Introduction to Phase Diagram

- There is a strong correlation between microstructure and mechanical properties. And the development of microstructure of an alloy is related to the characteristics of its phase diagram
- It is a type of chart used to show conditions at which thermodynamically distinct phases can occur at equilibrium.
- Provides valuable information about melting, casting, crystallization, and other phenomena

What is a Phase?

- The term ‘phase’ refers to a separate and identifiable state of matter in which a given substance may exist.
- Applicable to both crystalline and non-crystalline materials.
- An important refractory oxide silica is able to exist as three crystalline phases, quartz, tridymite and cristobalite, as well as a non-crystalline phase, silica glass, and as molten silica.
- Every pure material is considered to be a phase, so also is every solid, liquid, and gaseous solution.
- For example, the sugar–water syrup solution is one phase, and solid sugar is another.

Phase Equilibria: Solubility Limit

Introduction

- Solutions – solid solutions, single phase
- Mixtures – more than one phase

- Solubility Limit:

Max concentration for which only a single phase solution occurs.

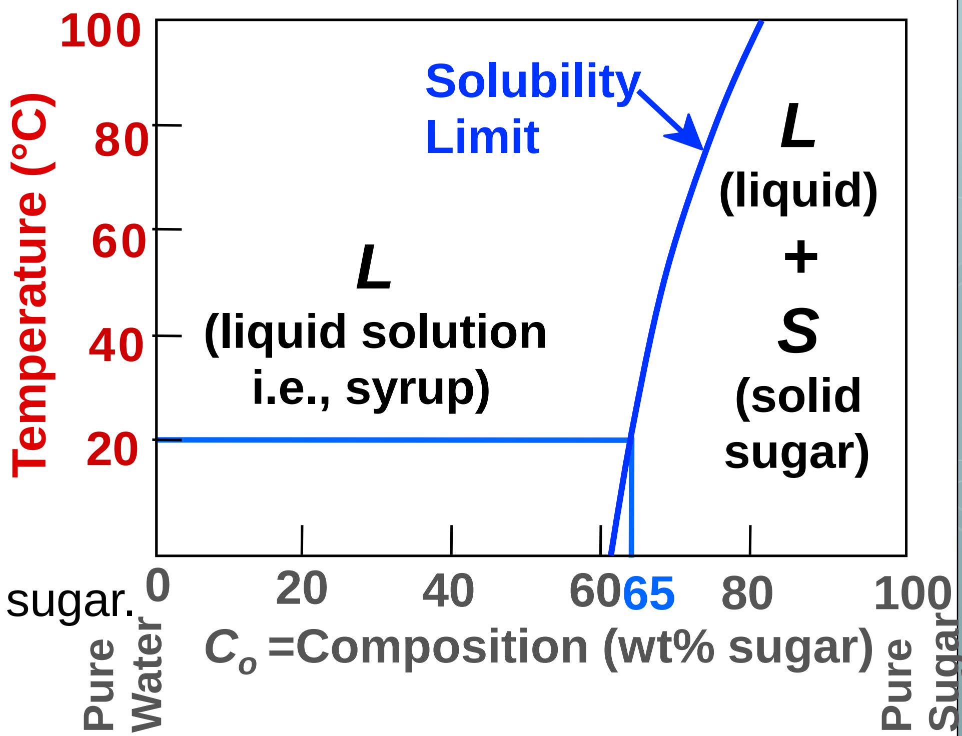
Question: What is the solubility limit at 20°C?

Answer: 65 wt% sugar.

If C_o < 65 wt% sugar: syrup

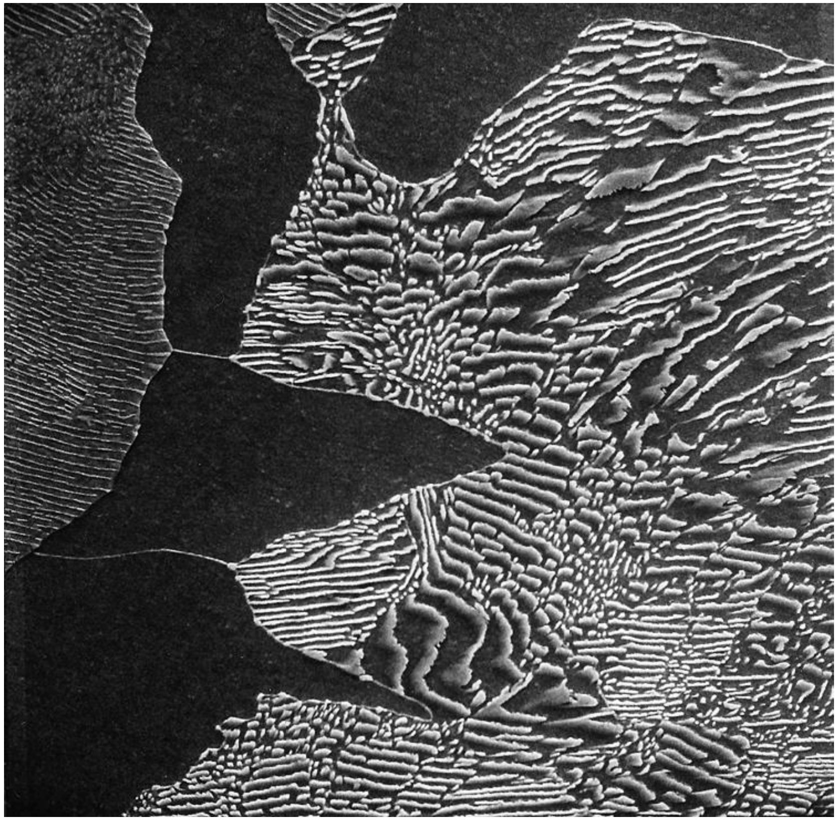
If C_o > 65 wt% sugar: syrup + sugar.

Sucrose/Water Phase Diagram



Microstructure

- the structure of a prepared surface of material as revealed by a microscope above 25× magnification



Components and Phases

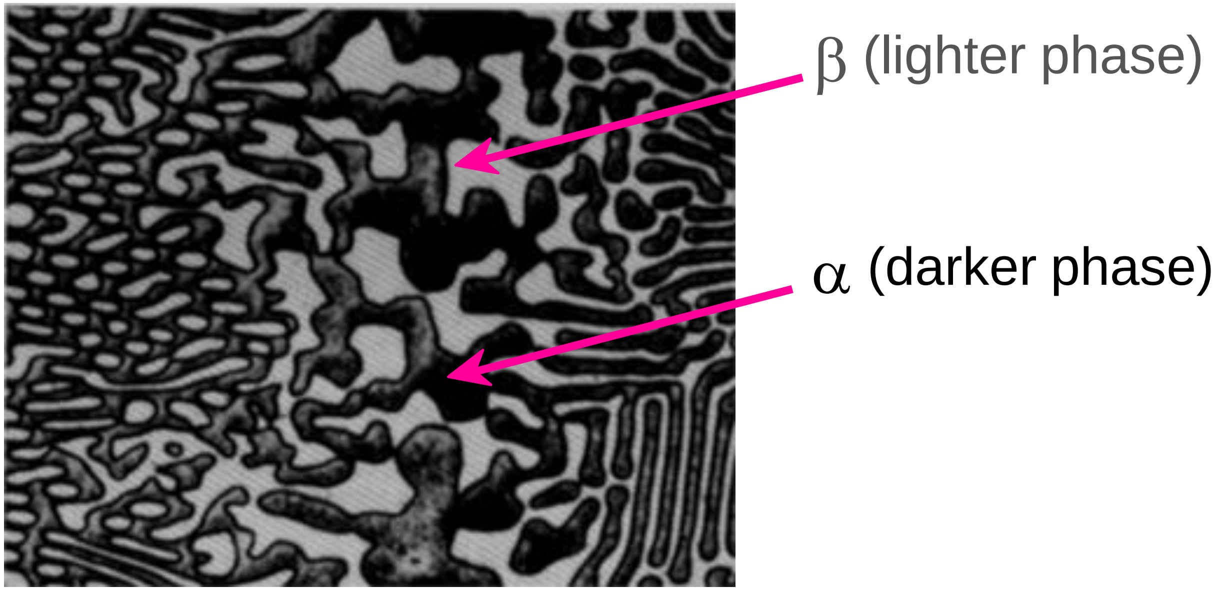
Components:

