Chapter 9: Phase Diagrams

ISSUES TO ADDRESS...

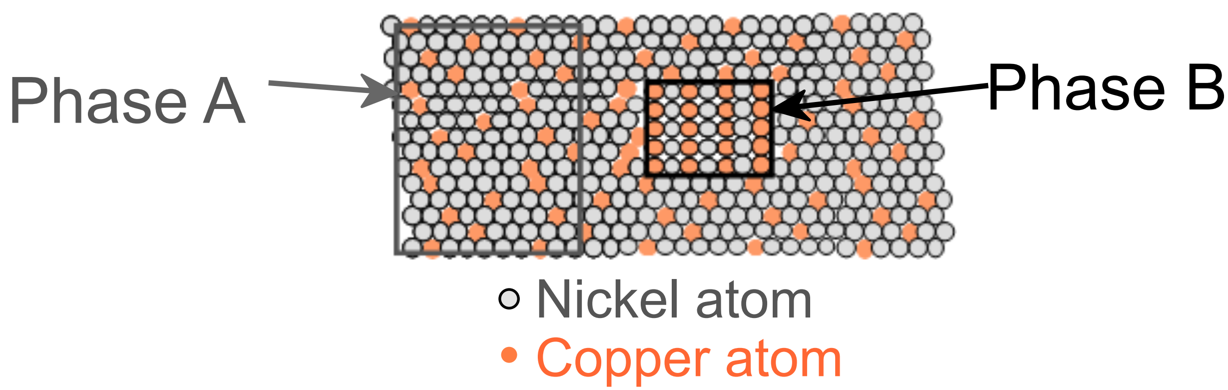
- When we combine two elements...
  what equilibrium state do we get?
- In particular, if we specify...
  --a composition (e.g., wt% Cu - wt% Ni), and
  --a temperature (*T*)

then...

How many phases do we get?

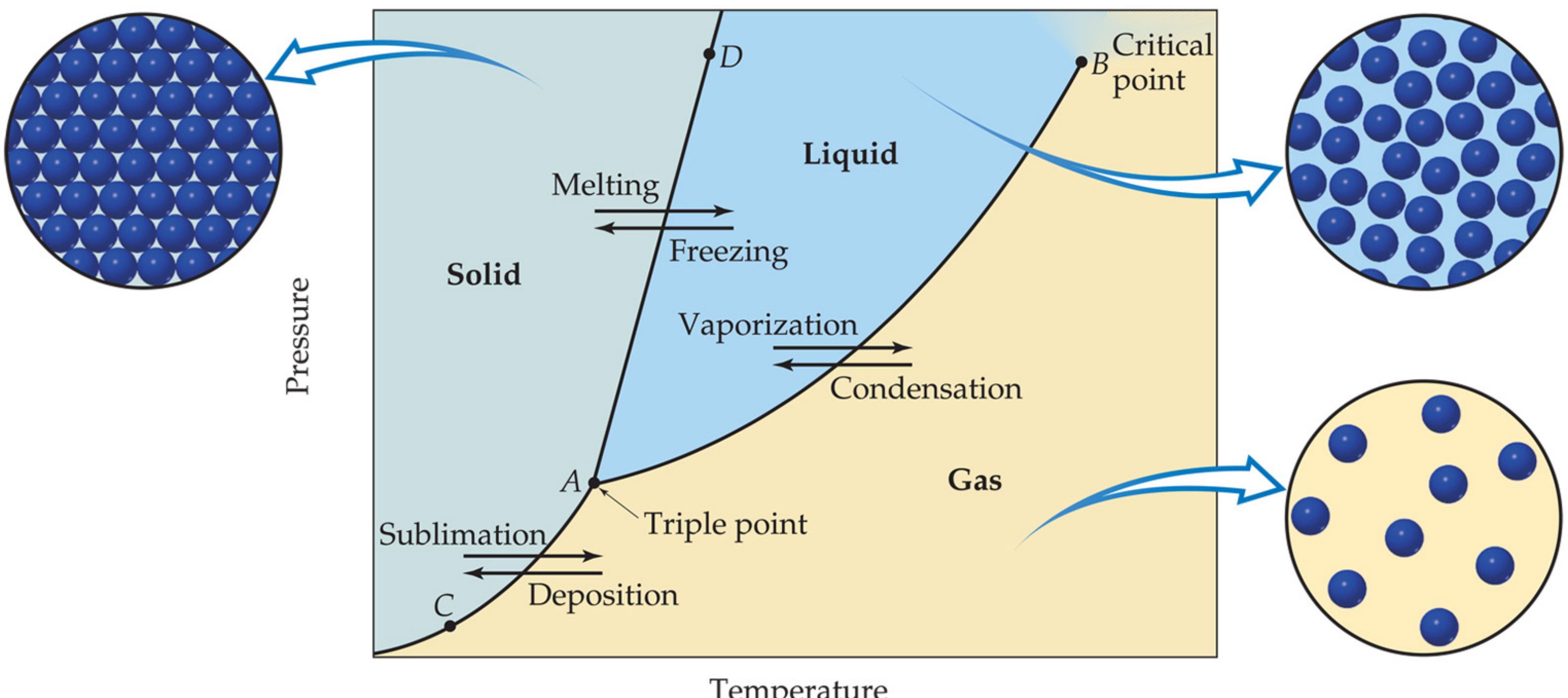
What is the composition of each phase?

How much of each phase do we get?



