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%Al - wt%Cu), and

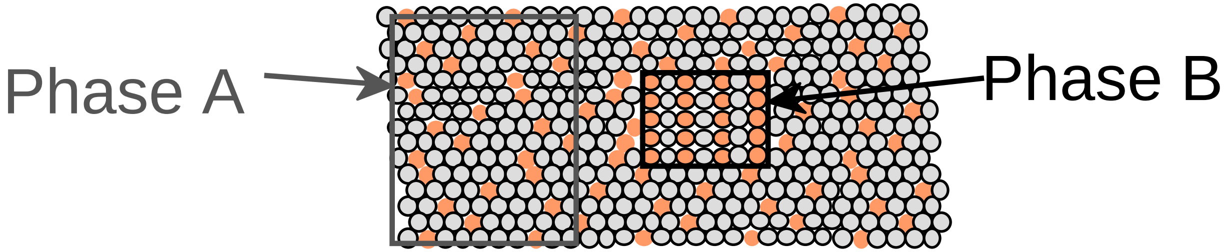
  --a temperature (T)

  then...

  How many phases do we get?

  What is the composition of each phase?

  How much of each phase do we get?



○Aluminum atom

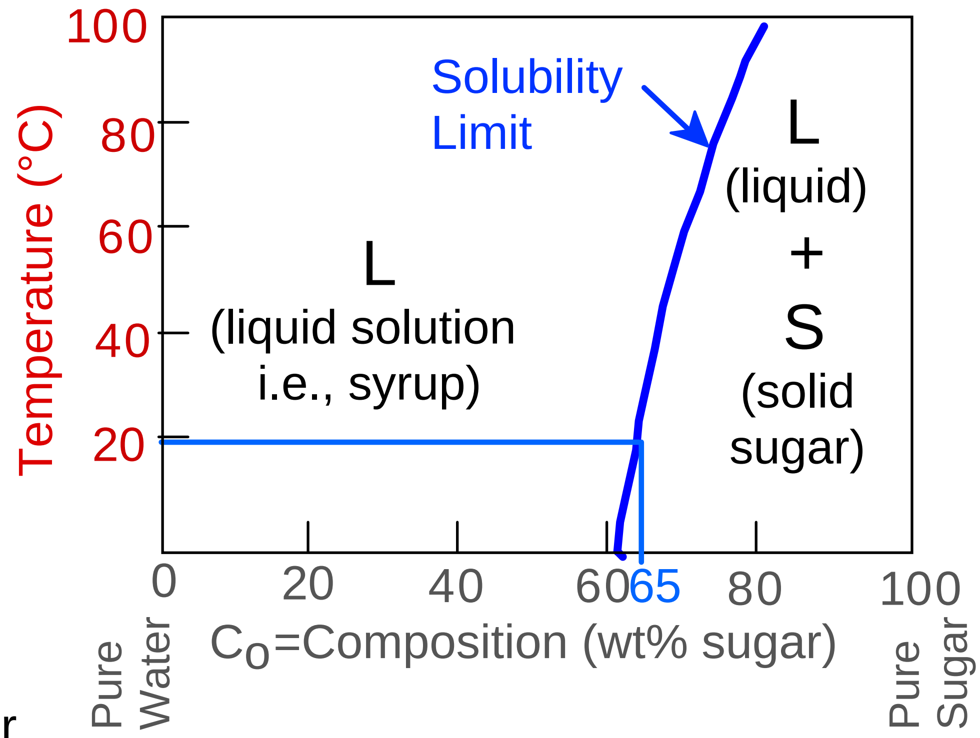
•Copper atom

The Solubility limit

- Solubility Limit:
  Max concentration for which only a solution occurs.

- Ex: Phase Diagram:
  Water-Sugar System

  Question: What is the solubility limit at 20C?
  Answer: 65wt% sugar.
  If C_o < 65wt% sugar: sugar
  If C_o > 65wt% sugar: syrup + sugar.



Adapted from Fig. 9.1, *Callister 6e.*

- Solubility limit increases with T:
  e.g., if T = 100C, solubility limit = 80wt% sugar.

Components and phases

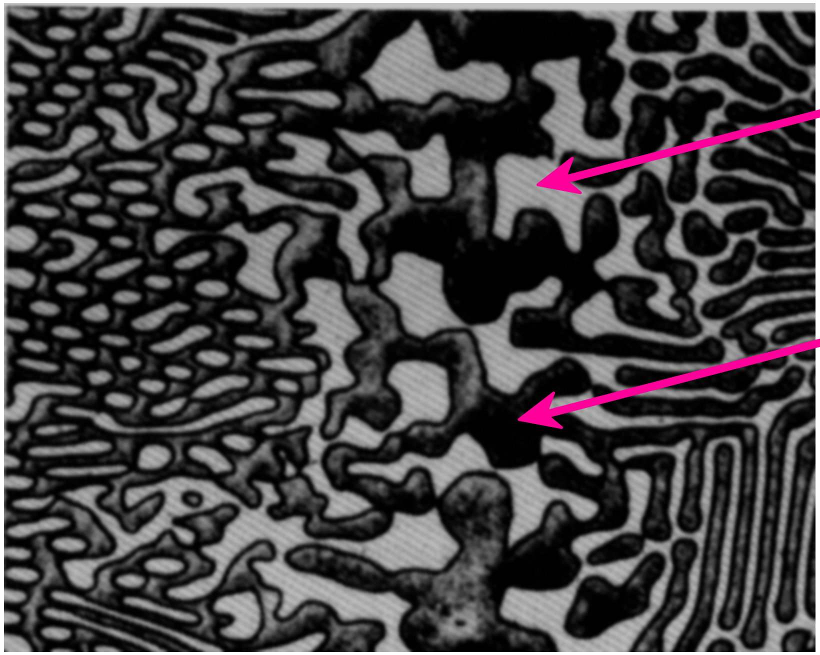
- **Components**:

  The elements or compounds which are mixed initially (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)

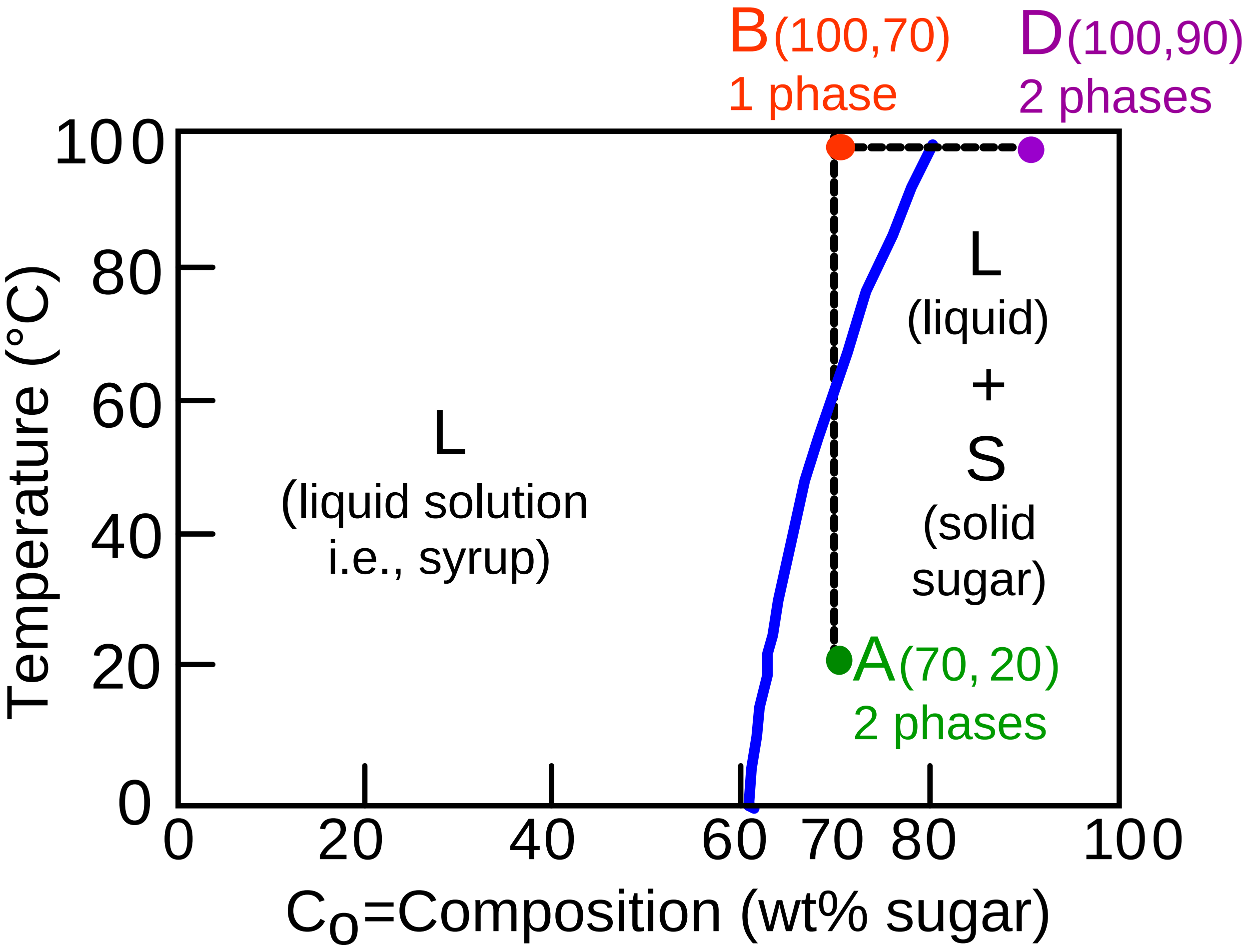
α (darker phase)