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

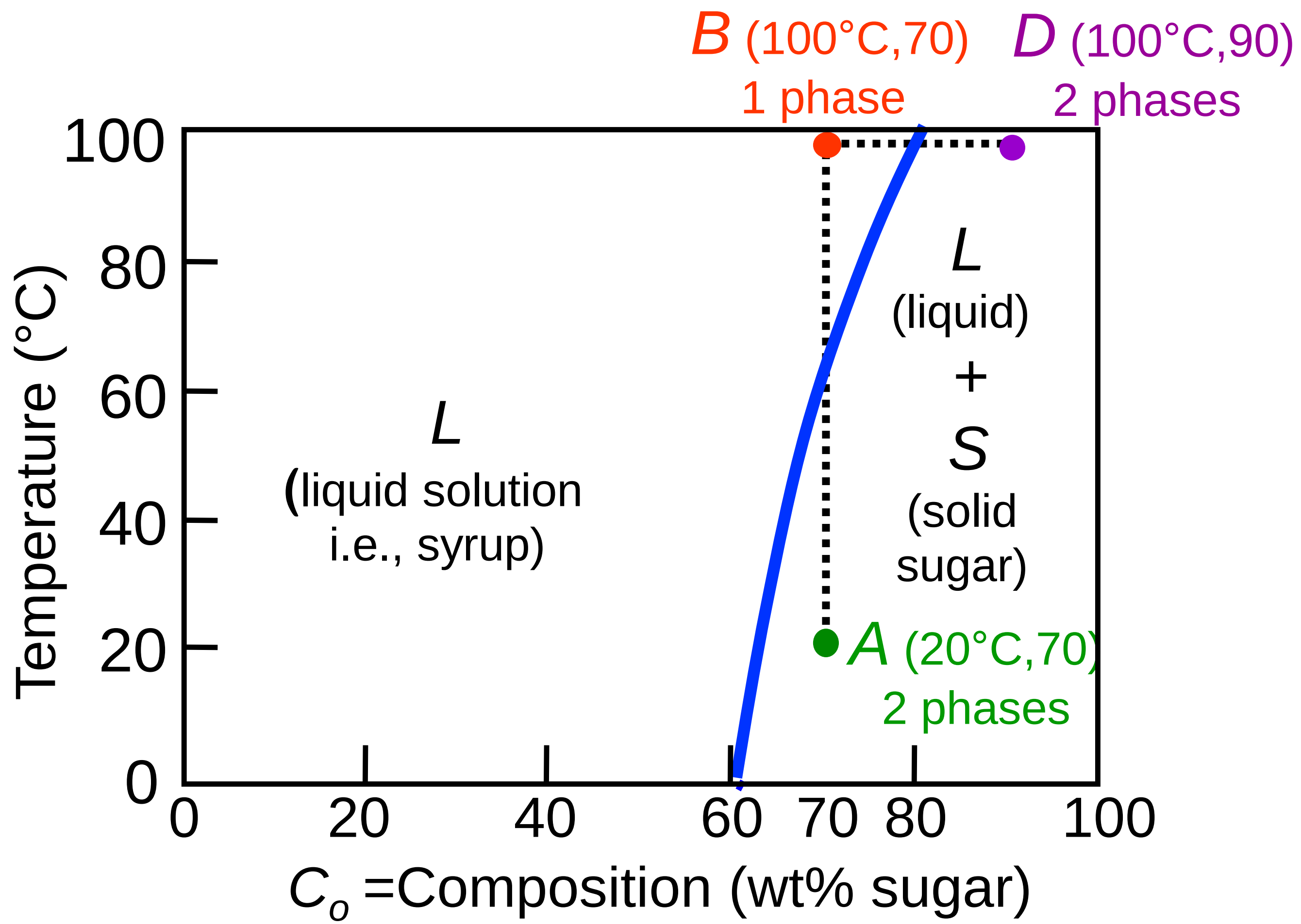


Adapted from chapter-opening photograph, Chapter 9, *Callister 3e.*

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



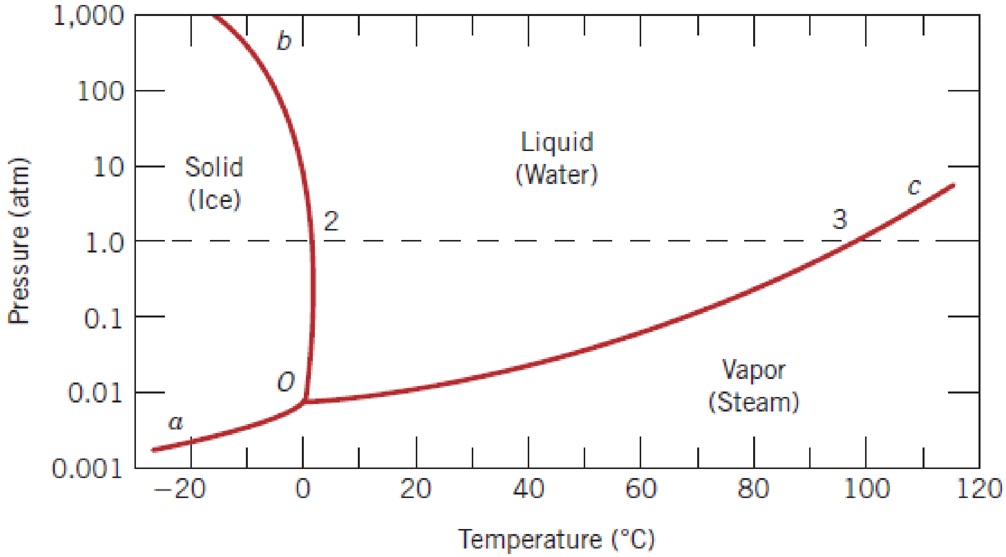
Adapted from Fig. 9.1, *Callister 7e.*

PHASE EQUILIBRIA

- Free Energy -> a function of the internal energy of a system and also the disorder of the atoms or molecules (or entropy).
- A system is at equilibrium if its free energy is at a minimum under some specified combination of temperature, pressure, and composition.
- A change in temperature, pressure, and/or composition for a system in equilibrium will result in an increase in the free energy.
- And in a possible spontaneous change to another state whereby the free energy is lowered

Pressure-Temperature Diagram (Water)

- Each of the phases will exist under equilibrium conditions over the temperature–pressure ranges of its corresponding area
- The three curves (*aO*, *bO*, and *cO*) are phase boundaries; at any point on these curves, the two phases on either side of the curve are in equilibrium with one another
- Point on a *P–T* phase diagram where three phases are in equilibrium, is called a *triple point*.



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

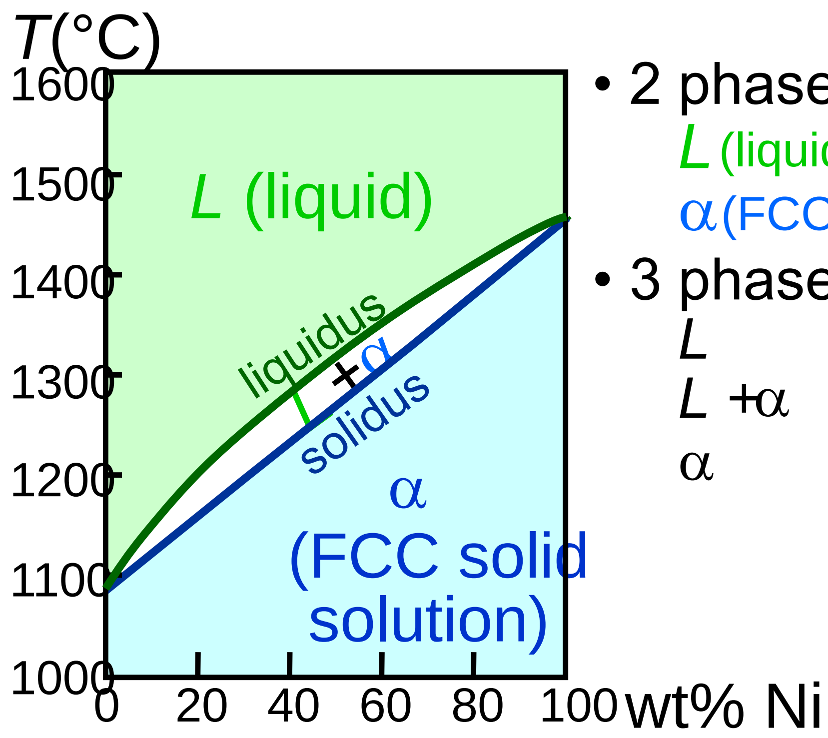
- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.
- Ni and Cu are totally miscible in all proportions.