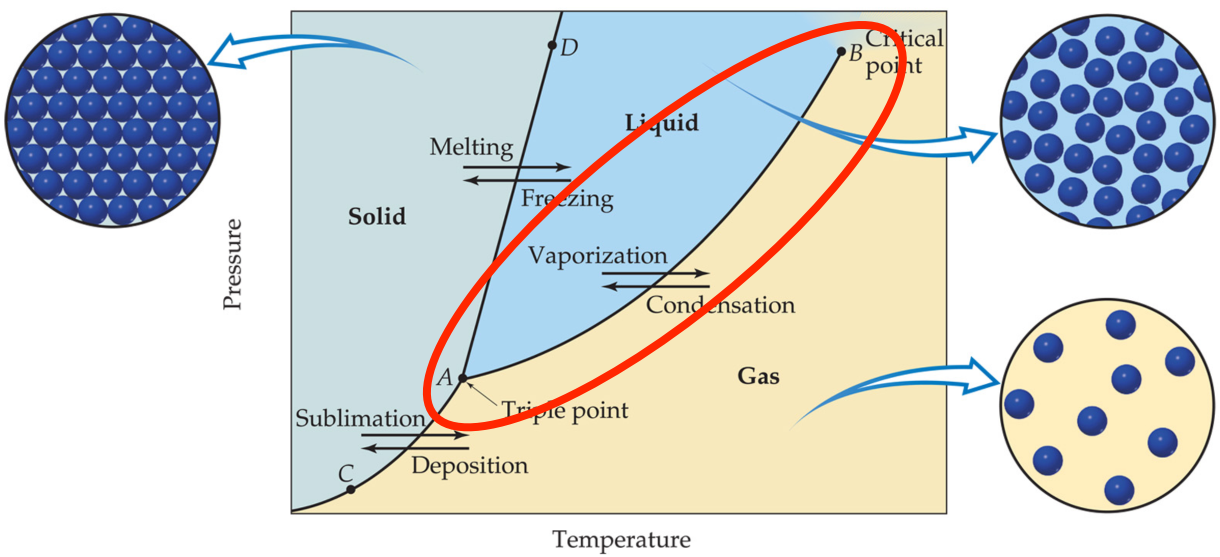
Phase Diagrams

Phase diagrams display the state of a substance at various pressures and temperatures and the places where equilibria exist between phases.



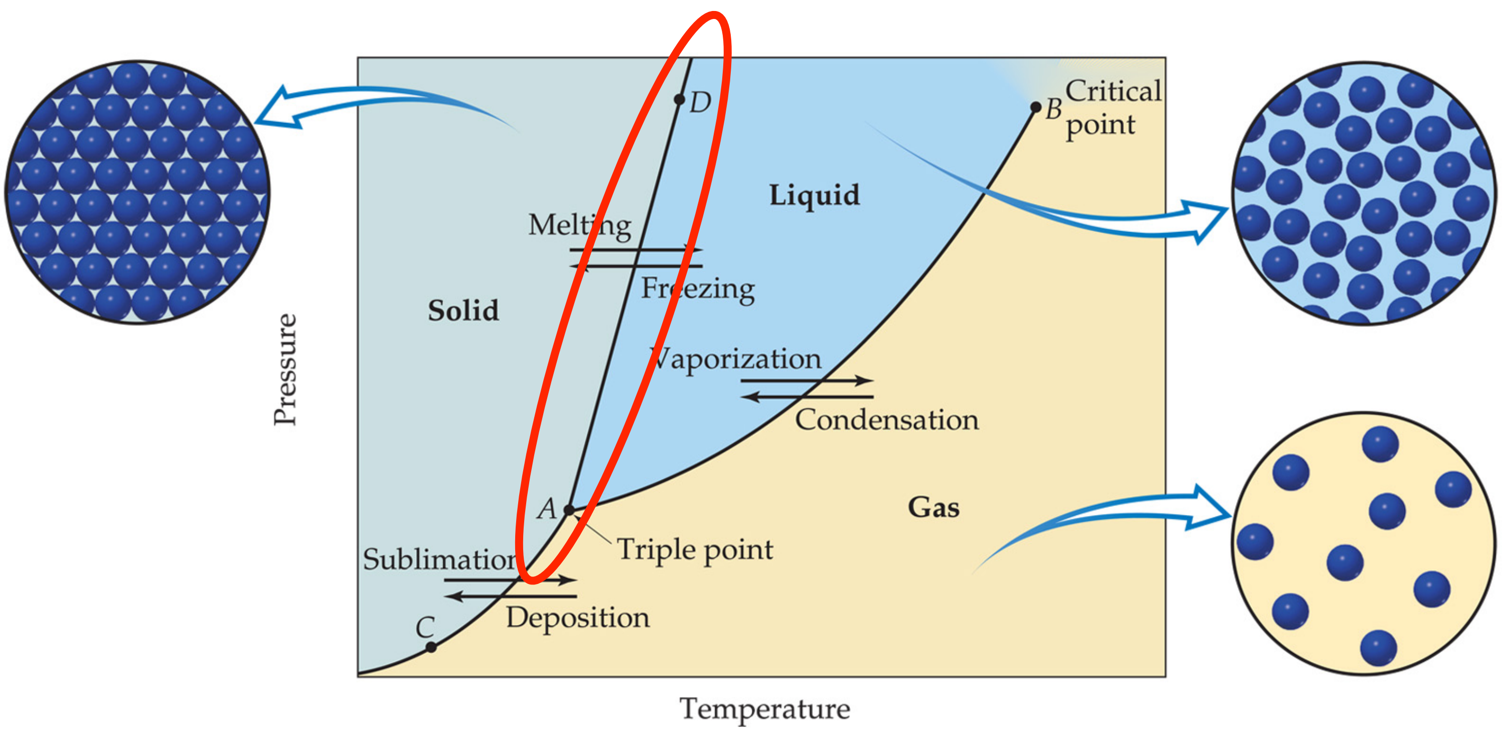
Phase Diagrams

- *The AB line is the **liquid-vapor interface**. Eq^m btw liquid and gas phases.*
- *It starts at the **triple point (A)**, the point at which all three states are in equilibrium.*
- *Each point along this line is the **boiling point** of the substance at that pressure.*



