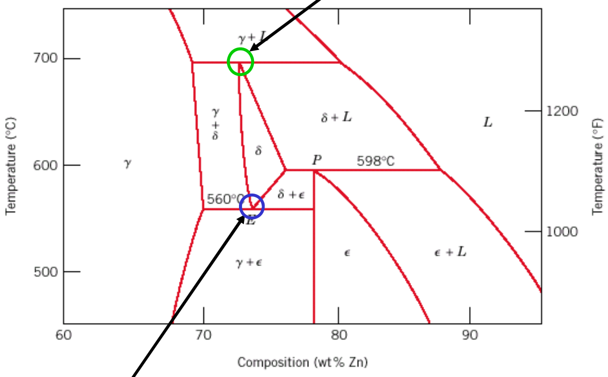
  $S_1 + L \rightleftharpoons S_2$

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

# Eutectoid & Peritectic

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

Cu-Zn Phase diagram



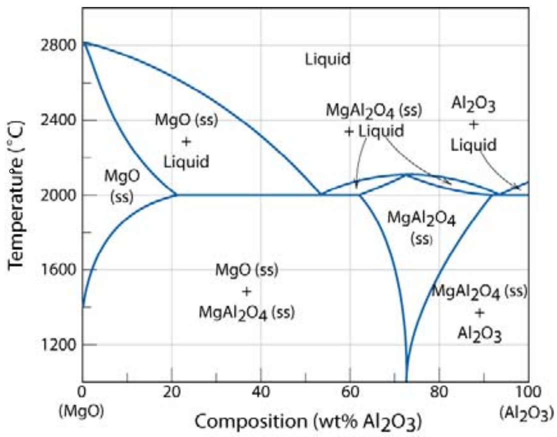

Adapted from Fig. 10.21, *Callister & Rethwisch 3e.*

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



# Ceramic Phase Diagrams

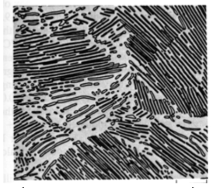
MgO-$Al_2O_3$ diagram:




Adapted from Fig. 10.24, *Callister & Rethwisch 3e.*

# Iron-Carbon (Fe-C) Phase Diagram

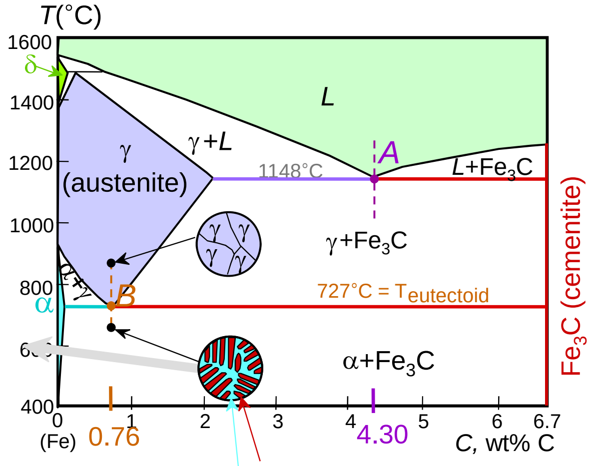
- 2 important points
  - Eutectic (*A*): $L \Rightarrow \gamma + Fe_3C$
  - Eutectoid (*B*): $\gamma \Rightarrow \alpha + Fe_3C$



120 μm

Result: Pearlite = alternating layers of $\alpha$ and $Fe_3C$ phases

(Adapted from Fig. 10.31, *Callister & Rethwisch 3e.*)