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

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).



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

Phase Diagrams:

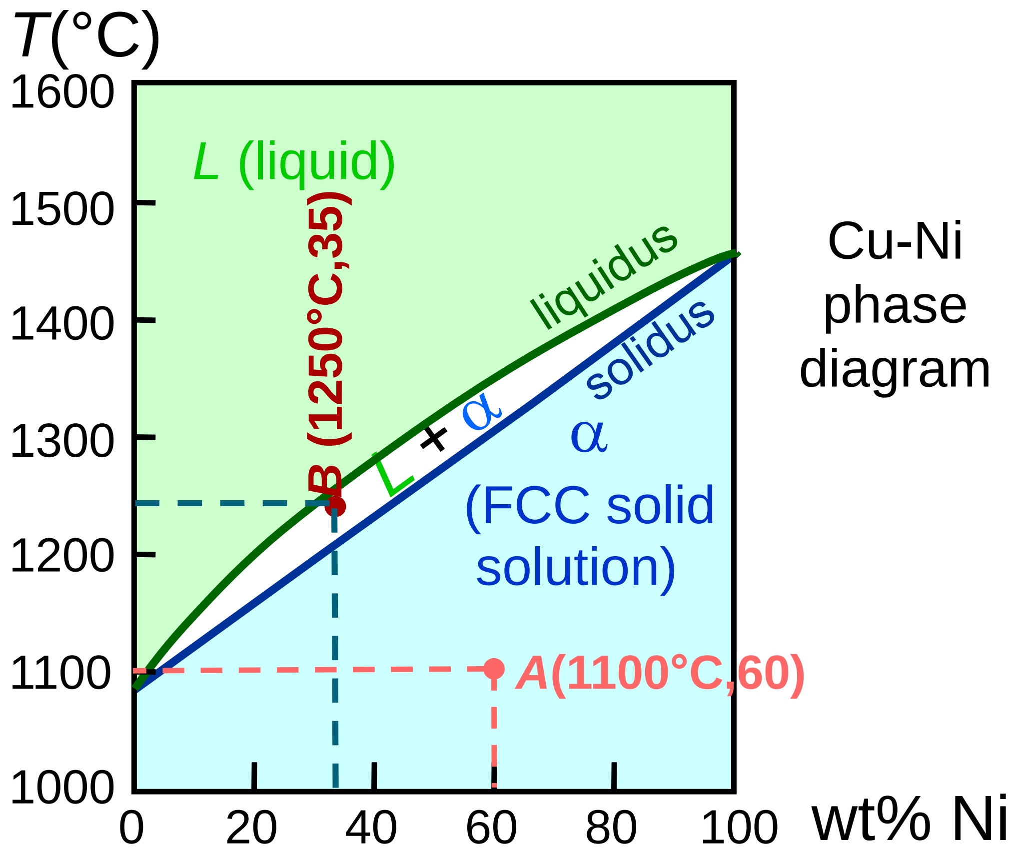
and types of phases

- 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)

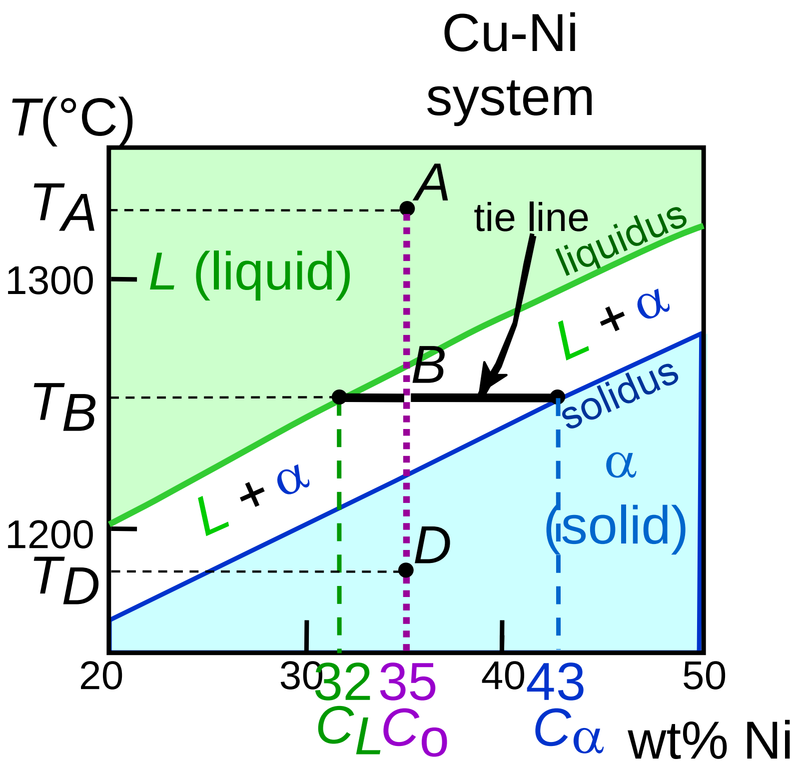
  C_α = C_o (= 35 wt% Ni)

  At T_B = 1250°C:

  Both α and L

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

  C_α = $C_{solidus}$ (= 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.)

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_α = 0

At T_D: Only Solid (α)

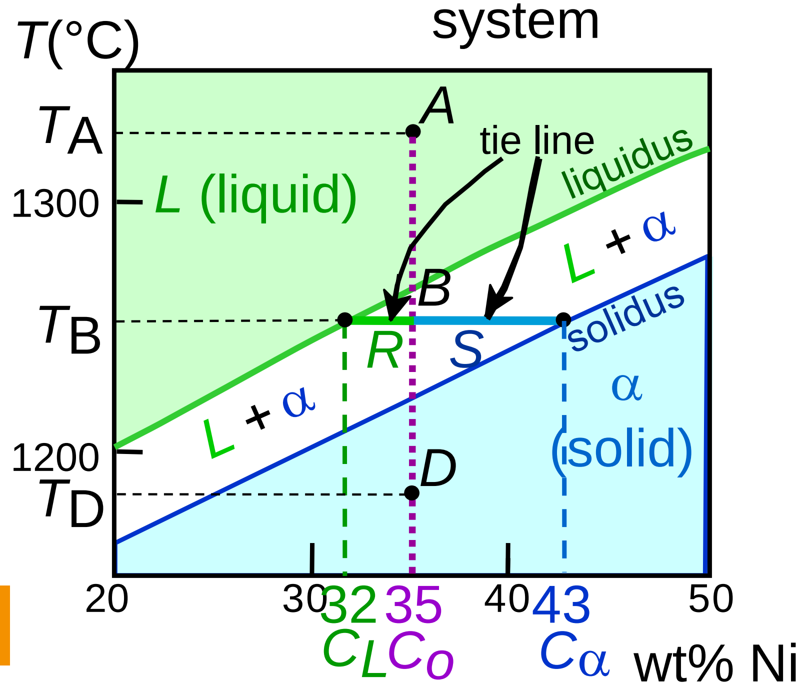
W_L = 0, W_α = 100 wt%

At T_B: Both α and L

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

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

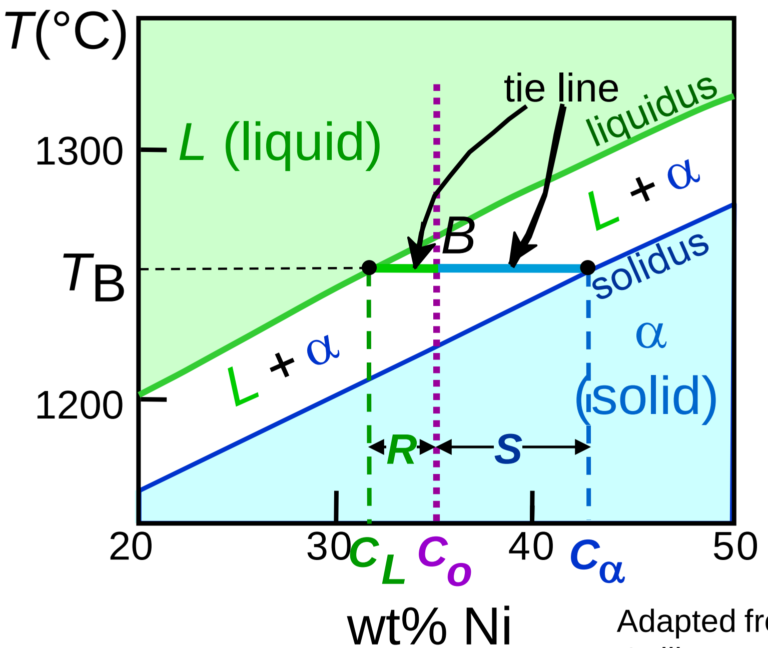
Cu-Ni system



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

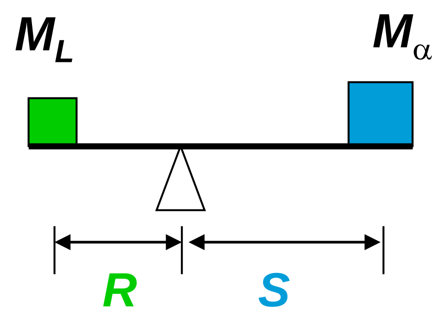
- Tie line – connects the phases in equilibrium with each other - essentially an isotherm



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

How much of each phase?