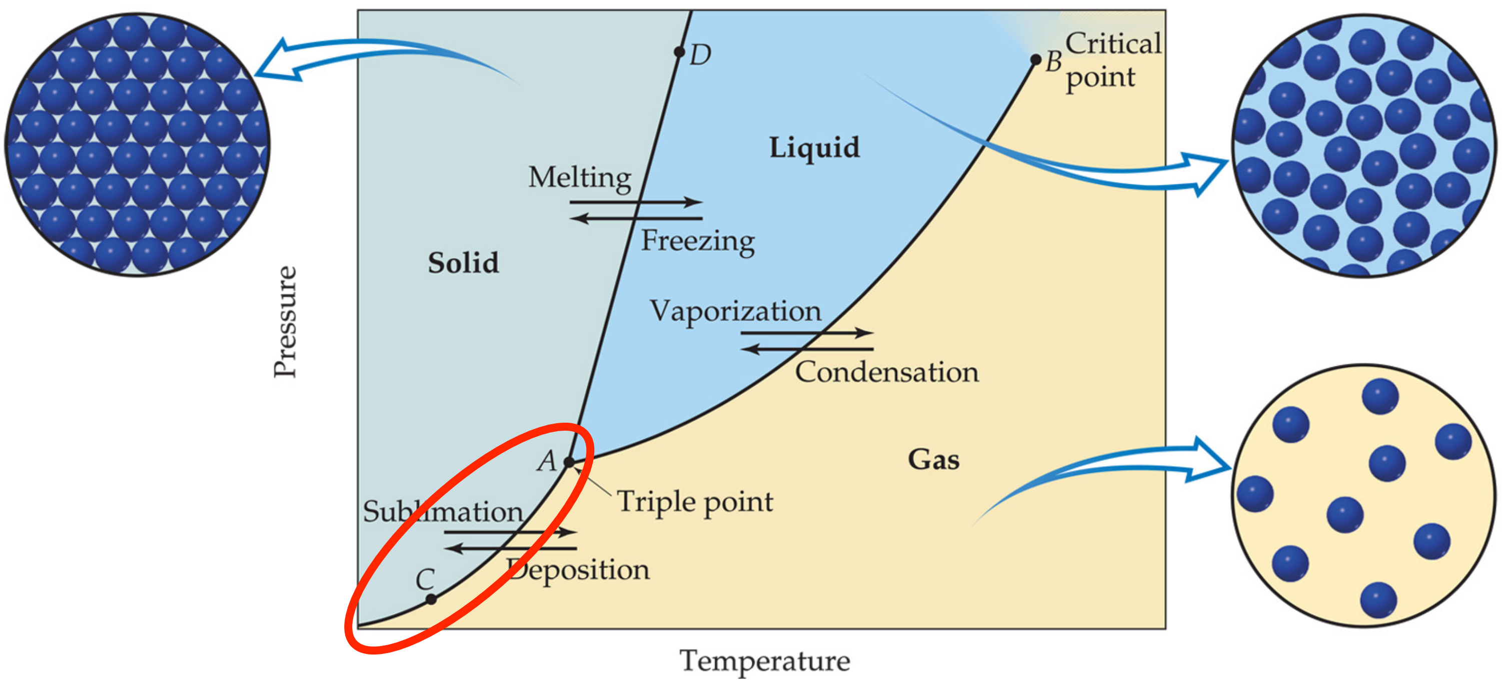
Phase Diagrams

- *The AD line is the interface between liquid and solid.*
- *An increase in pressure usually favors the more compact solid phase, thus, higher temperatures are required to melt the solid at higher pressures.*
- *The melting point at each pressure can be found along this line.*



Phase Diagrams

- *Below A the substance cannot exist in the liquid state.*
- *Along the AC line the solid and gas phases are in equilibrium; the sublimation point at each pressure is along this line.*



Phase Equilibria: Solubility Limit

Introduction

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

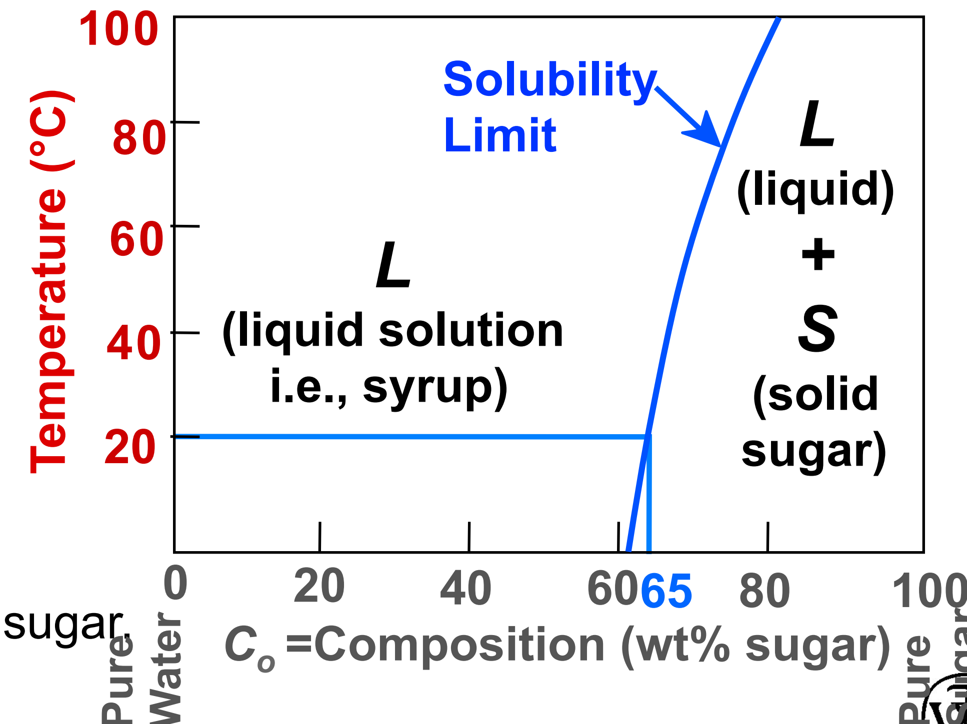
Adapted from Fig. 9.1, *Callister 7e.*

- 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_o < 65 wt% sugar: syrup
If C_o > 65 wt% sugar: syrup + sugar.