Adapted from Fig. 10.28, *Callister & Rethwisch 3e.*

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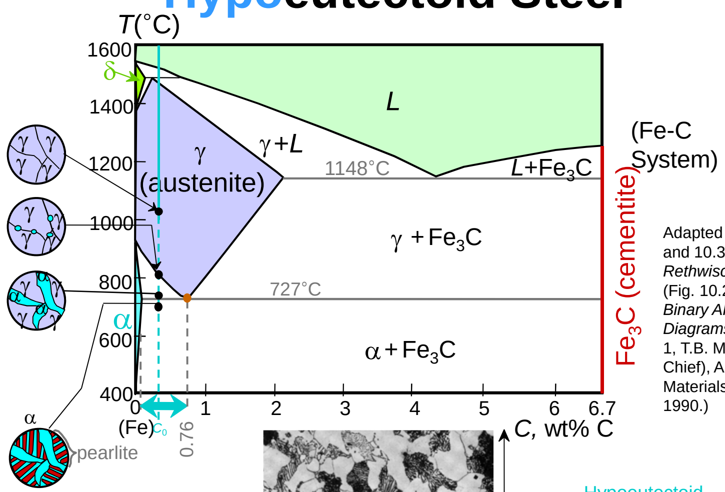
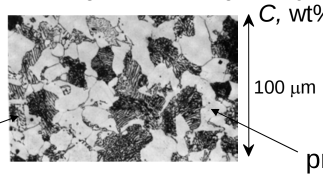
# Hypoeutectoid Steel




Adapted from Figs. 10.28 and 10.33, *Callister & Rethwisch 3e.