Think of it as a lever (teeter-totter)



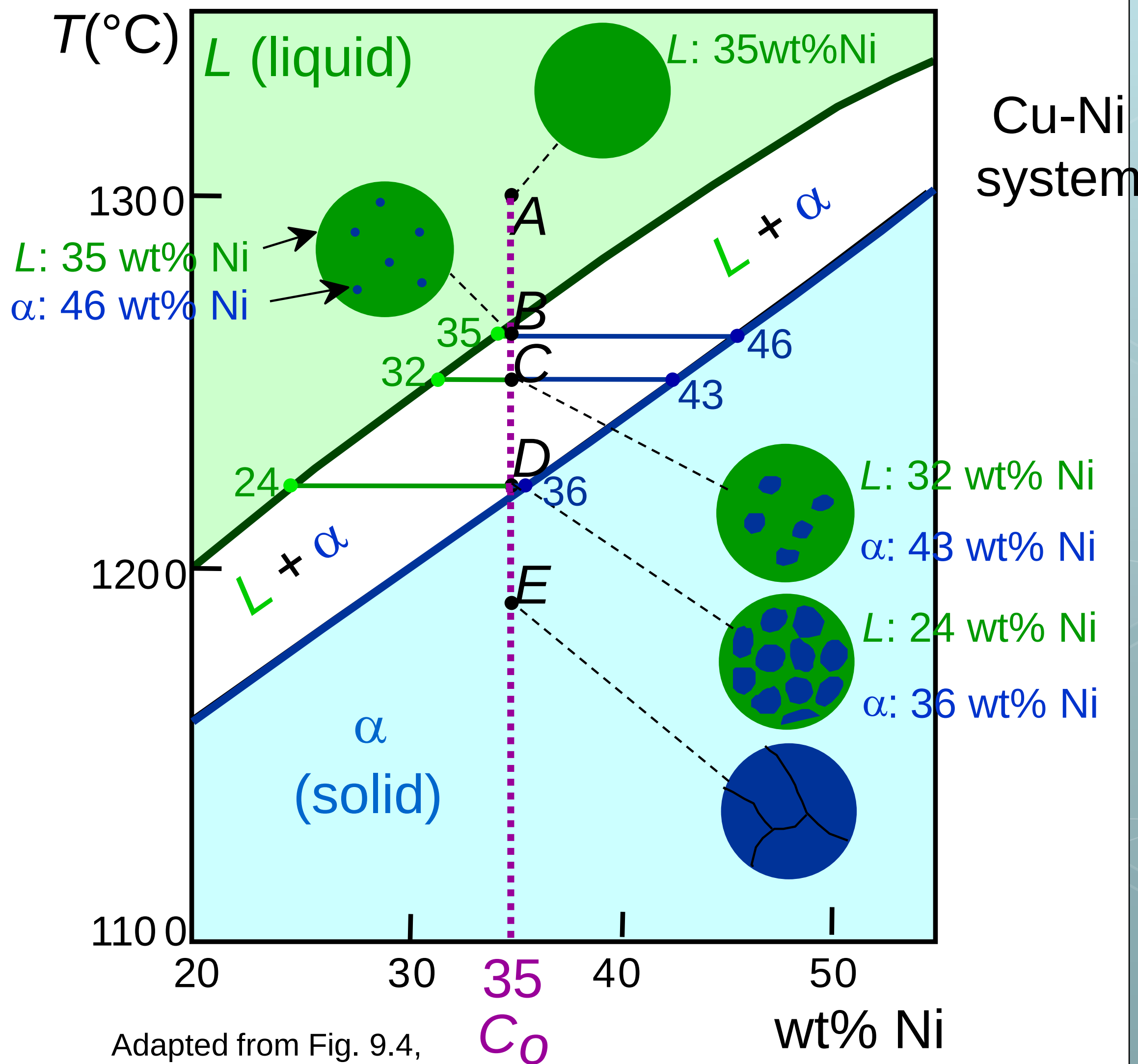
$$M_\alpha \cdot S = M_L \cdot R$$

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

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

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.