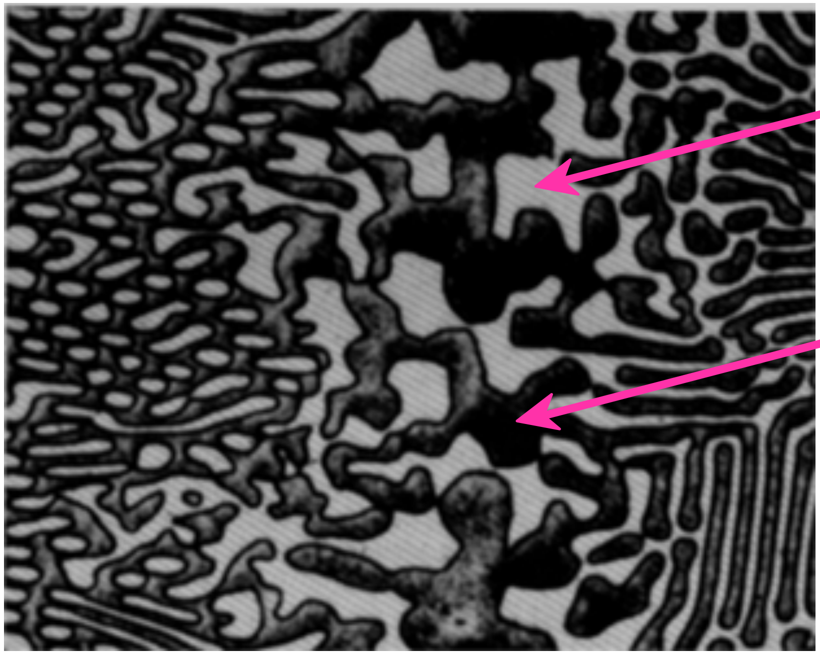
Sucrose/Water Phase Diagram



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



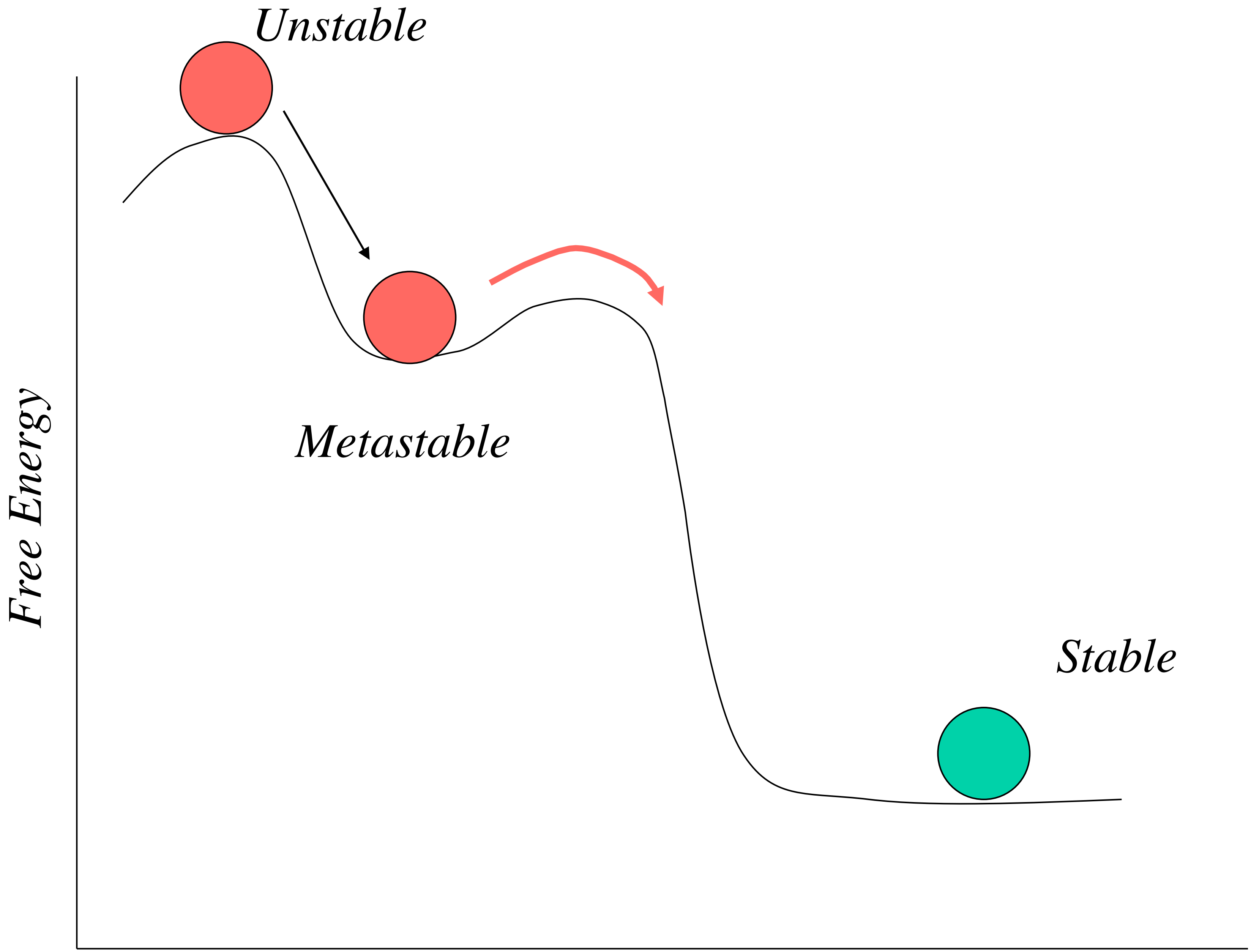
β (lighter phase)

α (darker phase)

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

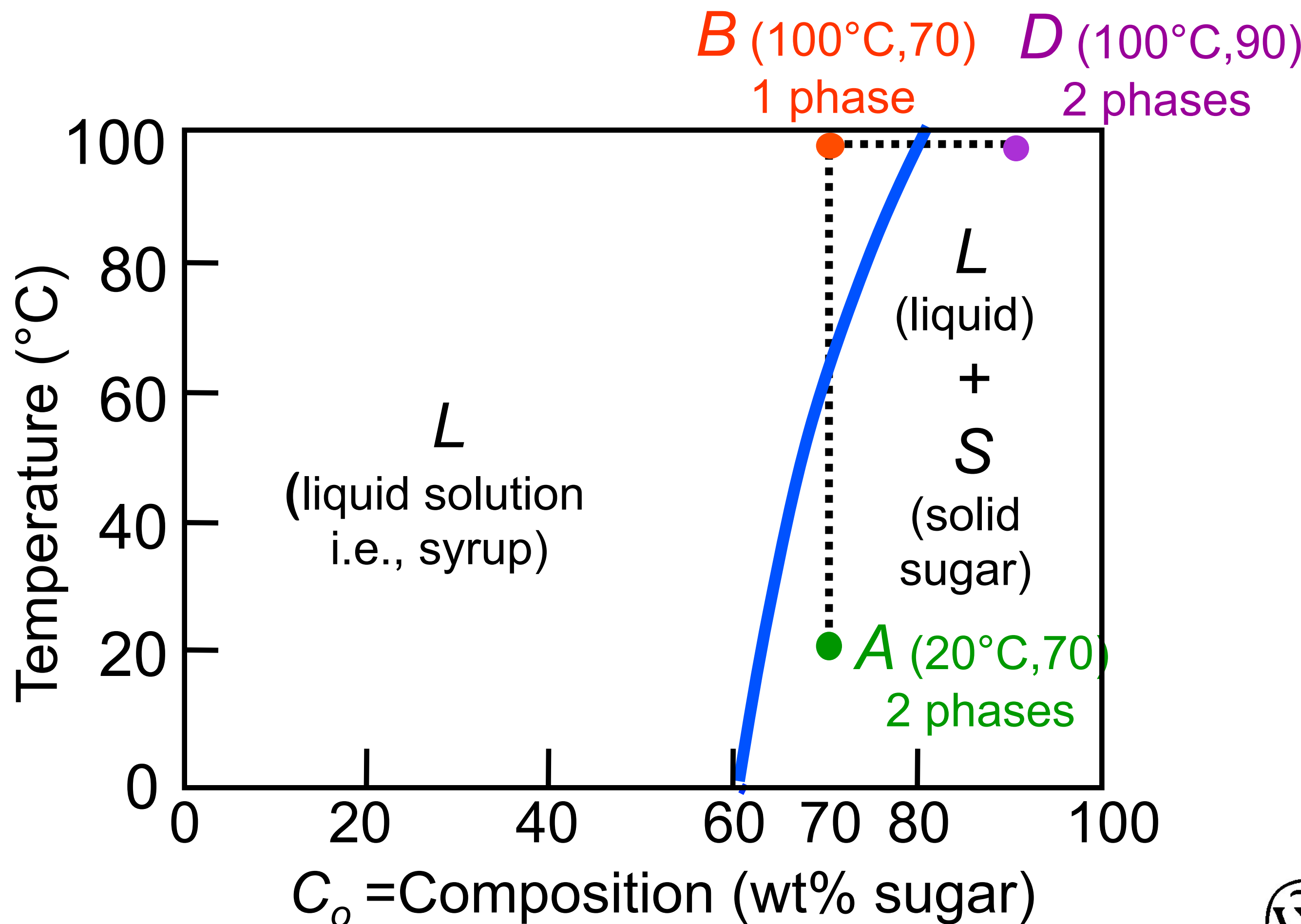
Nomenclature / Definitions / Basic Concepts (III)