* (Fig. 10.28 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. 10.34, *Callister & Rethwisch 3e.*

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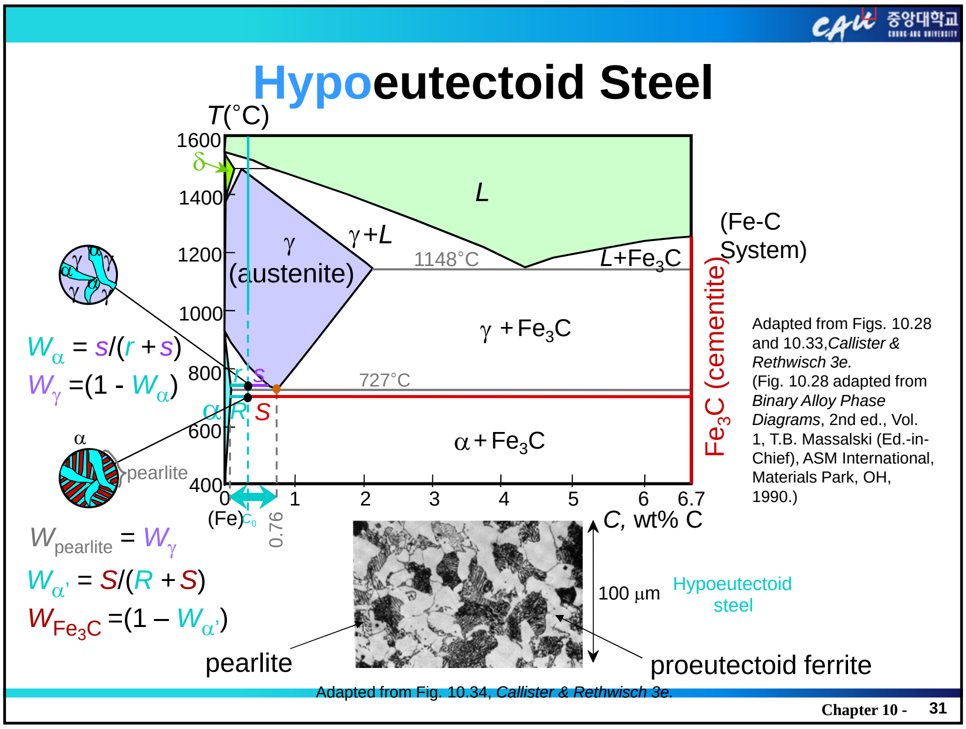
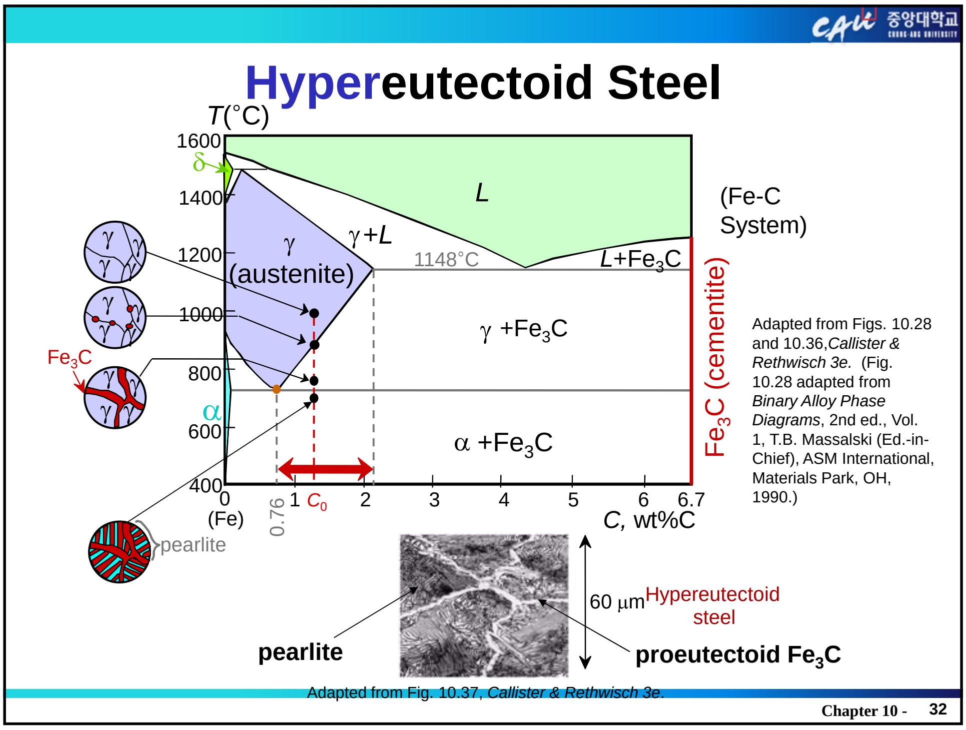
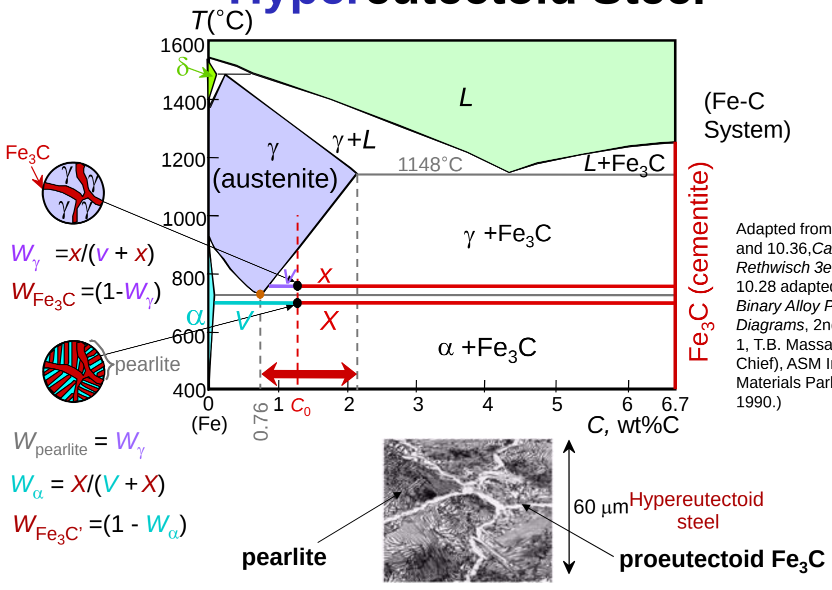