Adapted from Fig. 9.0, *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

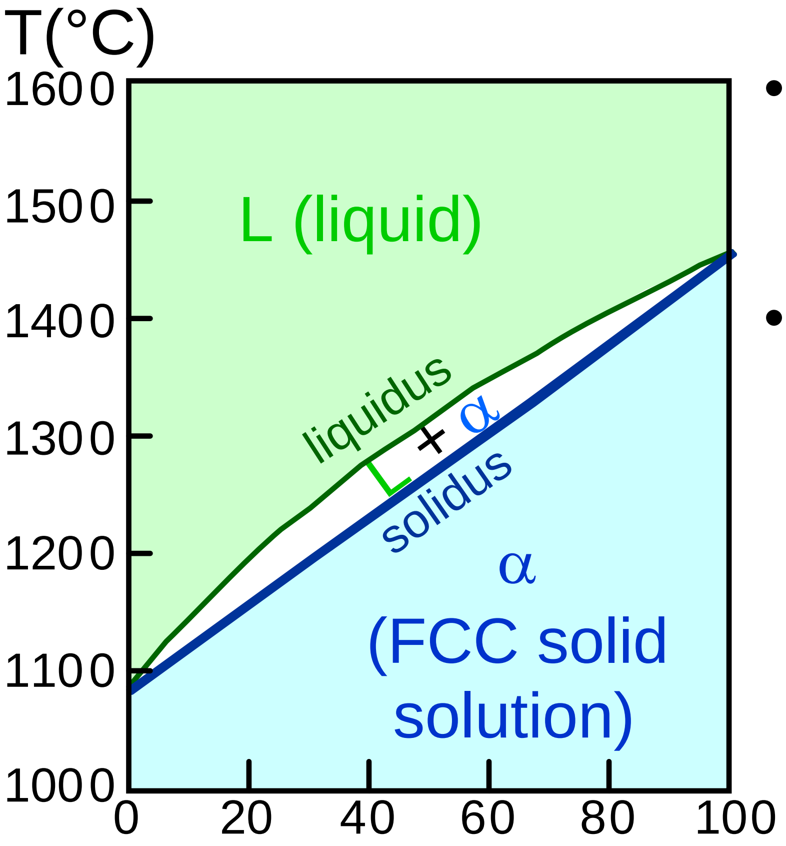


Adapted from
Fig. 9.1,
Callister 6e.

Phase diagrams

- Tell us about phases as function of T, C_o, P.
- For this course:
  --binary systems: just 2 components.
  --independent variables: T and C_o (P = 1atm is always used).

- Phase Diagram for Cu-Ni system



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

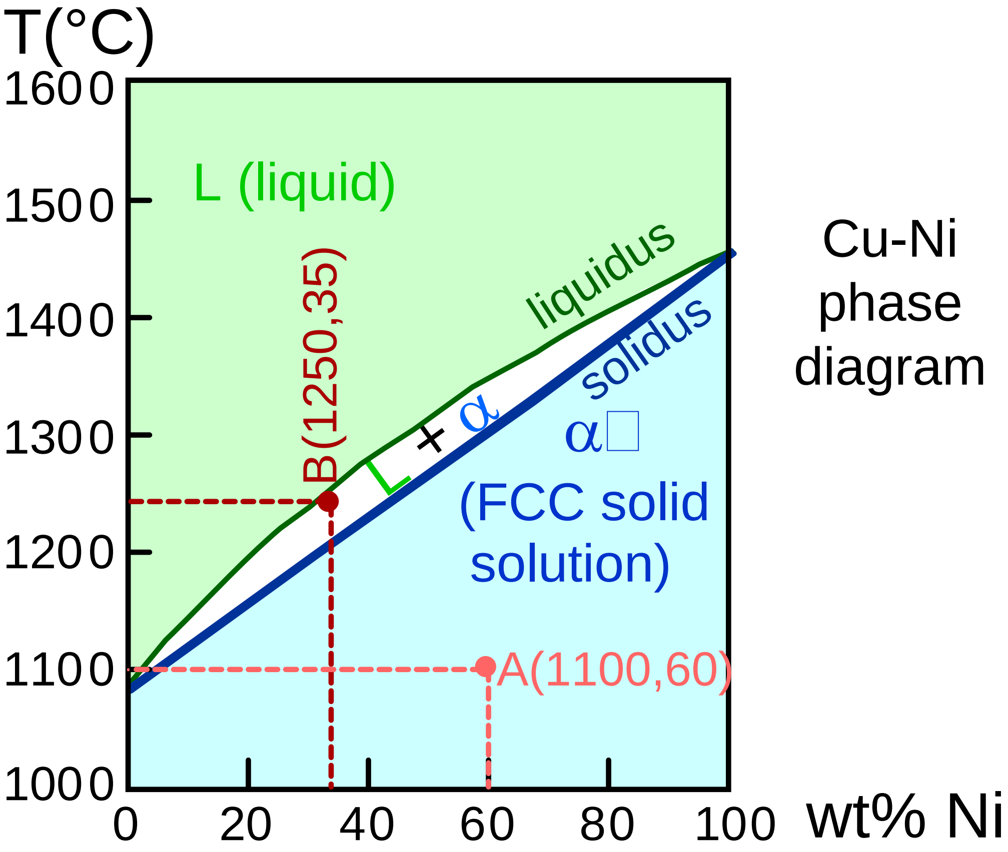
Adapted from Fig. 9.2(a), *Callister 6e.* (Fig. 9.2(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

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, 60):
  1 phase: α

  B(1250, 35):
  2 phases: L + α



Cu-Ni phase diagram

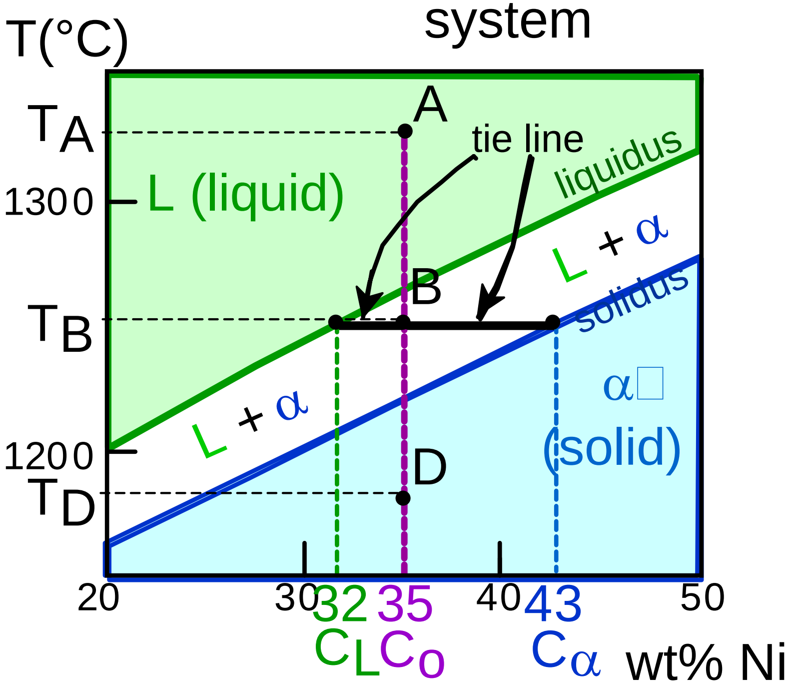
Adapted from Fig. 9.2(a), *Callister 6e.* (Fig. 9.2(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991).

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 = 35wt%Ni
  At T_A:
  Only Liquid (L)
  $C_L = C_o$ (= 35wt% Ni)
  At T_D:
  Only Solid (α)
  $C_\alpha = C_o$ (= 35wt% Ni)
  At T_B:
  Both α and L
  $C_L = C_{liquidus}$ (= 32wt% Ni here)
  $C_\alpha = C_{solidus}$ (= 43wt% Ni here)

Cu-Ni system



Adapted from Fig. 9.2(b), *Callister 6e.* (Fig. 9.2(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 = 35wt%Ni

At T_A: Only Liquid (L)

W_L = 100wt%, W_α = 0

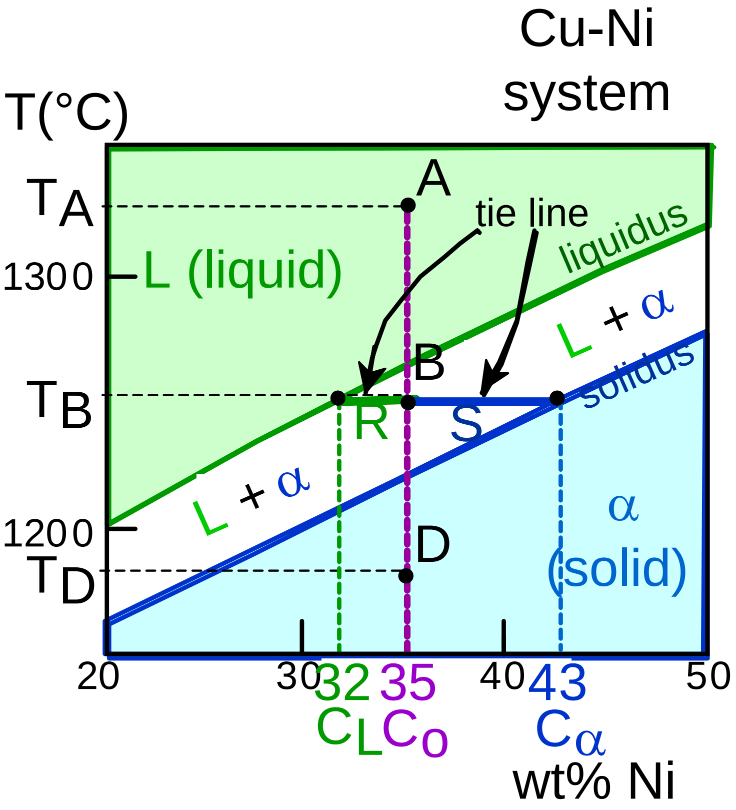
At T_D: Only Solid (α)

W_L = 0, W_α = 100wt%

At T_B: Both α and L

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

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



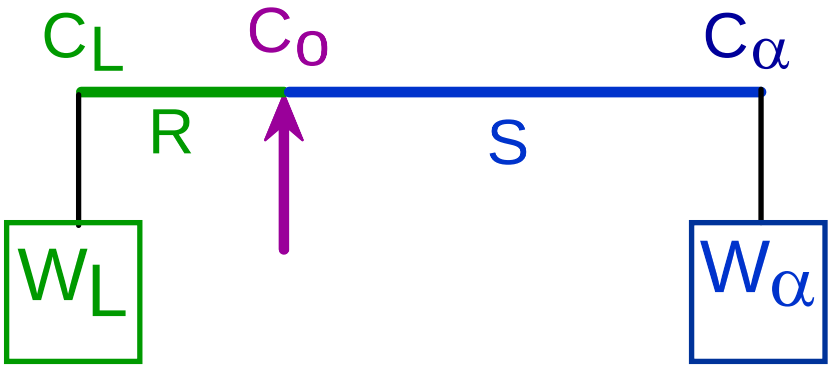
The lever rule: a proof

- Sum of weight fractions: $W_L + W_\alpha = 1$
- Conservation of mass (Ni): $C_o = W_L C_L + W_\alpha C_\alpha$
- Combine above equations:

$$\boxed{W_L = \frac{C_\alpha - C_o}{C_\alpha - C_L} = \frac{S}{R+S}}$$

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

- A geometric interpretation:



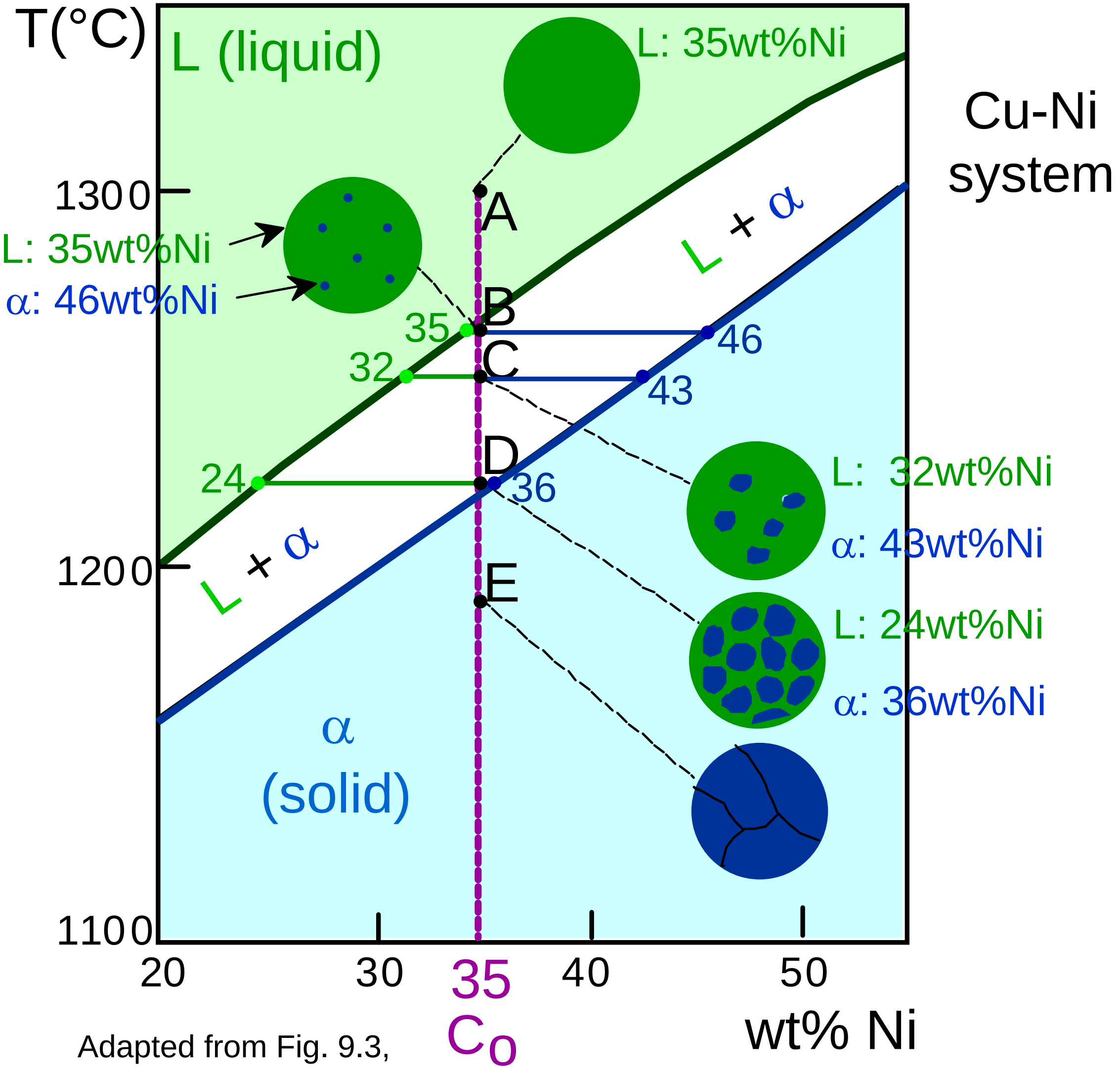
moment equilibrium:

$$\underset{\boxed{1-W_\alpha}}{\underset{\nwarrow}{\boxed{W_L}}}\, R = W_\alpha S$$

solving gives Lever Rule

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 100wt% Ni.
- Consider
  C_o = 35wt%Ni.

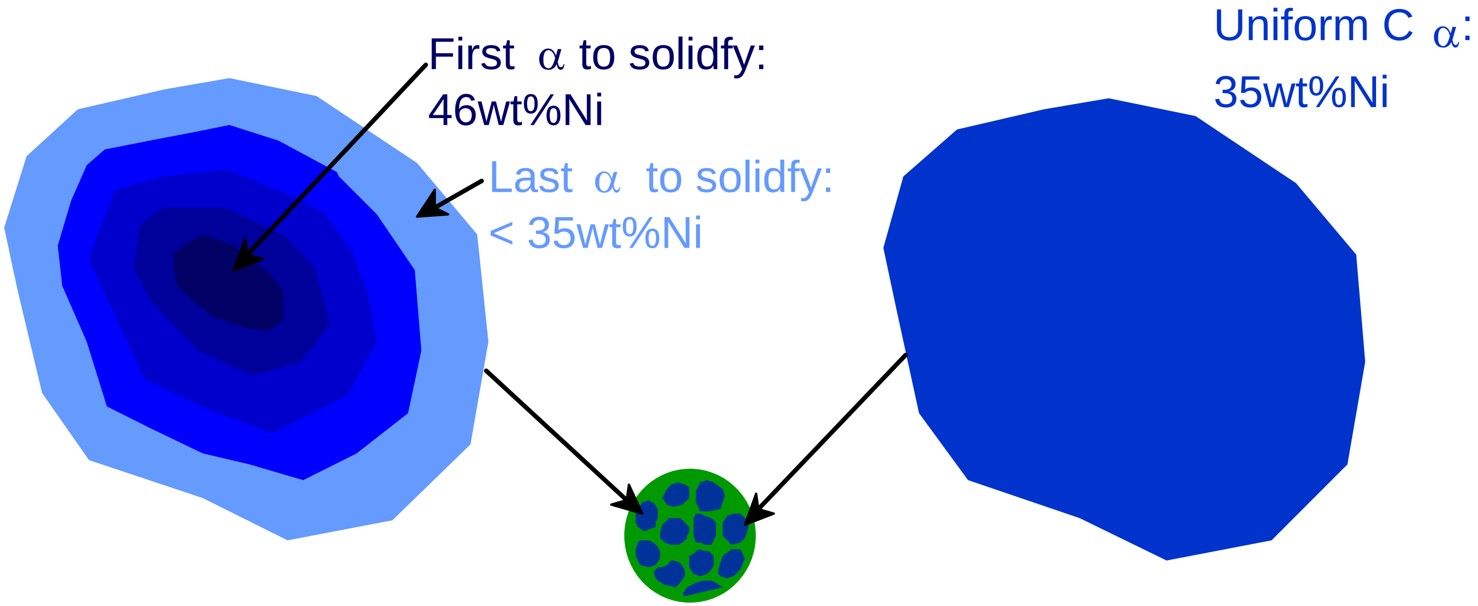


Adapted from Fig. 9.3, *Callister 6e.*

Cored vs equilibrium phases

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

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



First α to solidfy:
46wt%Ni

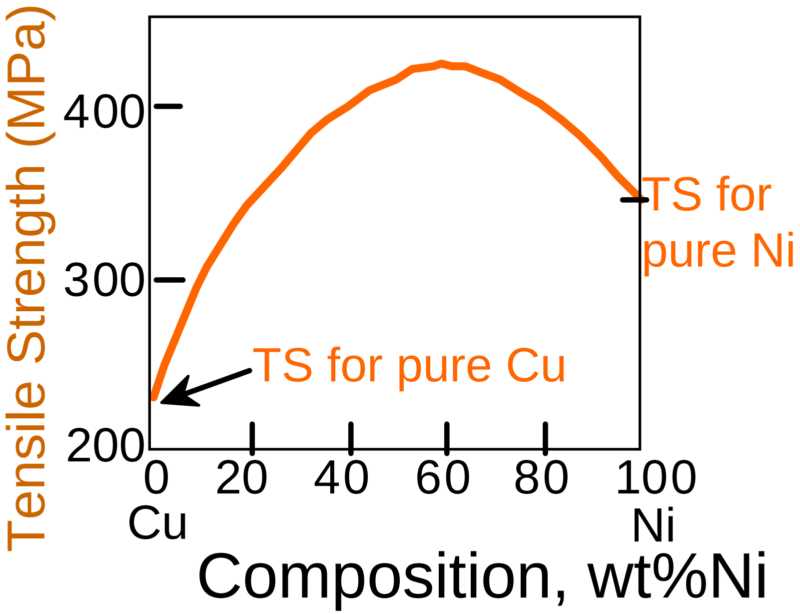
Last α to solidfy:
< 35wt%Ni

Uniform C α:
35wt%Ni

Mechanical properties: Cu-Ni System

- Effect of solid solution strengthening on:

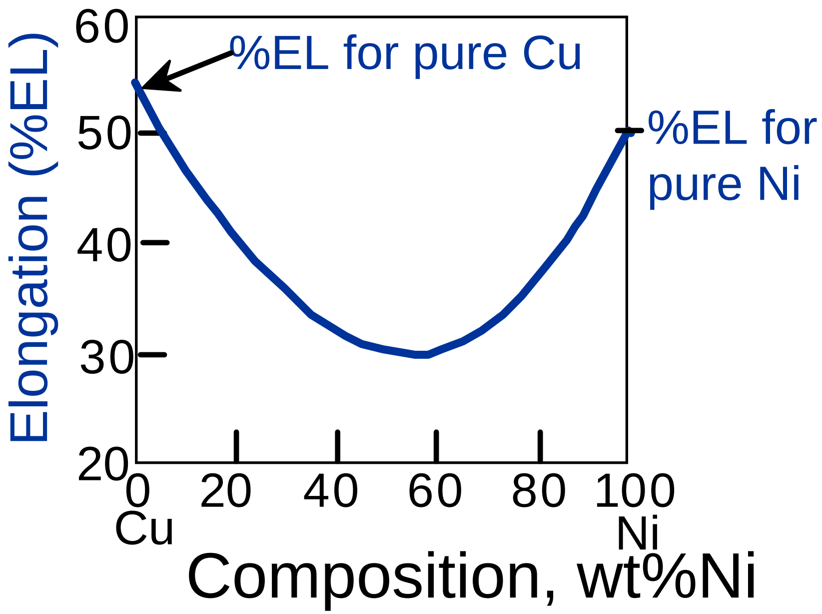
--Tensile strength (TS)