- A system is at equilibrium if at constant temperature, pressure and composition the system is chemically and structurally stable, not changing with time.
- Equilibrium is the state that is achieved given sufficient time. But sometimes it will take too much time to achieve equilibrium due the kinetics. This is called a meta-stable state.
- In thermodynamics the equilibrium is described as the state of system that corresponds to the minimum of thermodynamic function called the free energy.
  - Thermodynamics tells us that
    - under conditions of a constant temperature and pressure and composition, the direction of any spontaneous change is toward a lower free energy.
    - the state of stable thermodynamic equilibrium is the one with minimum free energy.
    - a system at a metastable state is trapped in a local minimum of free energy that is not the global one.


Unstable
Metastable
Stable
Free Energy

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*.

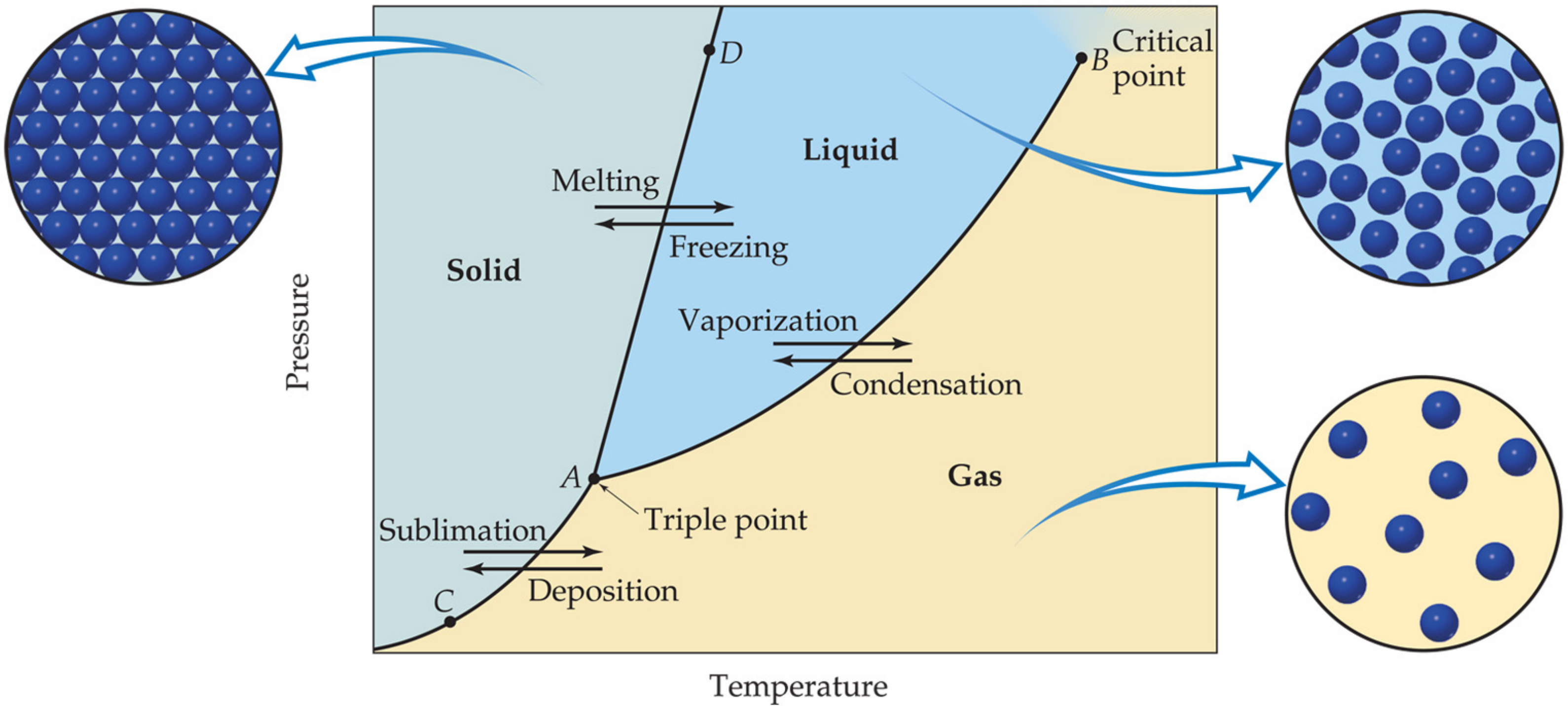


water-sugar system

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

One Component (Uniary) Phase Diagram

Phase diagrams display the state of a substance at various pressures and temperatures and the places where equilibria exist between phases.