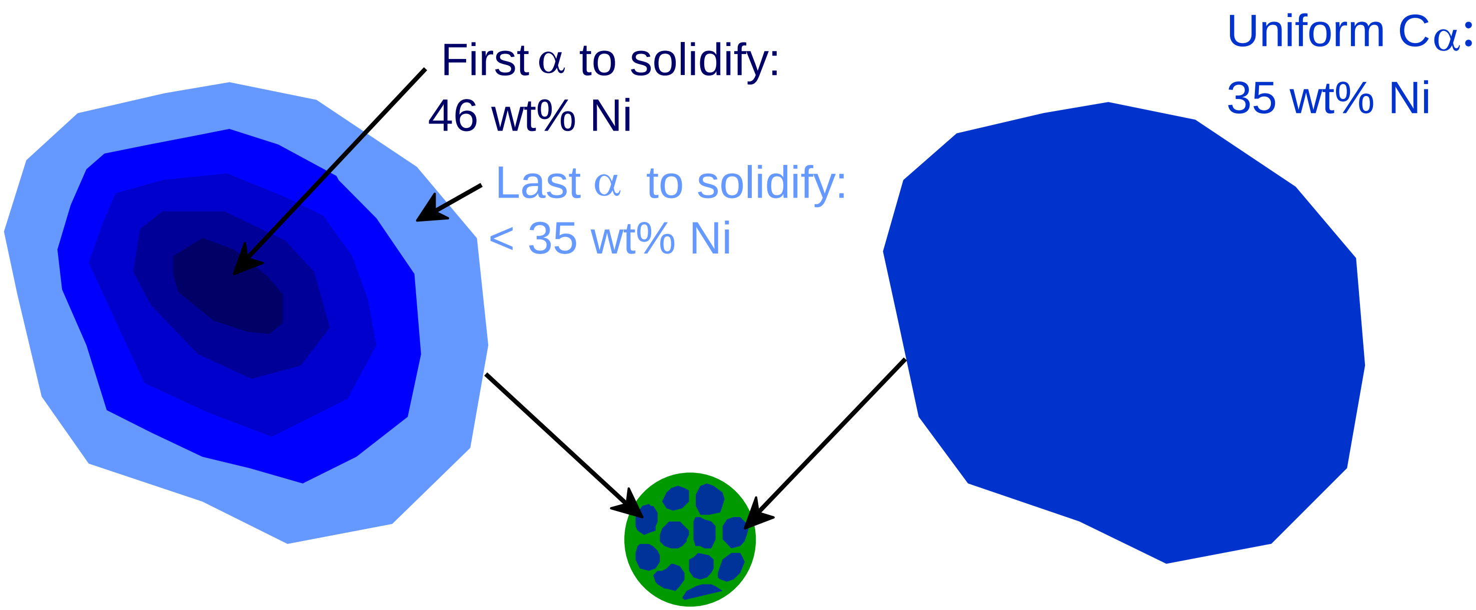


Adapted from Fig. 9.4, *Callister 7e.*

Cored vs Equilibrium Phases

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

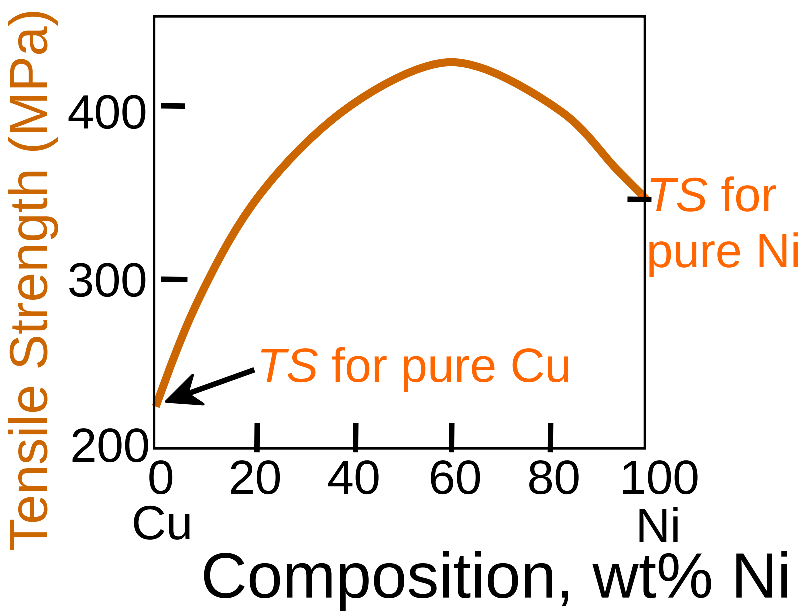
- Fast rate of cooling:
  Cored structure
- Slow rate of cooling:
  Equilibrium structure



Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

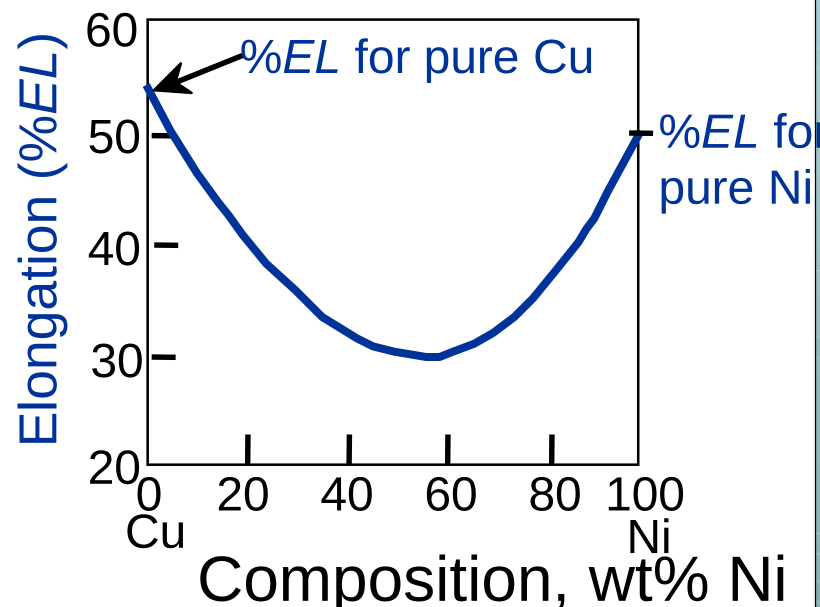
--Tensile strength (*TS*)



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

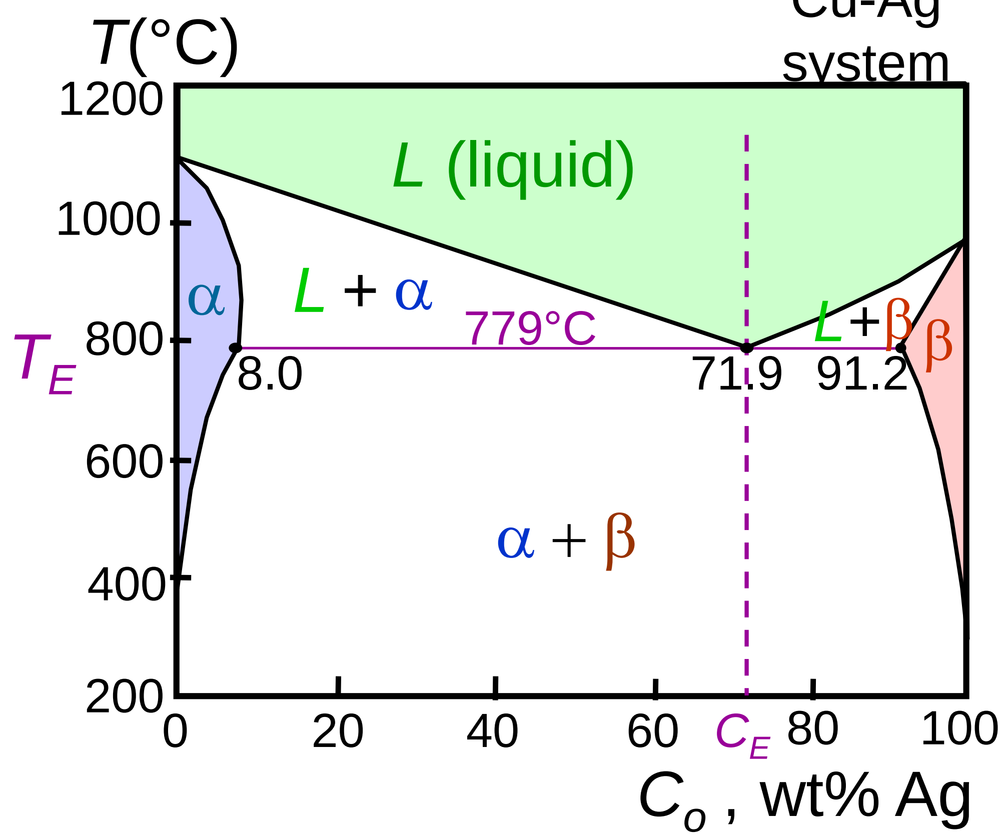
has a special composition with a min. melting T.

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

- **Eutectic transition**

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



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

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

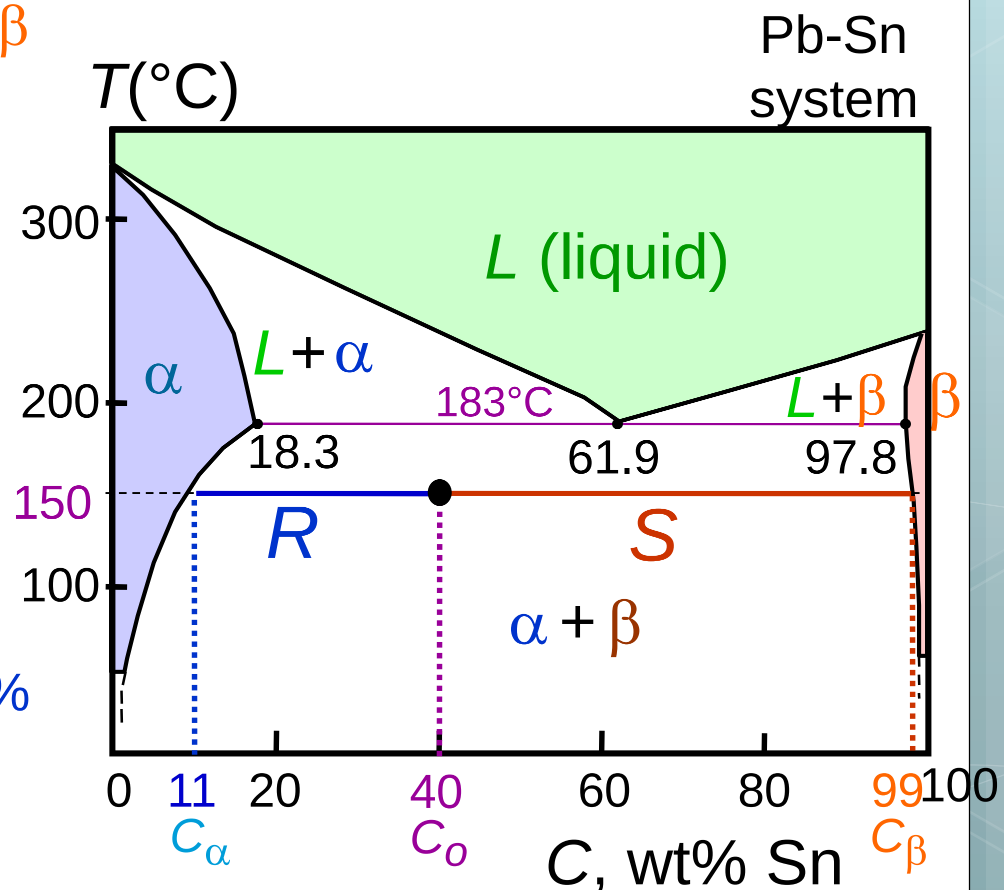
  --the relative amount of each phase:

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

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

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

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



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

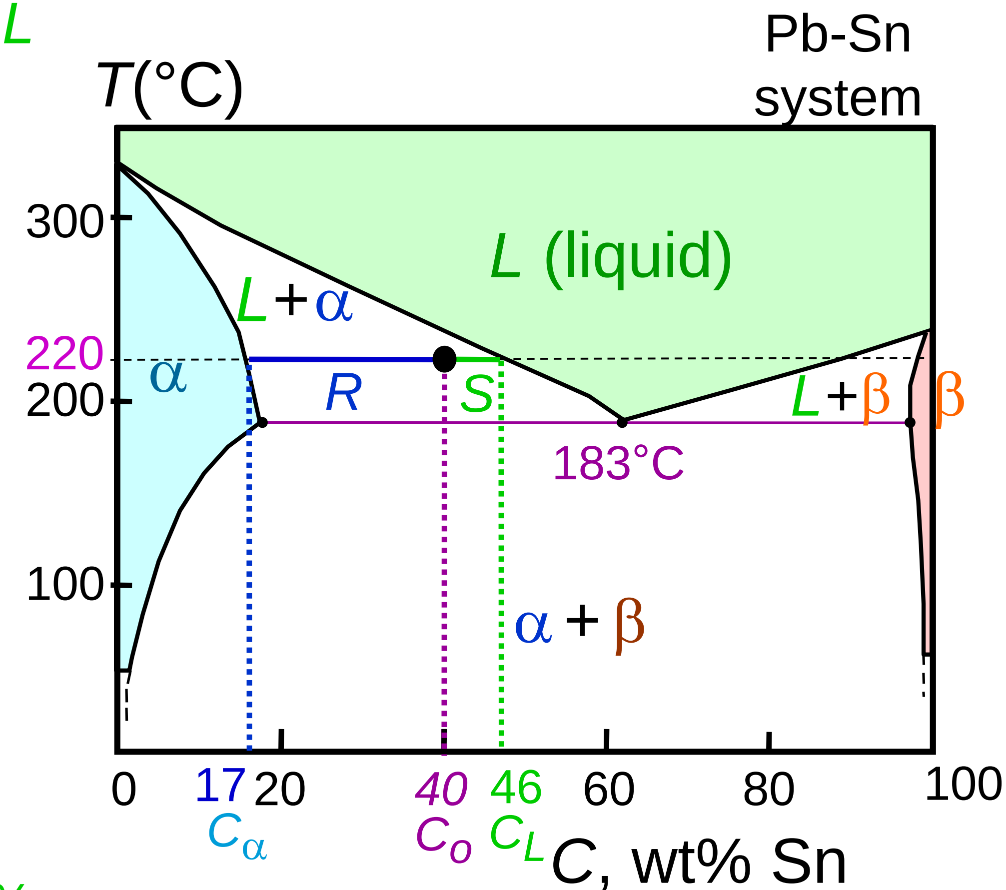
C_α = 17 wt% Sn

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.*

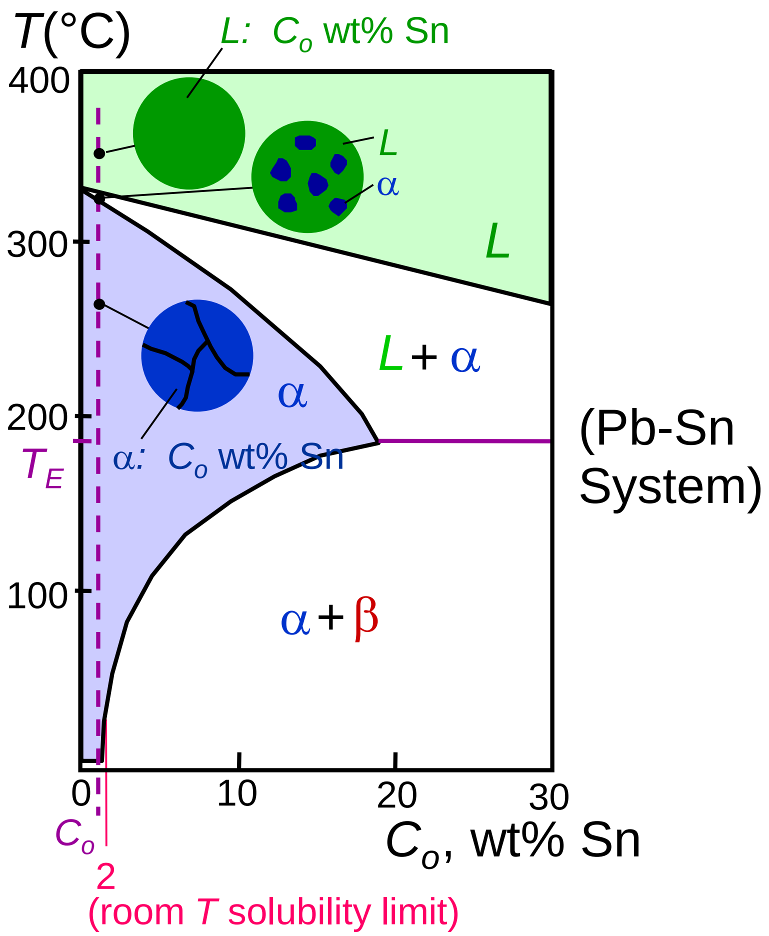
Microstructures in Eutectic Systems: I

- C_o < 2 wt% Sn
- Result:

  --at extreme ends

  --polycrystal of α grains

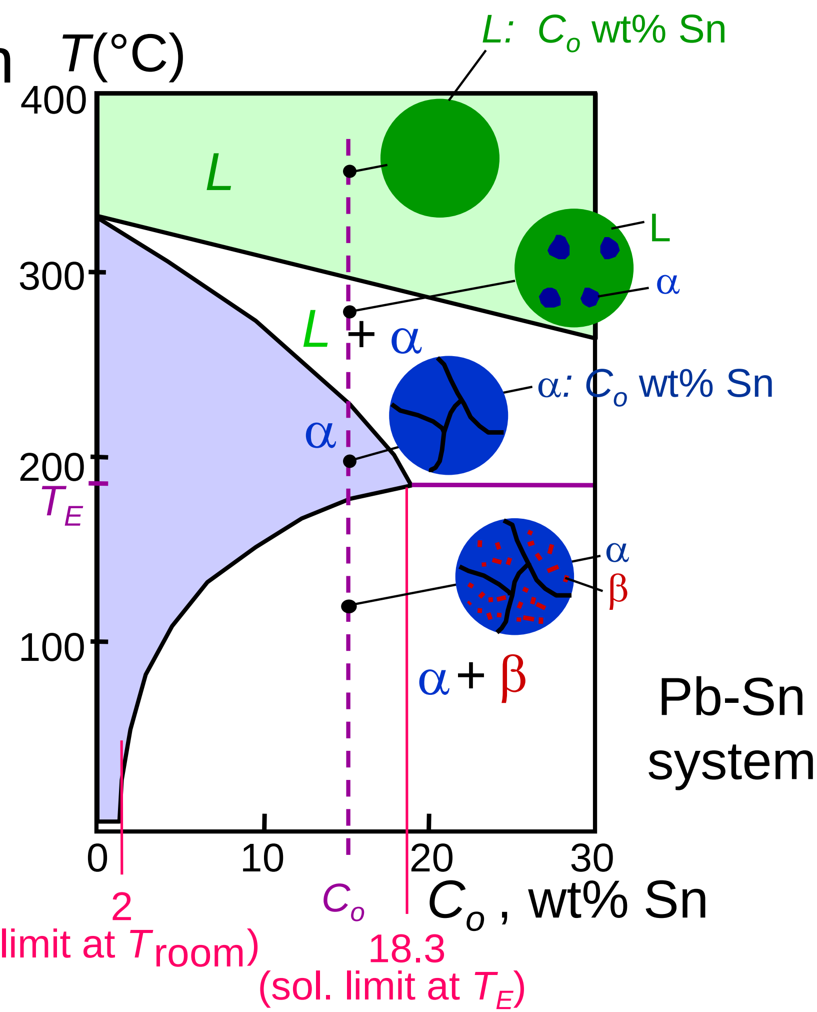
  i.e., only one solid phase.