Adapted from Fig. 9.5(a), *Callister 6e.*

--Peak as a function of C_o

--Ductility (%EL,%AR)



Adapted from Fig. 9.5(b), *Callister 6e.*

--Min. as a function of C_o

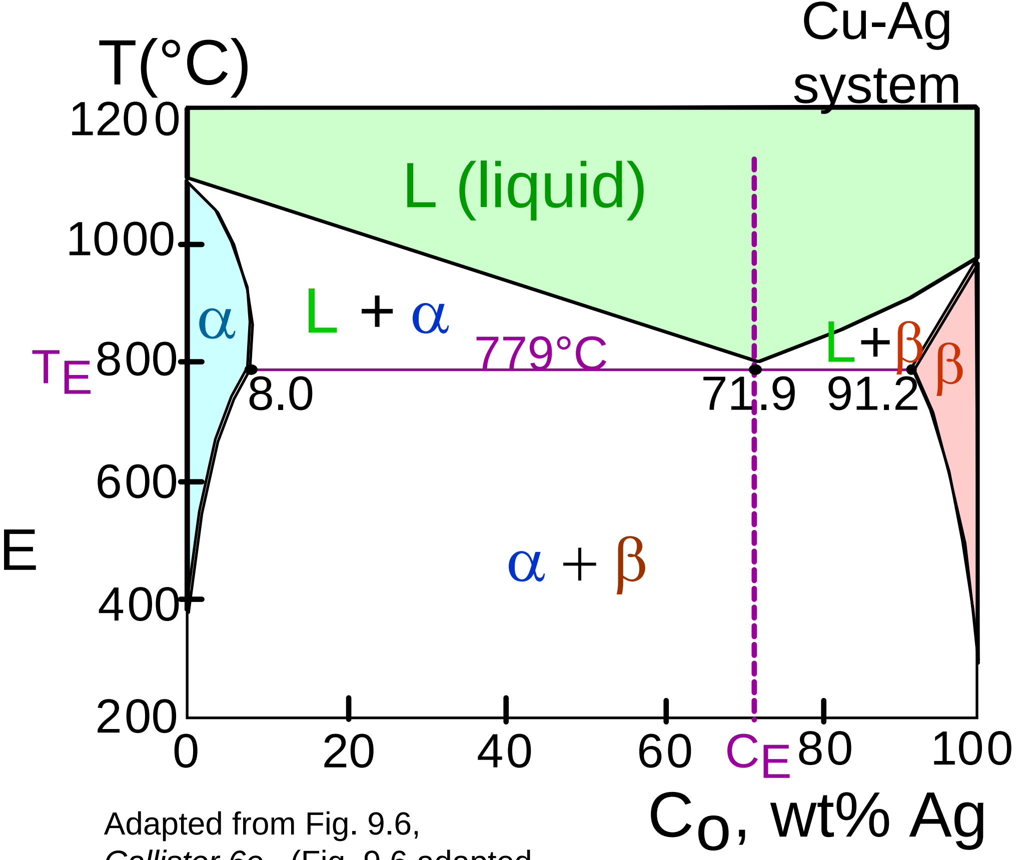
Binary-eutectic systems

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 Ni
- T_E: No liquid below T_E
- C_E: Min. melting T composition



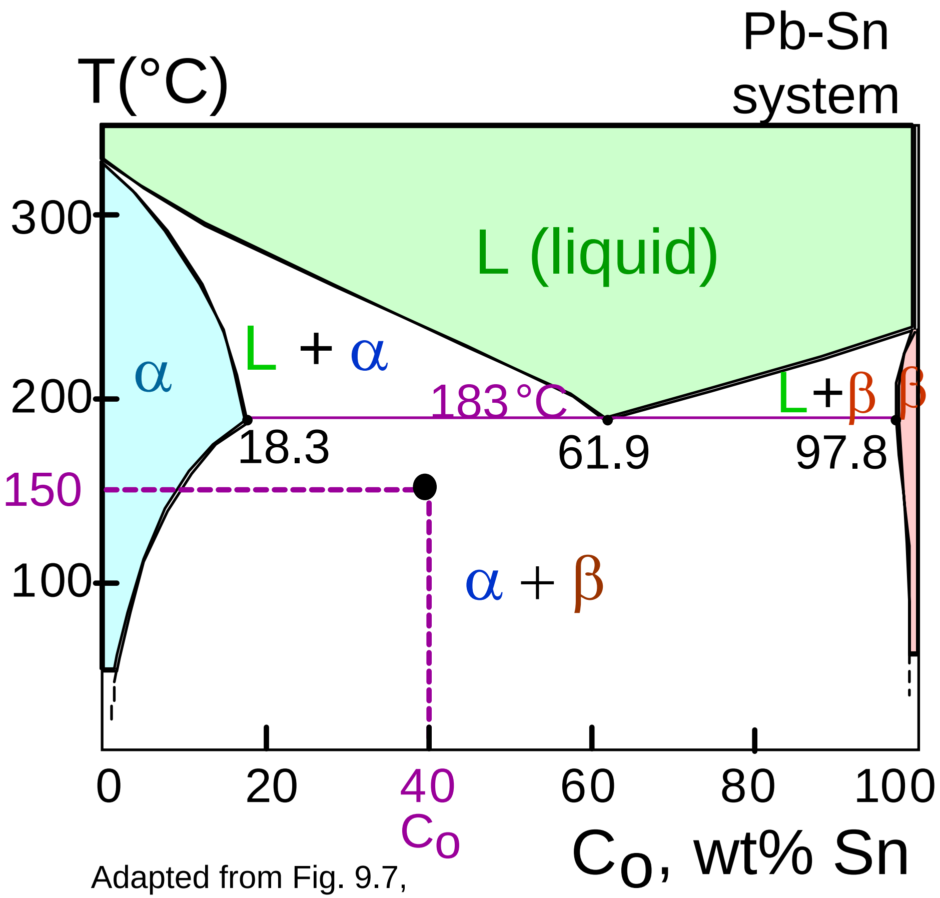
Adapted from Fig. 9.6, *Callister 6e.* (Fig. 9.6 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)

Ex: Pb-Sn eutectic system (1)

- For a 40wt%Sn-60wt%Pb alloy at 150C, find...
  - --the phases present:

    $\alpha + \beta$

  - --the compositions of the phases:



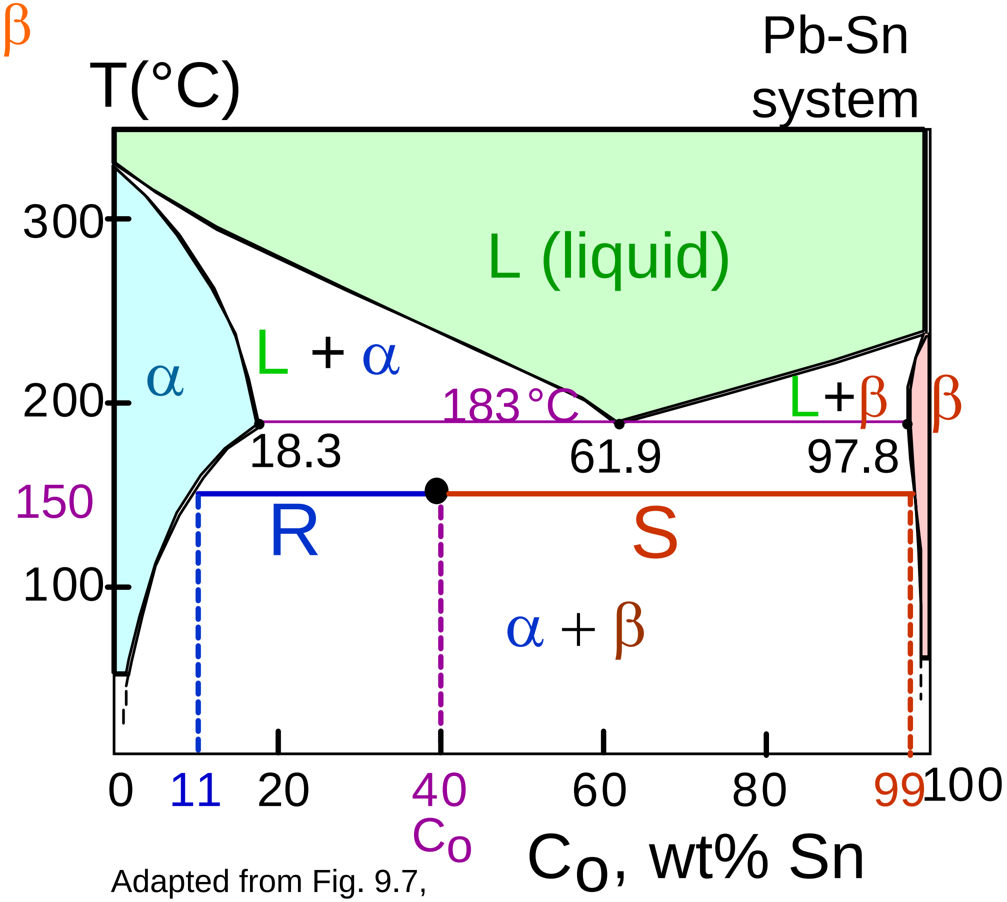
Adapted from Fig. 9.7, *Callister 6e.* (Fig. 9.7 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)

Ex: Pb-Sn eutectic system (2)