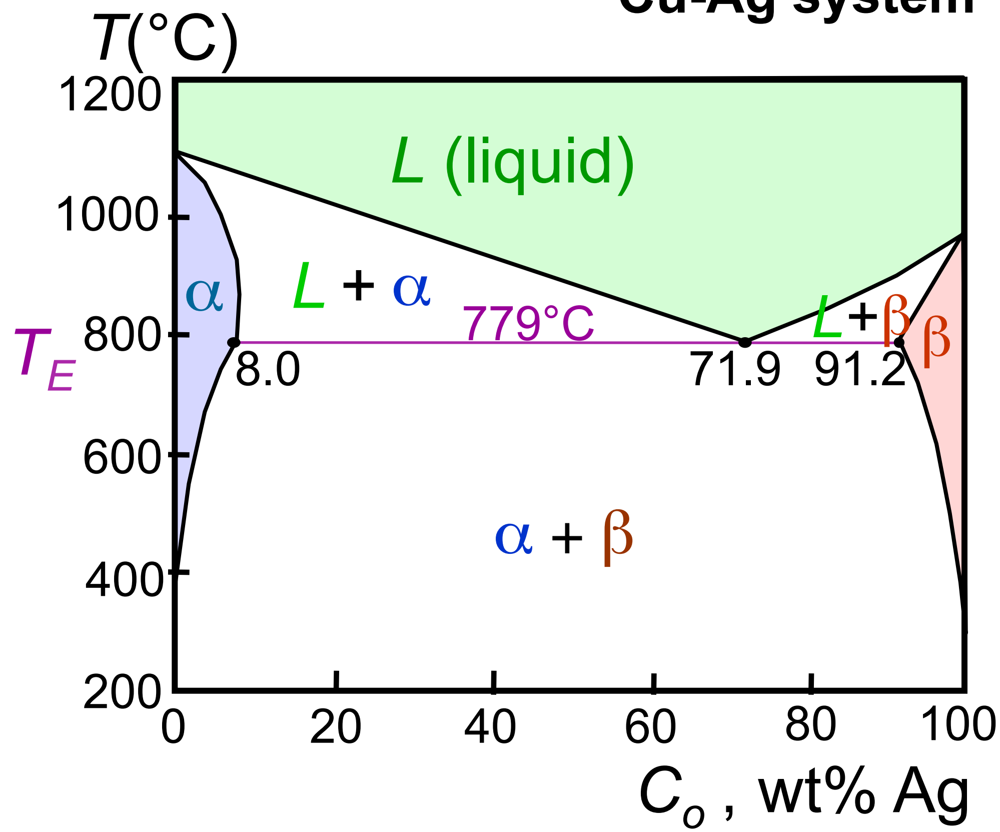
Binary Phase Diagram

2 components

Ex.: Cu-Ag system

- 3 single phase regions
  (L, α, β)
- Limited solubility:
  α: mostly Cu
  β: mostly Ag

Cu-Ag system



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

Phase Equilibria

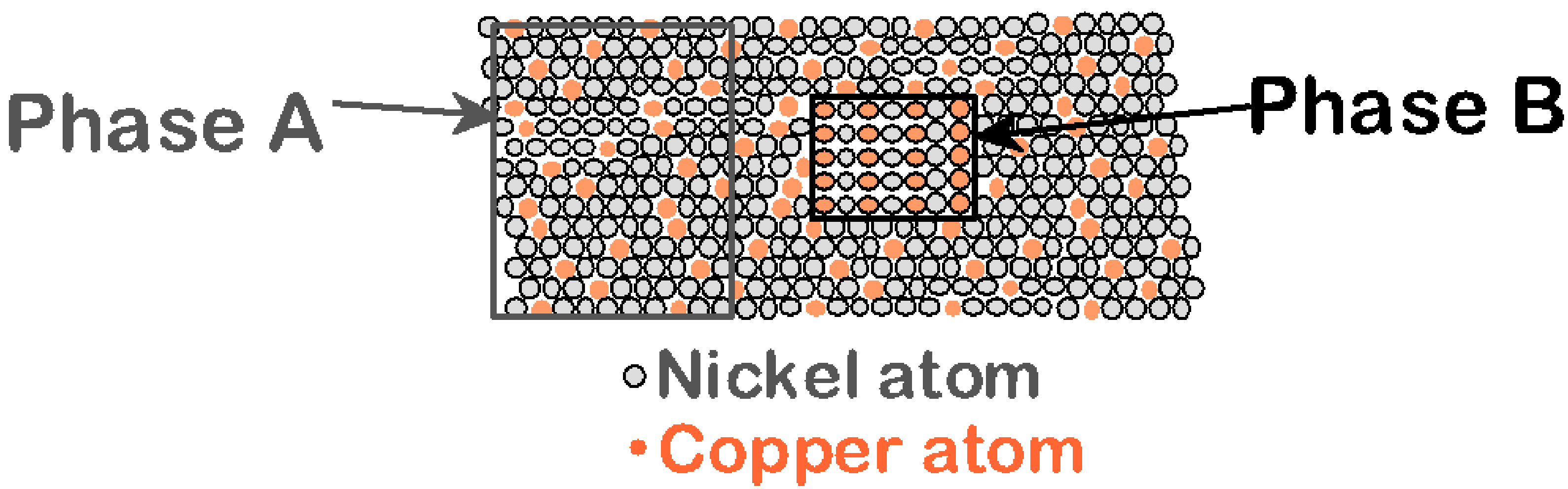
Simple solution system (e.g., Ni-Cu solution)

	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.