Hypoeutectoid Steel
T(°C)
1600
1400
1200
1000
800
600
400
δ
L
γ+L
γ
(austenite)
1148°C
L+Fe3C
γ + Fe3C
727°C
α + Fe3C
Fe3C (cementite)
(Fe-C System)
Wα = s/(r + s)
Wγ =(1 - Wα)
α
pearlite
r s
R S
0 1 2 3 4 5 6 6.7
(Fe) C0 0.76
C, wt% C
Wpearlite = Wγ
Wα' = S/(R + S)
WFe3C =(1 – Wα')
100 µm
Hypoeutectoid steel
pearlite
proeutectoid ferrite
Adapted from Figs. 10.28 and 10.33, Callister & Rethwisch 3e. (Fig. 10.28 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. 10.34, Callister & Rethwisch 3e.
Chapter 10 - 31


Hypereutectoid Steel
T(°C)
1600
1400
1200
1000
800
600
400
δ
L
γ+L
γ
(austenite)
1148°C
L+Fe3C
γ +Fe3C
α +Fe3C
Fe3C (cementite)
(Fe-C System)
Fe3C
α
pearlite
0 1 C0 2 3 4 5 6 6.7
(Fe) 0.76
C, wt%C
60 µm
Hypereutectoid steel
pearlite
proeutectoid Fe3C
Adapted from Figs. 10.28 and 10.36, Callister & Rethwisch 3e. (Fig. 10.28 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. 10.37, Callister & Rethwisch 3e.
Chapter 10 - 32

## Hypereutectoid Steel




Adapted from Figs. 10.28 and 10.36, *Callister & Rethwisch 3e.* (Fig. 10.28 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. 10.37, *Callister & Rethwisch 3e.*



## 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 ($\alpha$).

b) The amount of cementite (in grams) that forms in 100 g of steel.

c) The amounts of pearlite and proeutectoid ferrite ($\alpha$) in the 100 g.

# Solution to Example Problem

a) Using the *RS* tie line just below the eutectoid

$C_\alpha$ = 0.022 wt% C
$C_{Fe_3C}$ = 6.70 wt% C

b) Using the lever rule with the tie line shown

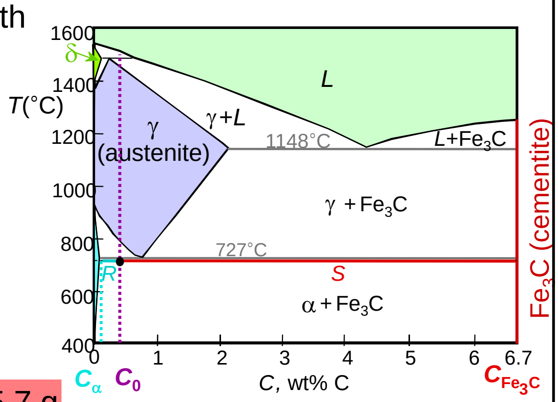
$$W_{Fe_3C} = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha}$$

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

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
$C_\alpha$ = 0.022 wt% C
$C_{pearlite} = C_\gamma$ = 0.76 wt% C

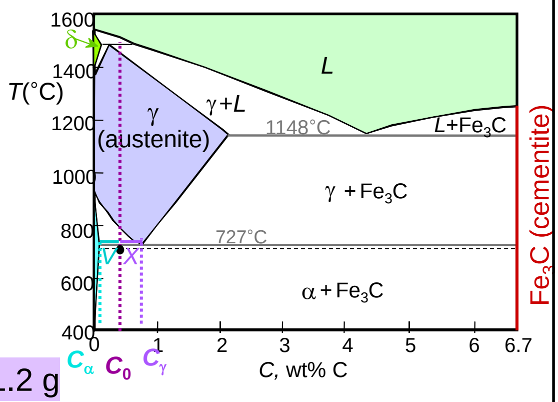
$$W_{pearlite} = \frac{V}{V+X} = \frac{C_0 - C_\alpha}{C_\gamma - C_\alpha}$$

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

Amount of pearlite in 100 g

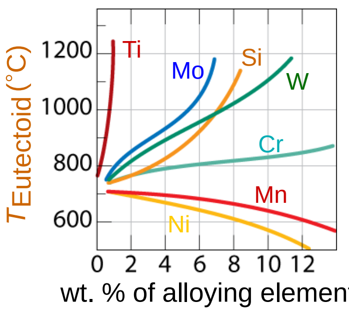
= (100 g)$W_{pearlite}$

= (100 g)(0.512) = 51.2 g



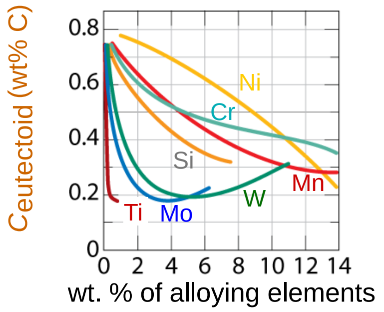
# Alloying with Other Elements

- $T_{eutectoid}$ changes:




Adapted from Fig. 10.38,*Callister & Rethwisch 3e*. (Fig. 10.38 from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)

- $C_{eutectoid}$ changes:




Adapted from Fig. 10.39,*Callister & Rethwisch 3e*. (Fig. 10.39 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.