- For a 40wt%Sn-60wt%Pb alloy at 150C, find...
  - --the phases present: $\alpha + \beta$
  - --the compositions of the phases:
    - $C\alpha$ = 11wt%Sn
    - $C\beta$ = 99wt%Sn
  - --the relative amounts of each phase:

$$W_\alpha = \frac{59}{88} = 67\,\text{wt}\,\%$$

$$W_\beta = \frac{29}{88} = 33\,\text{wt}\,\%$$

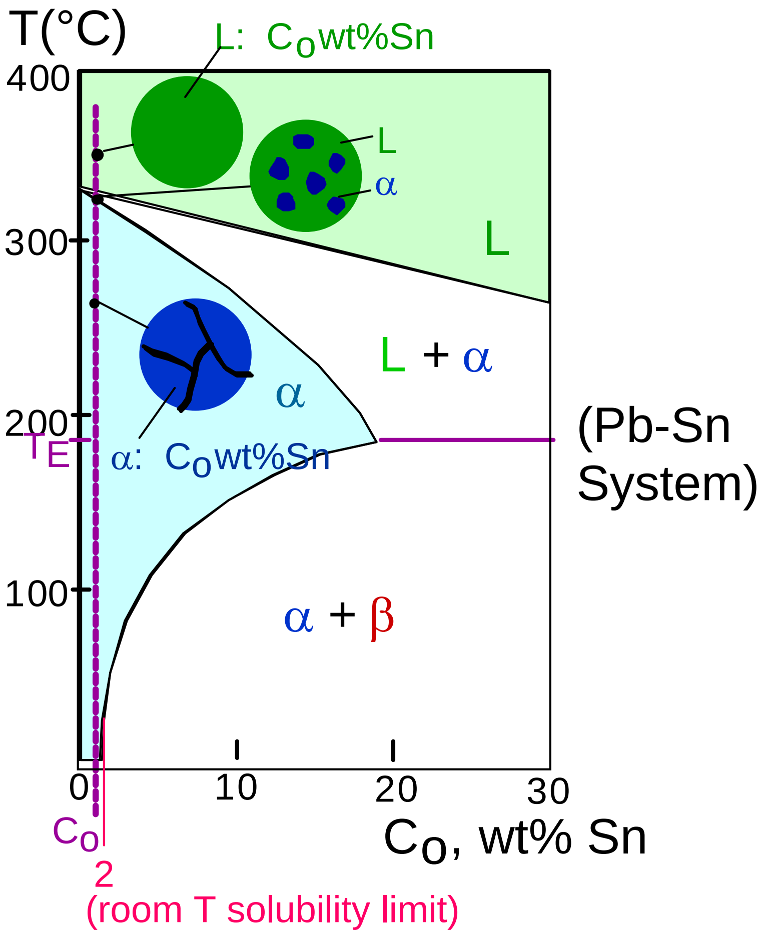


Adapted from Fig. 9.7, *Callister 6e.* (Fig. 9.7 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)

Microstructures in eutectic systems-I

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

  --polycrystal of α grains.

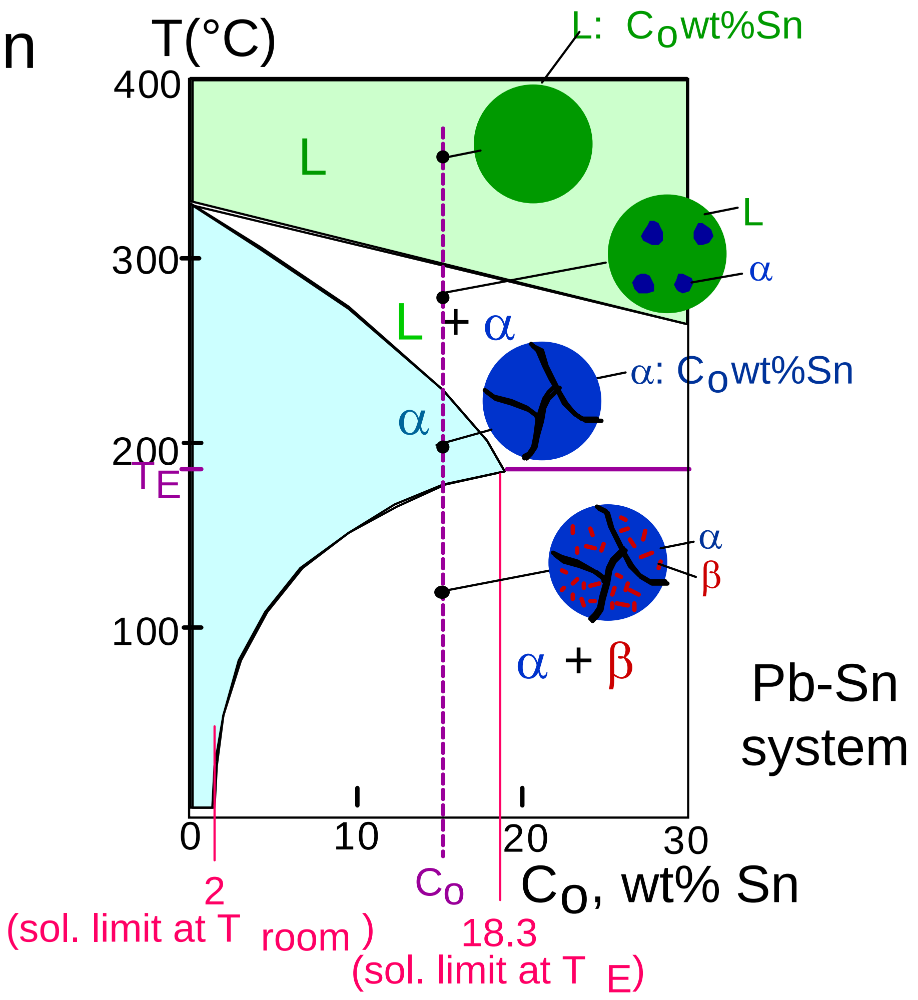


Adapted from Fig. 9.9, *Callister 6e.*

Microstructures in eutectic systems-II

- 2wt%Sn < C_o < 18.3wt%Sn
- Result:

  --α polycrystal with fine β crystals.

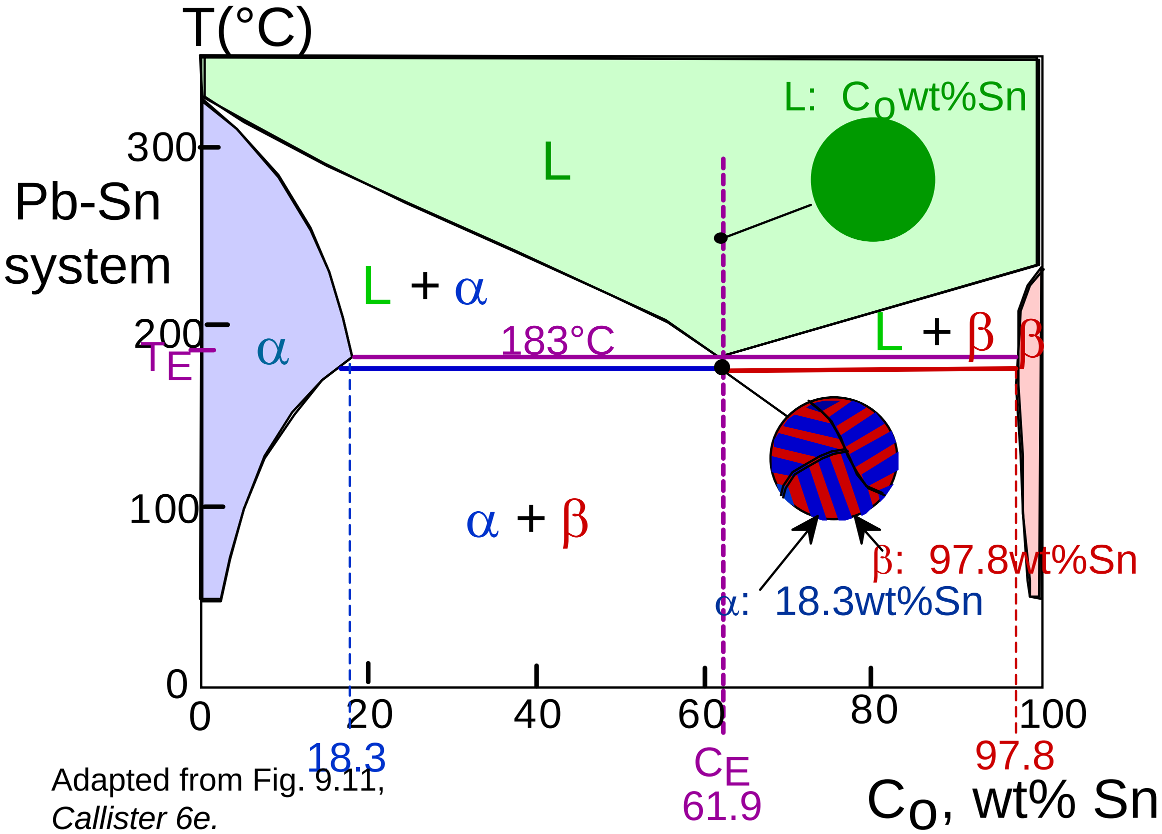


Adapted from Fig. 9.10, *Callister 6e.*

Microstructures in eutectic systems-III

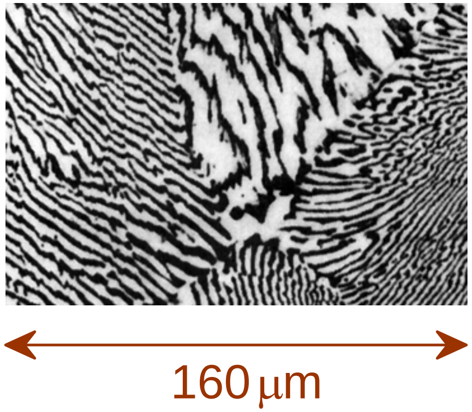
- $C_o = C_E$
- Result: Eutectic microstructure

  --alternating layers of α and β crystals.