CHAPTER 9: PHASE DIAGRAMS

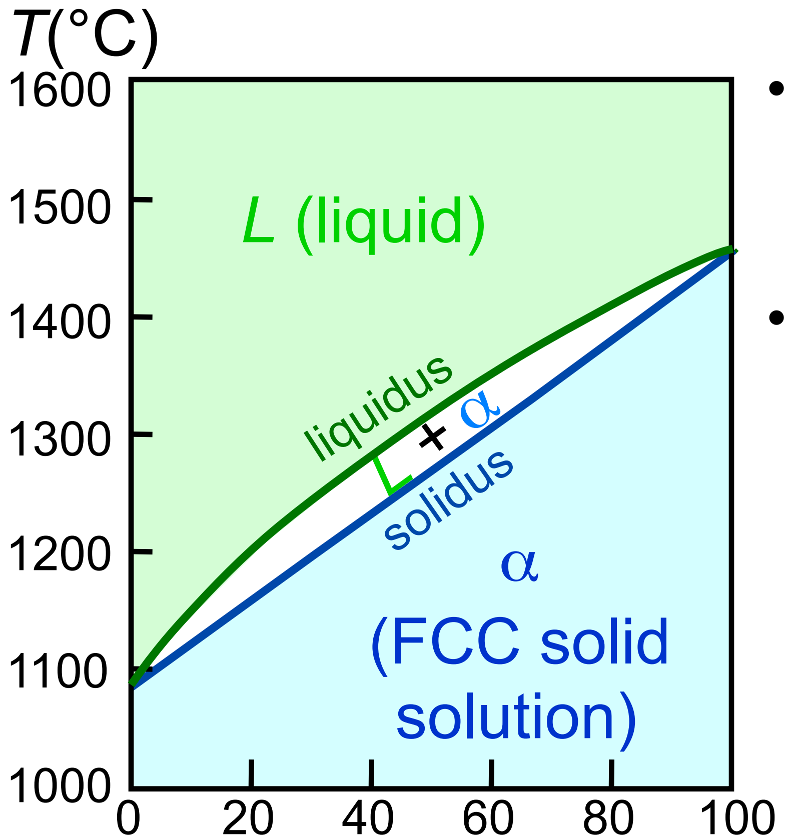
- *When we combine two elements, create an alloy or a compound what is the equilibrium structure like ?*
- *For a given composition and temperature*
  - *How many phases do we get ?*
  - *What is the composition of each phase ?*
  - *How much of each phase do we get ?*



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).

Interpretation of Phase Diagrams

- For a given temperature, T, and composition, C_O, we can use the phase diagram to determine:
  1. The # of phases that are present
  2. Compositions of these phases
  3. The relative fractions of the phases
- Finding the composition in a two phase region:
  1. Locate composition and temperature in the diagram
  2. In a two phase region draw the tie line or an isotherm
  3. Note the intersection with phase boundaries. Read compositions at the intersections.

The liquid and/or solid phases have these compositions.

LETS TRY

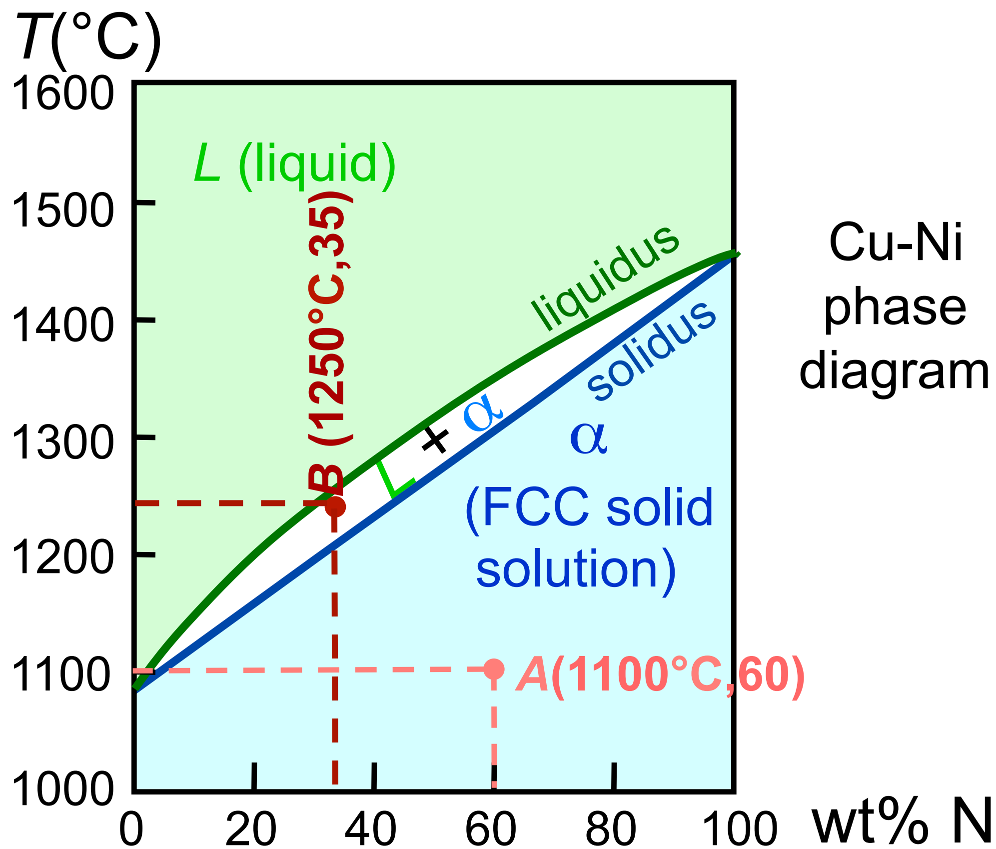
Phase Diagrams:
and types of phases

- 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)

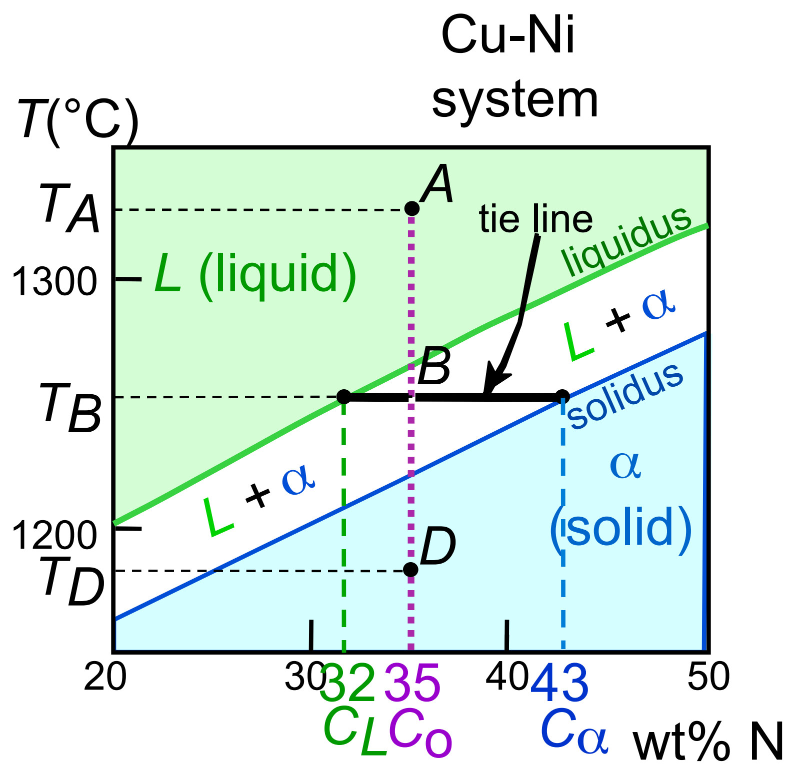
  $C_\alpha = C_o$ (= 35 wt% Ni)