Adapted from Fig. 9.11, *Callister 7e.*

Microstructures in Eutectic Systems: II

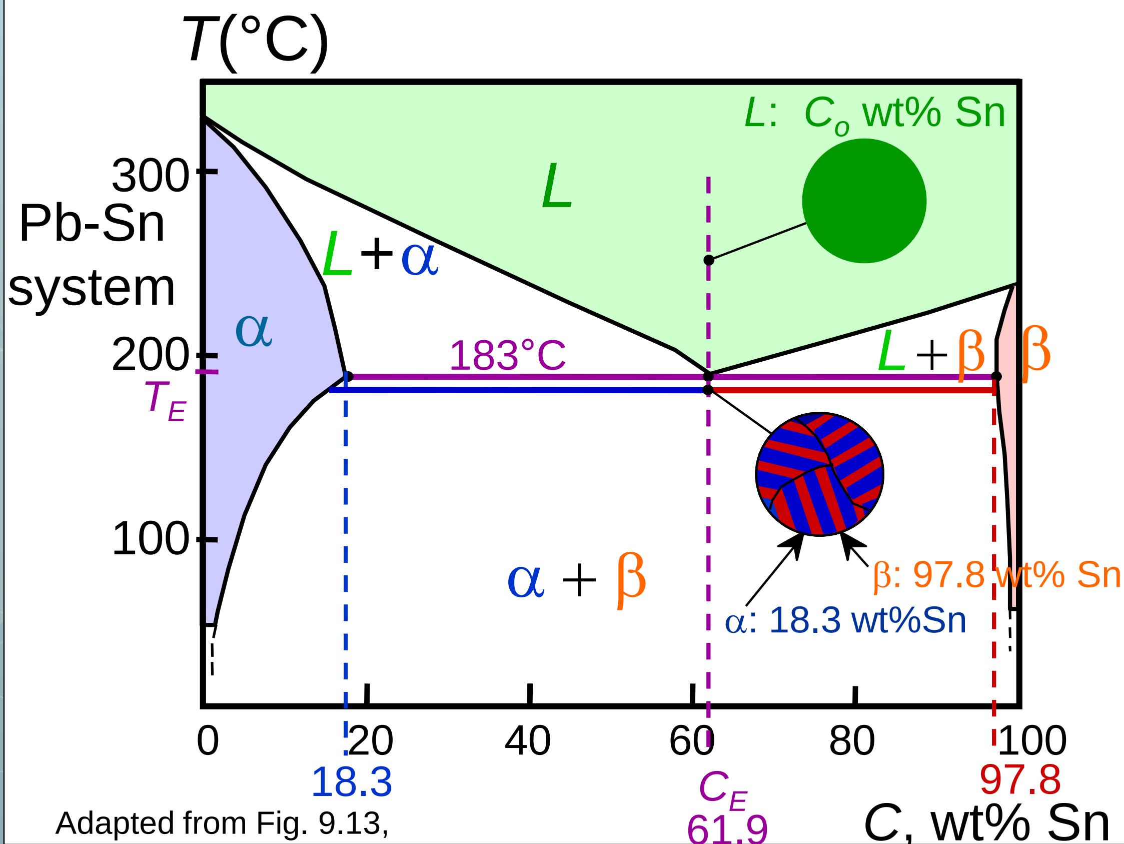
- 2 wt% Sn < C_o < 18.3 wt% Sn
- Result:
  - Initially liquid + α
  - then α alone
  - finally two phases
    - α polycrystal
    - fine β-phase inclusions



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

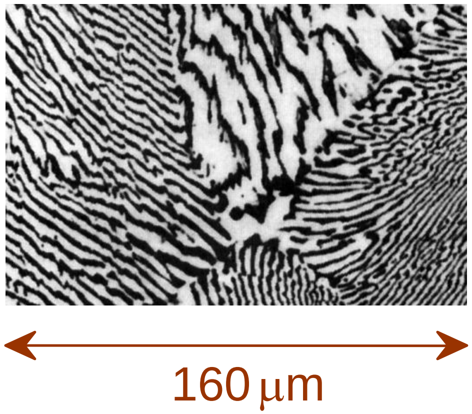
Microstructures in Eutectic Systems: III

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



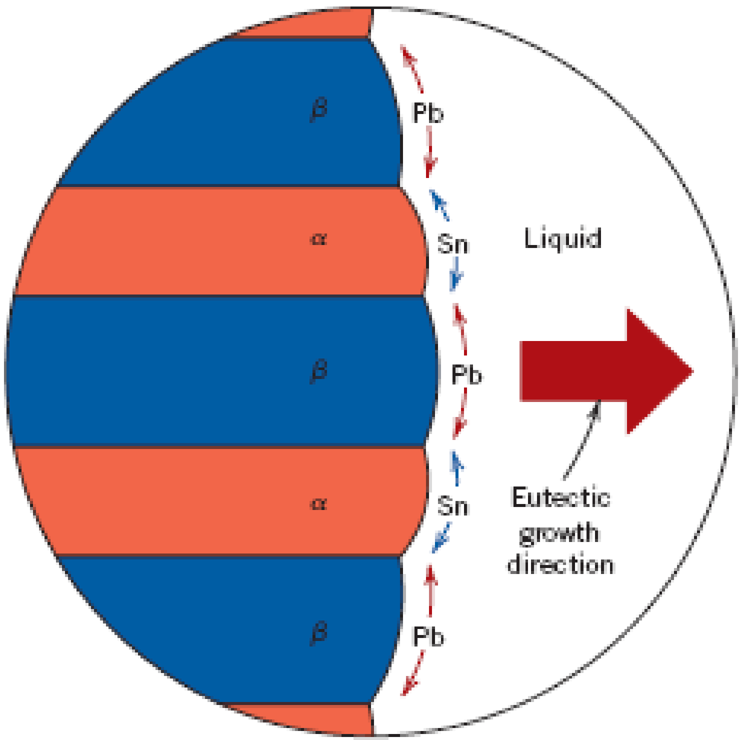
Adapted from Fig. 9.13, *Callister 7e.*

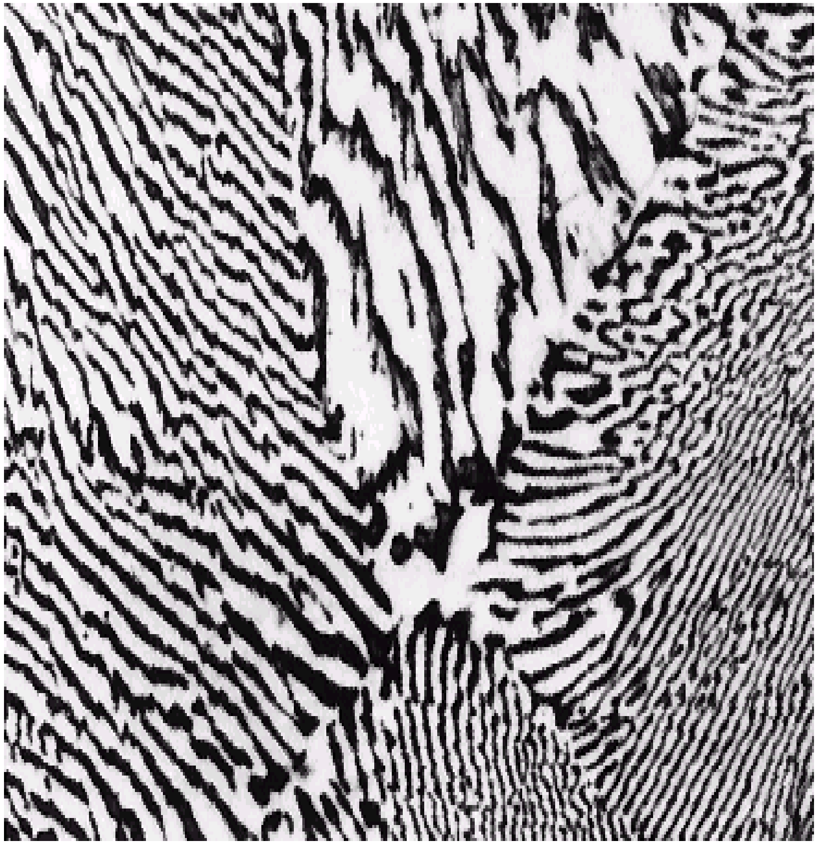
Micrograph of Pb-Sn eutectic microstructure