Adapted from Fig. 9.11, *Callister 6e.*

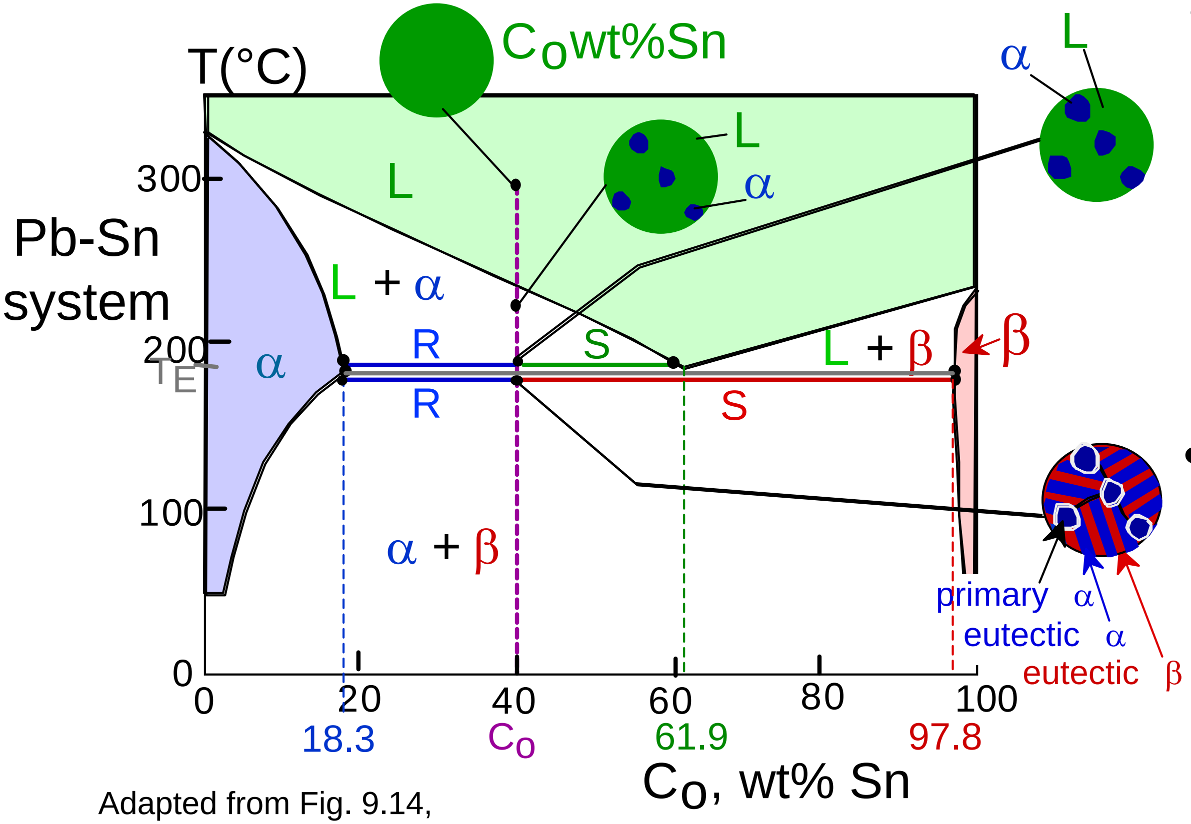
Micrograph of Pb-Sn eutectic microstructure



Adapted from Fig. 9.12, *Callister 6e.* (Fig. 9.12 from *Metals Handbook*, Vol. 9, 9th ed., *Metallography and Microstructures*, American Society for Metals, Materials Park, OH, 1985.)

Microstructures in eutectic systems-IV

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



Adapted from Fig. 9.14, *Callister 6e.*

- Just above T_E:

C_α = 18.3wt%Sn

C_L = 61.9wt%Sn

$$W_\alpha = \frac{S}{R+S} = 50\text{wt\%}$$

$$W_L = (1-W_\alpha) = 50\text{wt\%}$$

- Just below T_E:

C_α = 18.3wt%Sn

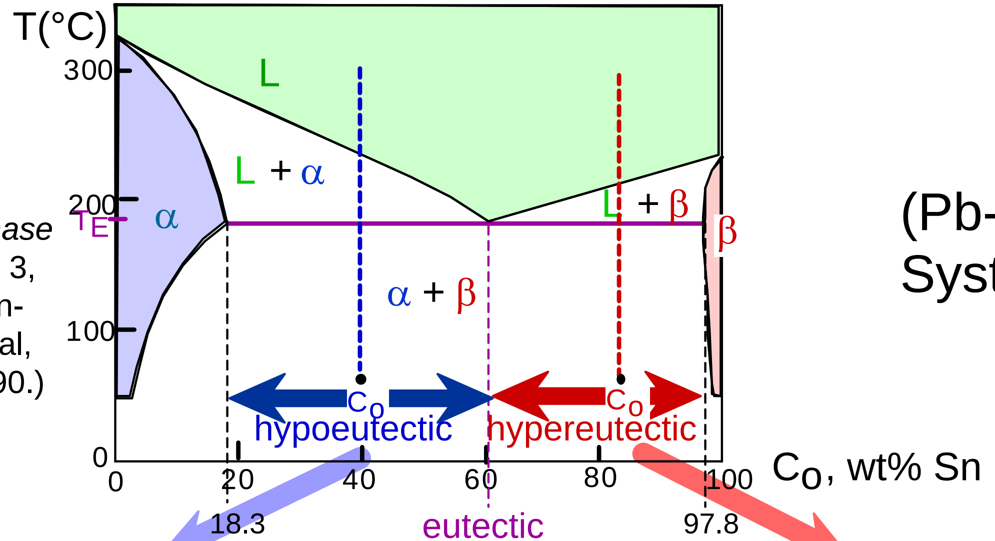
C_β = 97.8wt%Sn

$$W_\alpha = \frac{S}{R+S} = 73\text{wt\%}$$

$$W_\beta = 27\text{wt\%}$$

Hypoeutectic & Hypereutectic

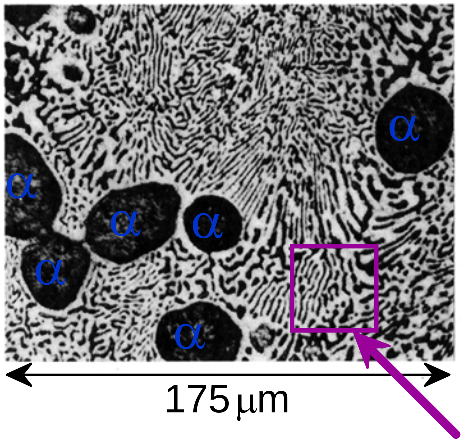
Adapted from Fig. 9.7, *Callister 6e.* (Fig. 9.7 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)



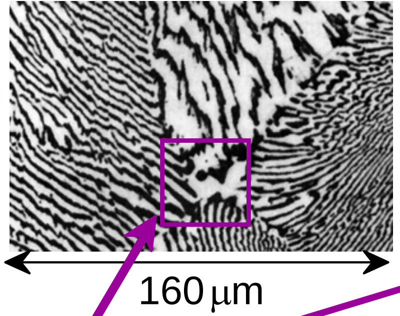
(Pb-Sn System)

(Figs. 9.12 and 9.15 from *Metals Handbook*, 9th ed., Vol. 9, *Metallography and Microstructures*, American Society for Metals, Materials Park, OH, 1985.)

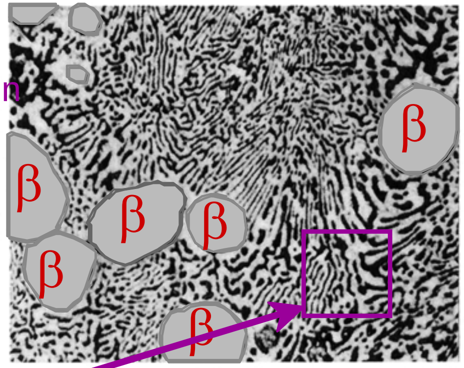
hypoeutectic: C_o=50wt%Sn



eutectic: C_o=61.9wt%Sn



hypereutectic: (illustration only)



eutectic micro-constituent

Adapted from Fig. 9.15, *Callister 6e.*

Adapted from Fig. 9.12, *Callister 6e.*

Adapted from Fig. 9.15, *Callister 6e.* (Illustration only)

Iron-carbon (Fe-C) phase diagram

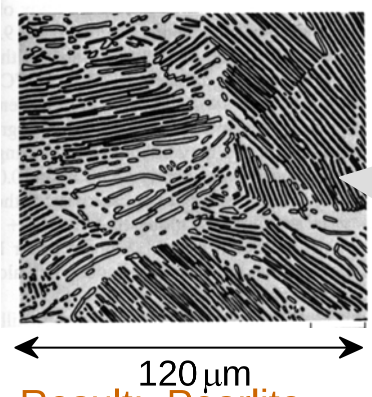
- 2 important points

-Eutectic (A):

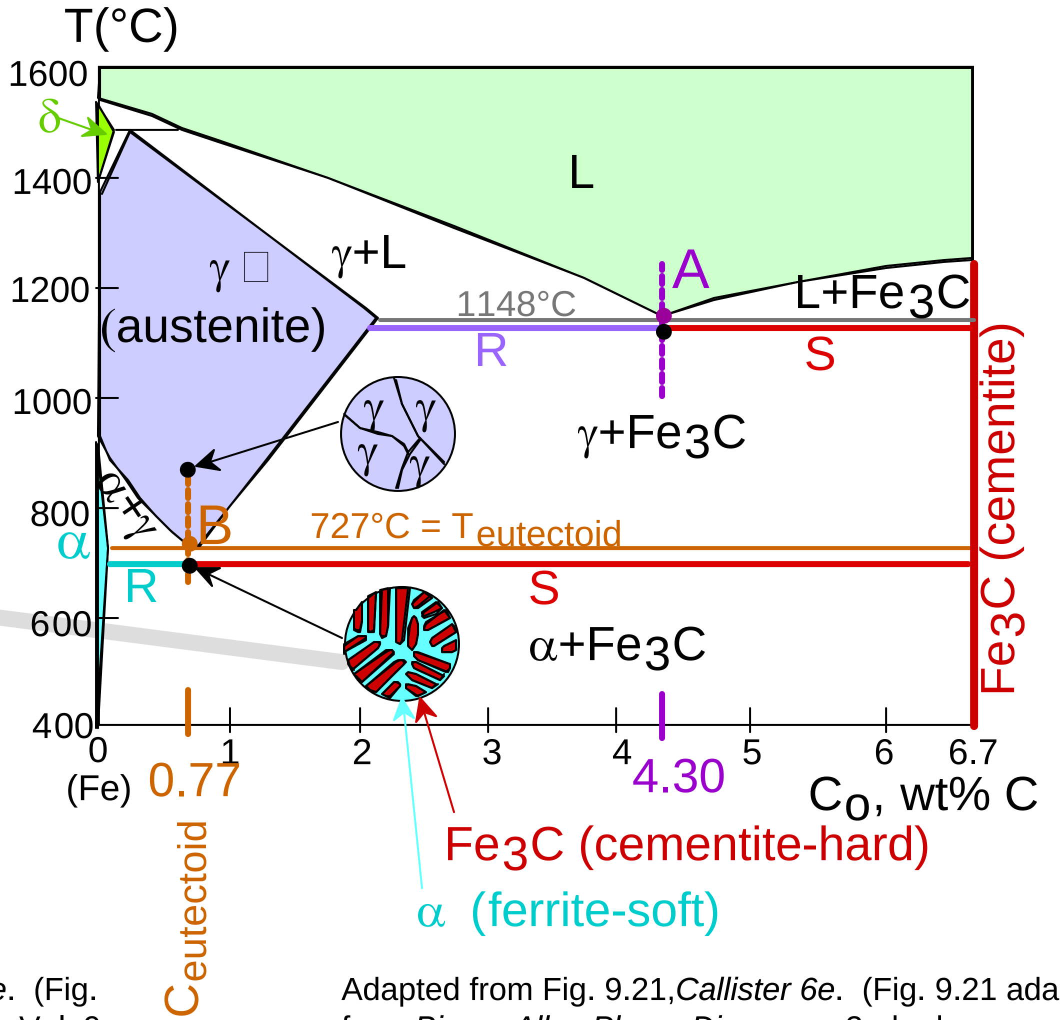
$L \Rightarrow \gamma + Fe_3C$

-Eutectoid (B):

$\gamma \Rightarrow \alpha + Fe_3C$



Result: Pearlite = alternating layers of α and Fe_3C phases.



(Adapted from Fig. 9.24, *Callister 6e*. (Fig. 9.24 from *Metals Handbook*, 9th ed., Vol. 9, *Metallography and Microstructures*, American Society for Metals, Materials Park, OH, 1985.)

Adapted from Fig. 9.21,*Callister 6e*. (Fig. 9.21 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

Eutectoid decomposition

Eutectoid reaction – All solid phases

$$\gamma \text{ (0.76 \%C)} \rightleftarrows \alpha \text{ (0.022 \%C)} + Fe_3C \text{ (6.7 \%C)}$$

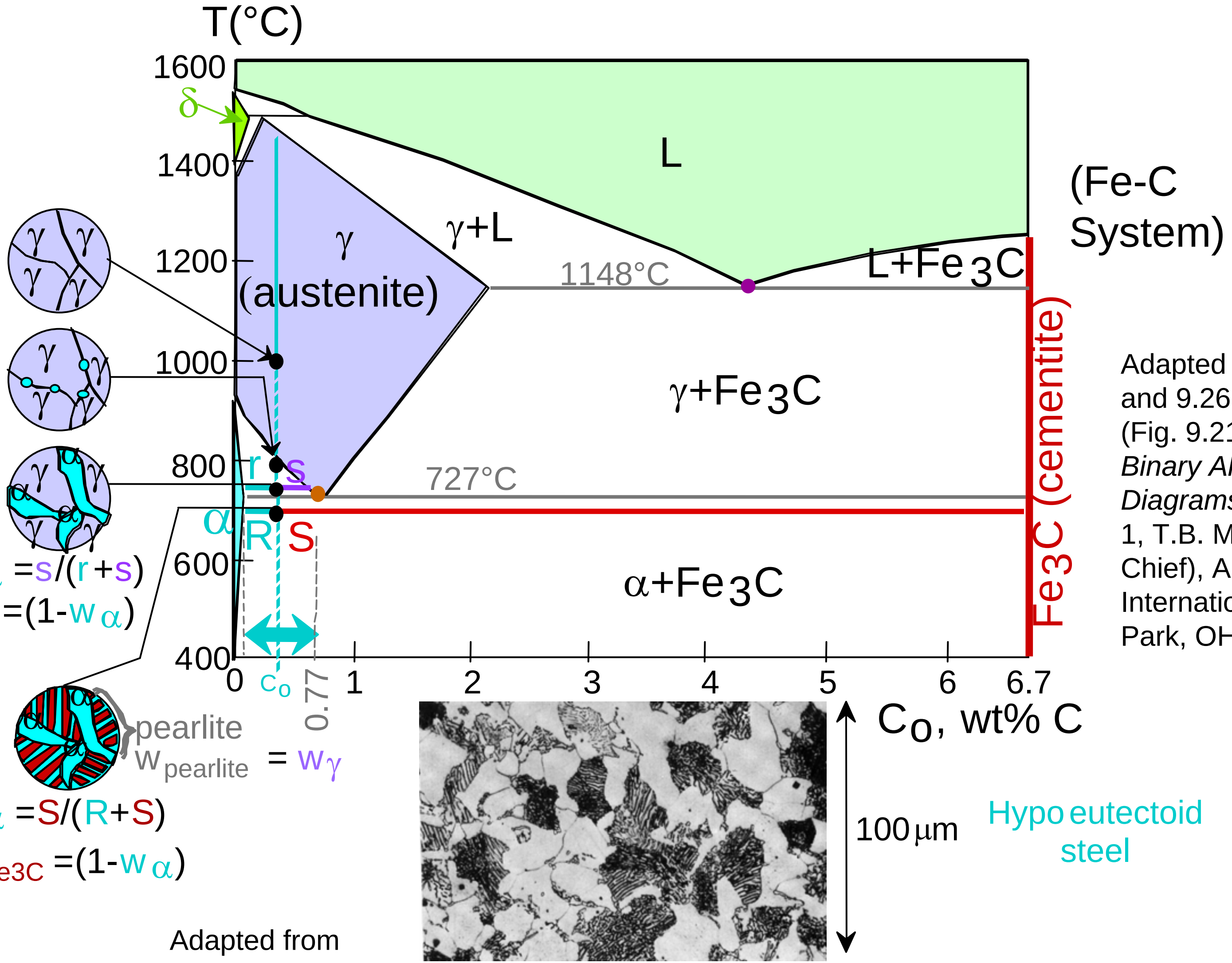
Austenite, FCC

Ferrite, bcc

Cementite, iron carbide
(Metastable, bct)

Pearlite (mixture of phases)

Hypoeutectoid steel



$w_{\alpha} = s/(r+s)$

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

$w_{pearlite} = w_{\gamma}$

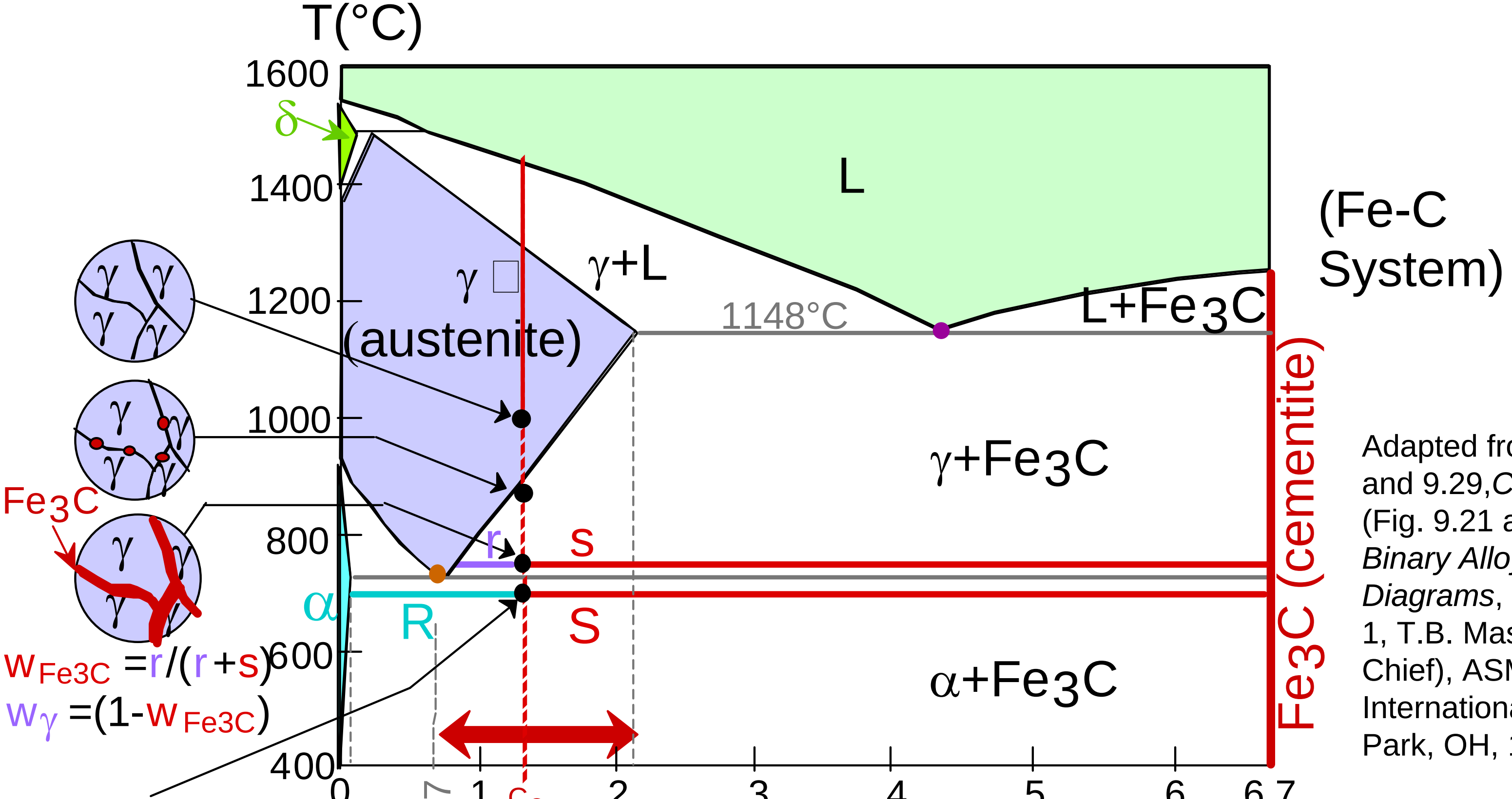
$w_{\alpha} = S/(R+S)$

$w_{Fe3C} = (1 - w_{\alpha})$

Adapted from Figs. 9.21 and 9.26, *Callister 6e*. (Fig. 9.21 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. 9.27, *Callister 6e*. (Fig. 9.27 courtesy Republic Steel Corporation.)