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

Lamellar Eutectic Structure

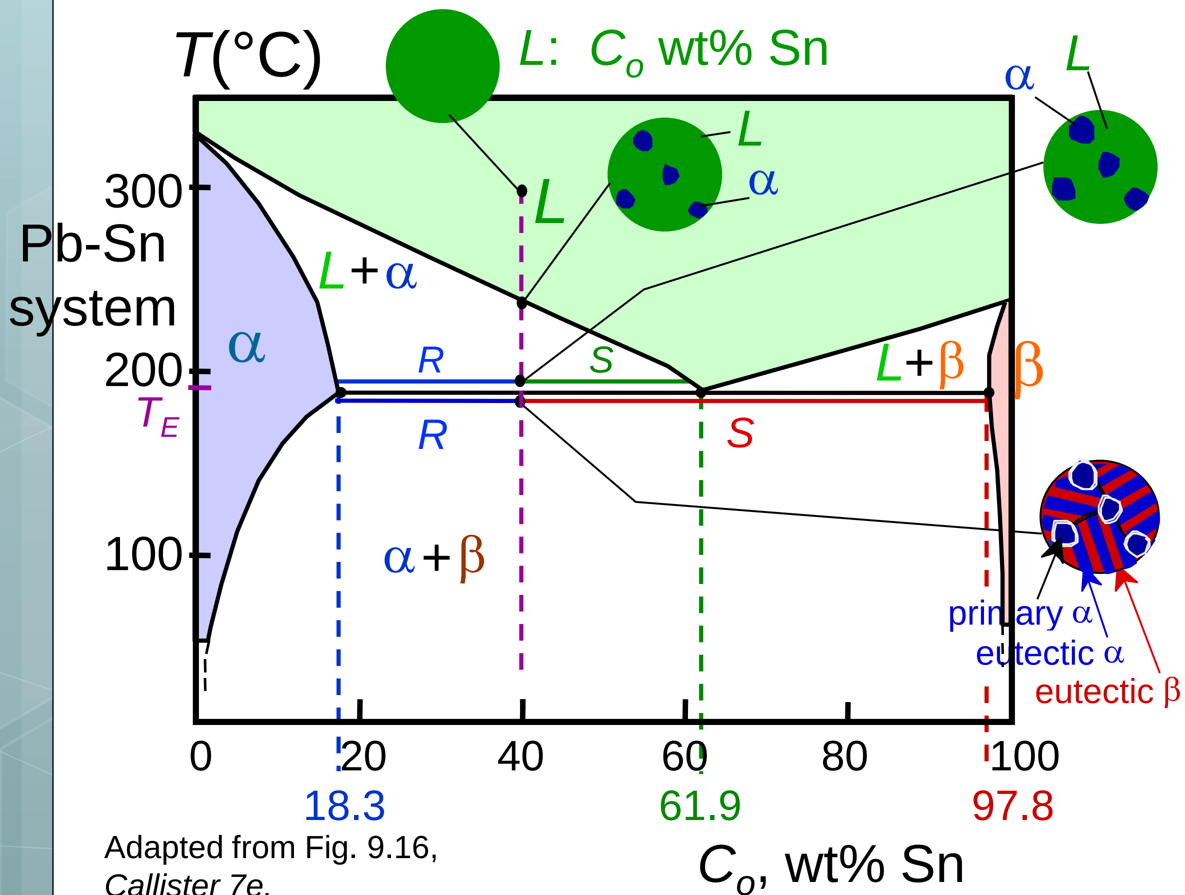




Adapted from Figs. 9.14 & 9.15, *Callister 7e.*

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

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

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

- Just below T_E :

C_α = 18.3 wt% Sn

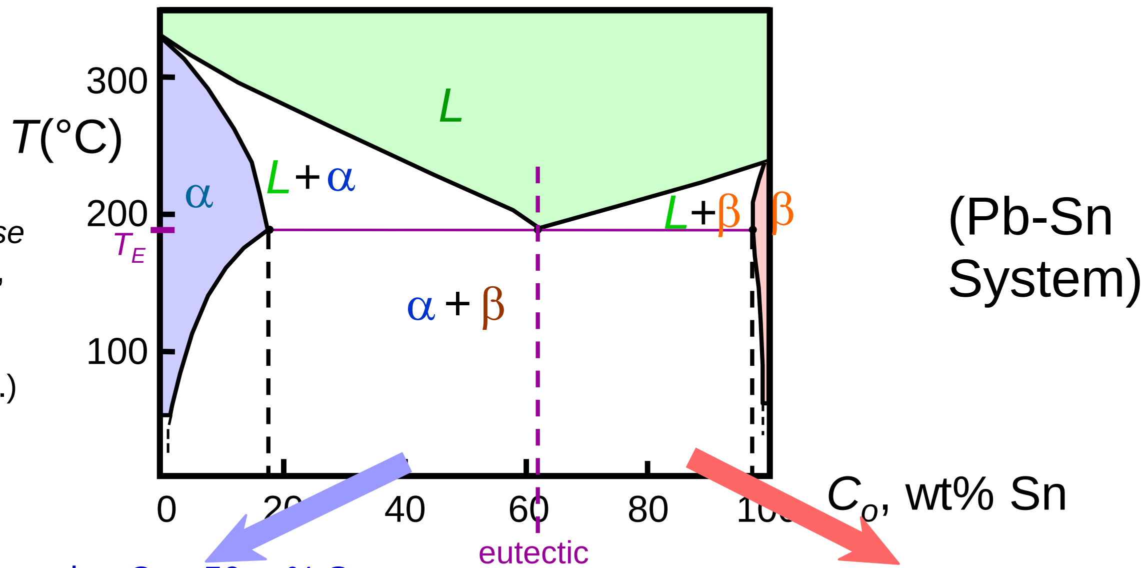
C_β = 97.8 wt% Sn

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

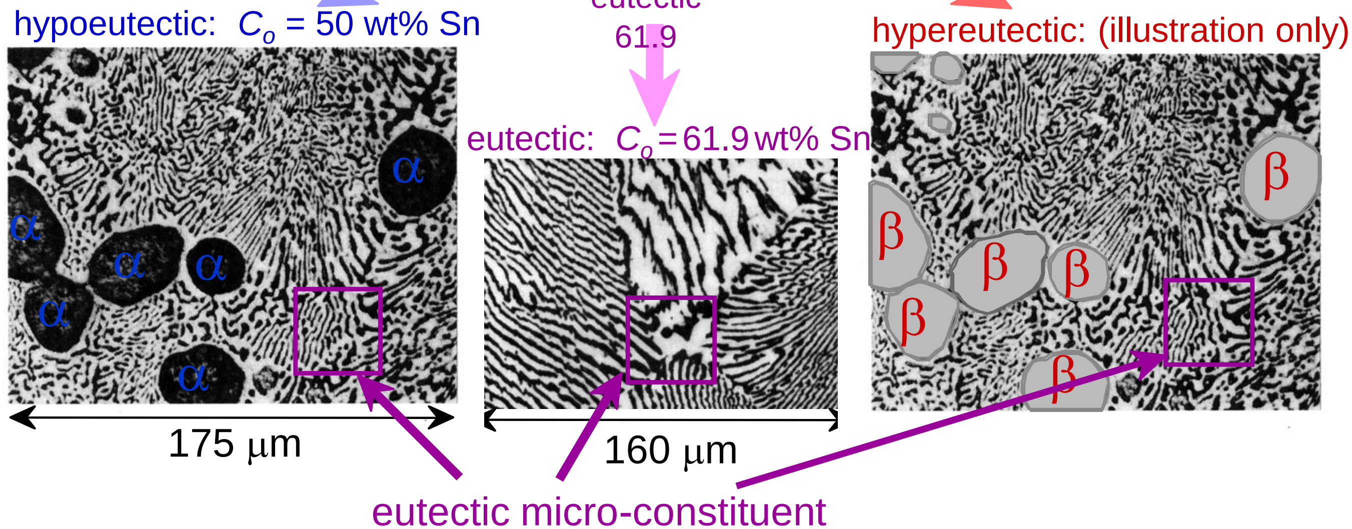
$$W_\beta = 27 \text{ wt\%}$$

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.)



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



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.