Hypereutectoid steel



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

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

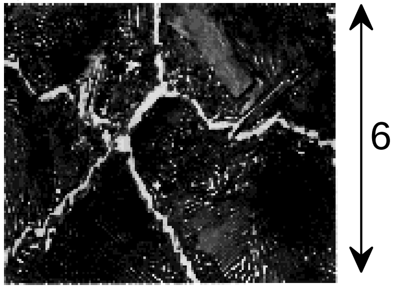
$w_{pearlite} = w_\gamma$

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

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

Co, wt% C

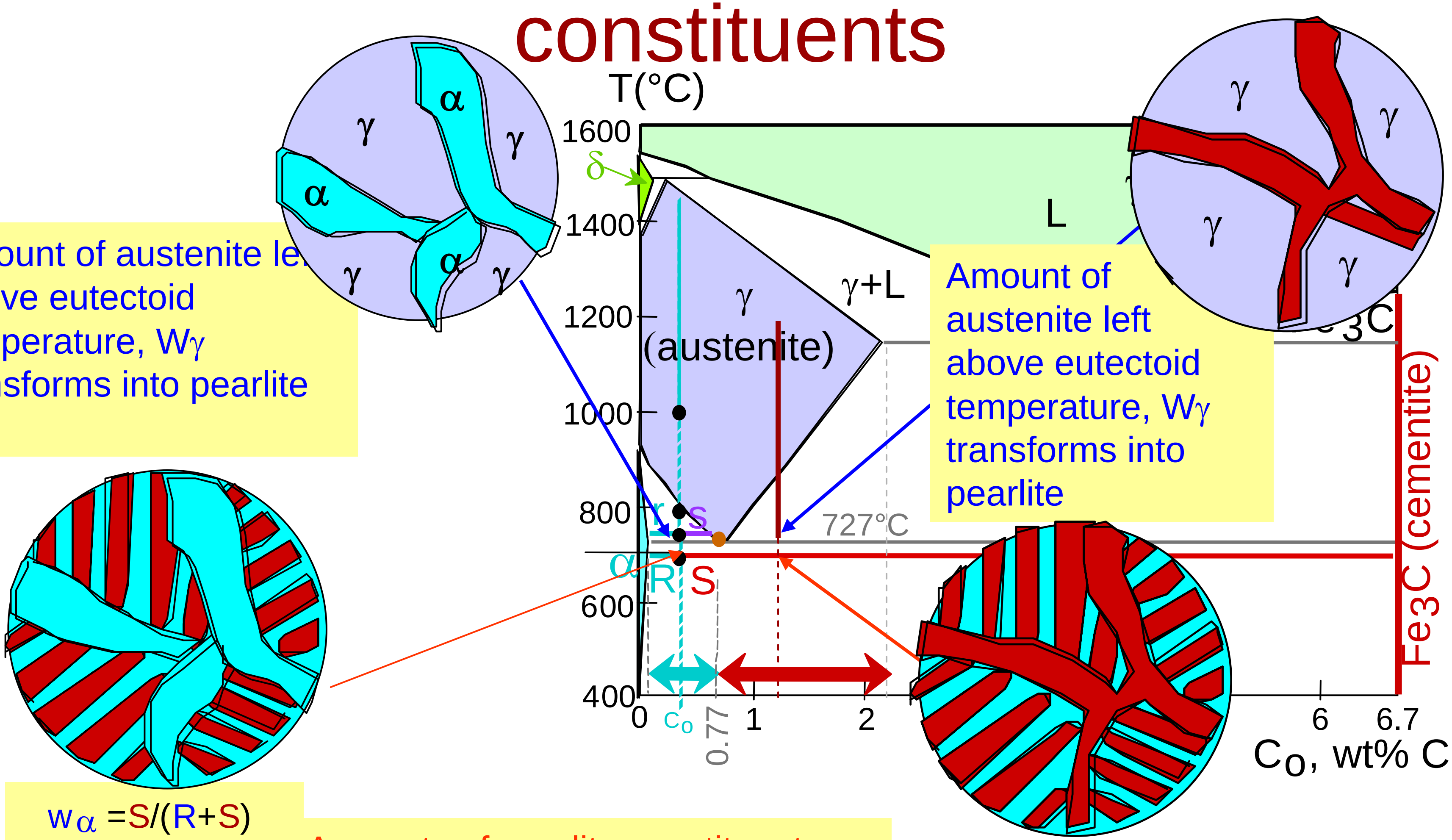
Adapted from Figs. 9.21 and 9.29,*Callister 6e*. (Fig. 9.21 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



Hypereutectoid steel

Adapted from Fig. 9.30,*Callister 6e*. (Fig. 9.30 copyright 1971 by United States Steel Corporation.)

Amounts of pearlite & pearlite constituents



Amount of austenite le above eutectoid temperature, Wγ transforms into pearlite

Amount of austenite left above eutectoid temperature, Wγ transforms into pearlite

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

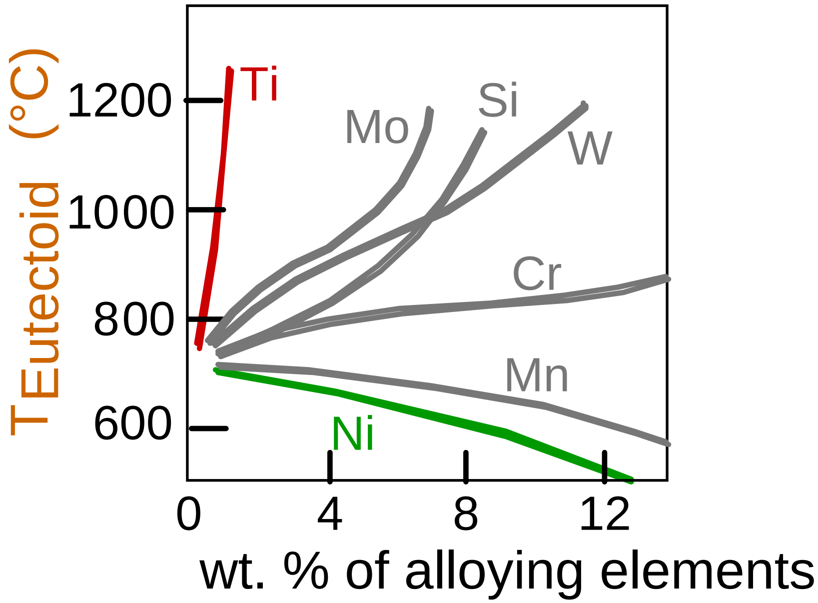
$w_{Fe3C} = (1-w_\alpha)$

Amounts of pearlite constituents

Amount of pearlite = Amount of austenite left above eutectoid temperature, Wγ

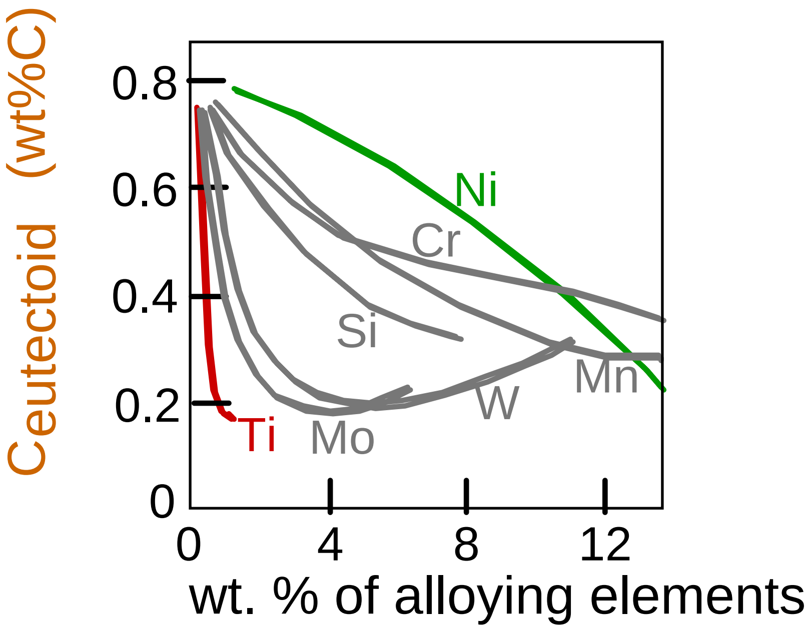
Alloying steel with more elements

- $T_{eutectoid}$ changes:



Adapted from Fig. 9.31,*Callister 6e*. (Fig. 9.31 from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)

- $C_{eutectoid}$ changes:



Adapted from Fig. 9.32,*Callister 6e*. (Fig. 9.32 from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)

Nomenclature for AISI and SAE steels

10xx	Plain carbon steels*
11xx	Plain-carbon (resulfurized for machinability)
15xx	Manganese (1.0-2.0%)
40xx	Molybdenum (0.2-0.3%)
41xx	Chromium (0.40-1.2%), molybdenum (0.08-0.25%)
43xx	Nickel (1.65-2.00%), chromium (0.40-0.90%), molybdenum (0.5%)
44xx	Molybdenum (0.5%)
46xx	Nickel (1.40-2.00%), molybdenum (0.15-0.30%)
48xx	Nickel (3.25-3.75%), molybdenum (0.20-0.30%)
51xx	Chromium (0.70-1.20%)
61xx	Chromium (0.70-1.10%), vanadium (0.10%)
81xx	Nickel (0.20-0.40%), chromium (0.30-0.55%), molybdenum (0.08-0.15%)
86xx	Nickel (0.30-0.70%), chromium (0.40-0.85%), molybdenum (0.08-0.25%)
87xx	Nickel (0.40-0.70%), chromium (0.40-0.60%), molybdenum (0.20-0.30%)
92xx	Silicon (1.80-2.20%)

xx - carbon content, 0.xx

All plain carbon steel contain 0.50% Mn

Summary

- Phase diagrams are useful tools to determine:

  -- the number and types of phases present,

  -- the composition of each phase

  -- and the fractional amount wt% of each phase,

  -- and the microstructure of the alloy

  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.