  At T_B = 1250°C:

  Both α and L

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

  $C_\alpha = C_{solidus}$ (= 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

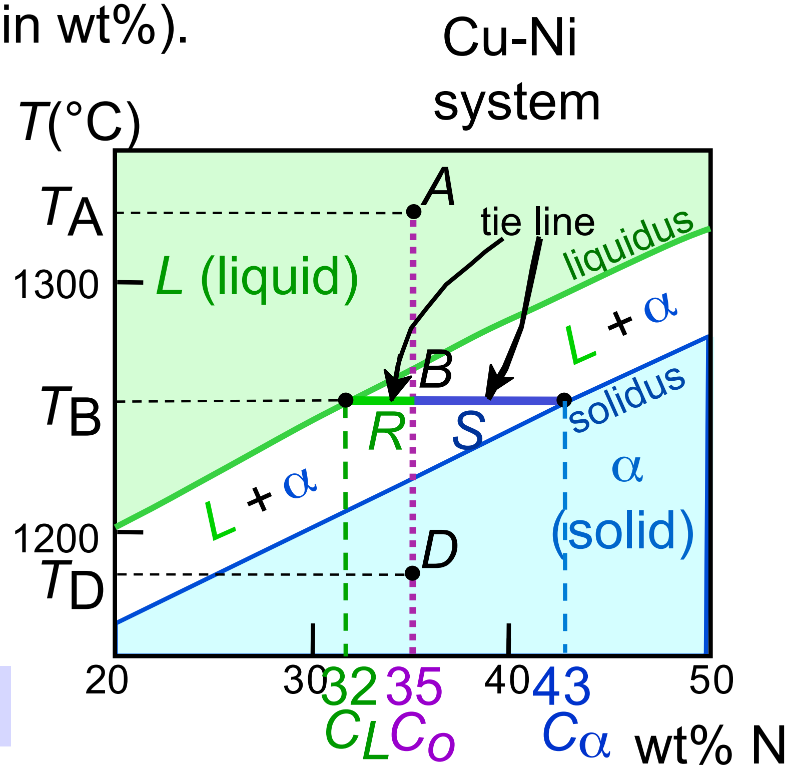
At T_D: Only Solid (α)

W_L = 0, W_α = 100 wt%

At T_B: Both α and L

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

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



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.)

Interpretation of Phase Diagrams : Lever Rule

- Finding the amounts of phases in a two phase region:
  1. Locate composition and temperature in diagram
  2. In two phase region draw the tie line or isotherm
  3. Fraction of a phase is determined by taking the length of the tie line to the phase boundary for the other phase, and dividing by the total length of tie line
- The lever rule is a mechanical analogy to the mass balance calculation. The tie line in the two-phase region is analogous to a lever balanced on a fulcrum.

- Proof

THE LEVER RULE: A PROOF

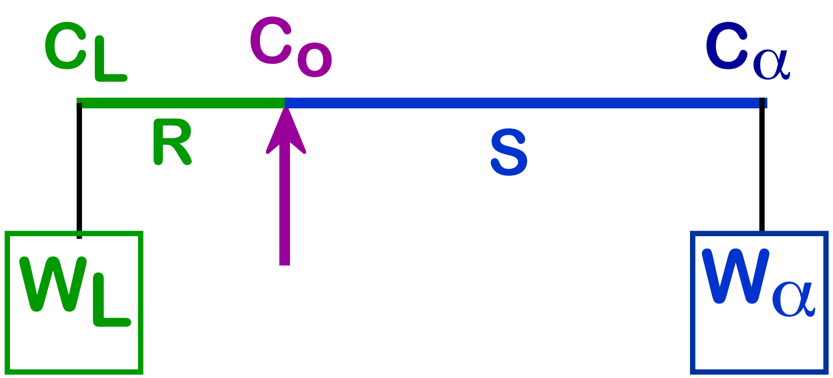
How much of each phase?
Think of it as a lever (teeter-totter)

- ***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:***

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

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

- ***A geometric interpretation:***



moment equilibrium:

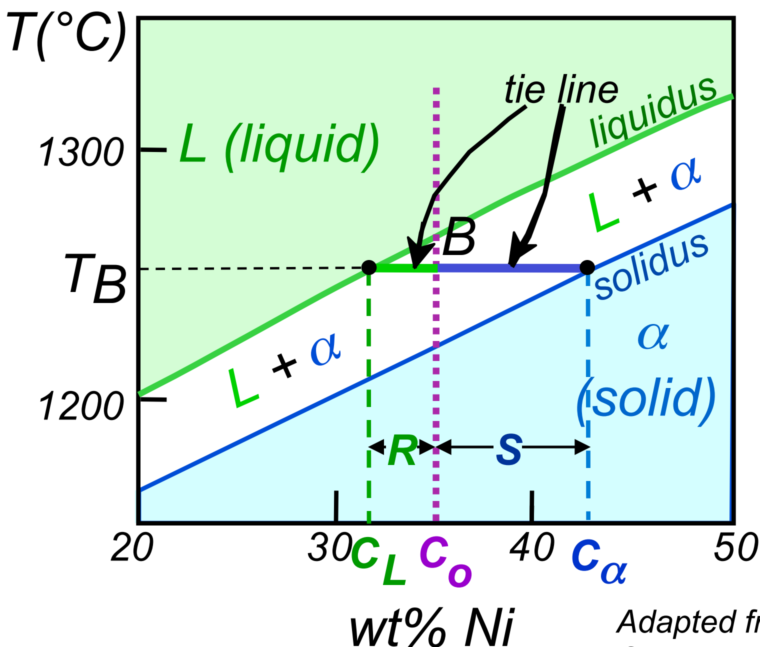
$$W_L R = W_\alpha S$$

$W_L = 1 - W_\alpha$

solving gives Lever Rule

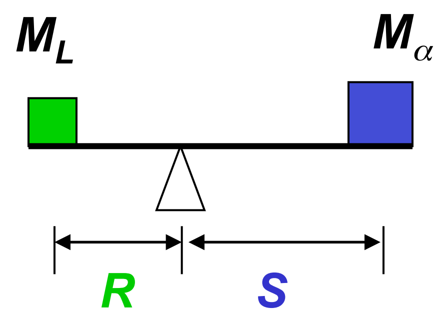
The Lever Rule

- 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)



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

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

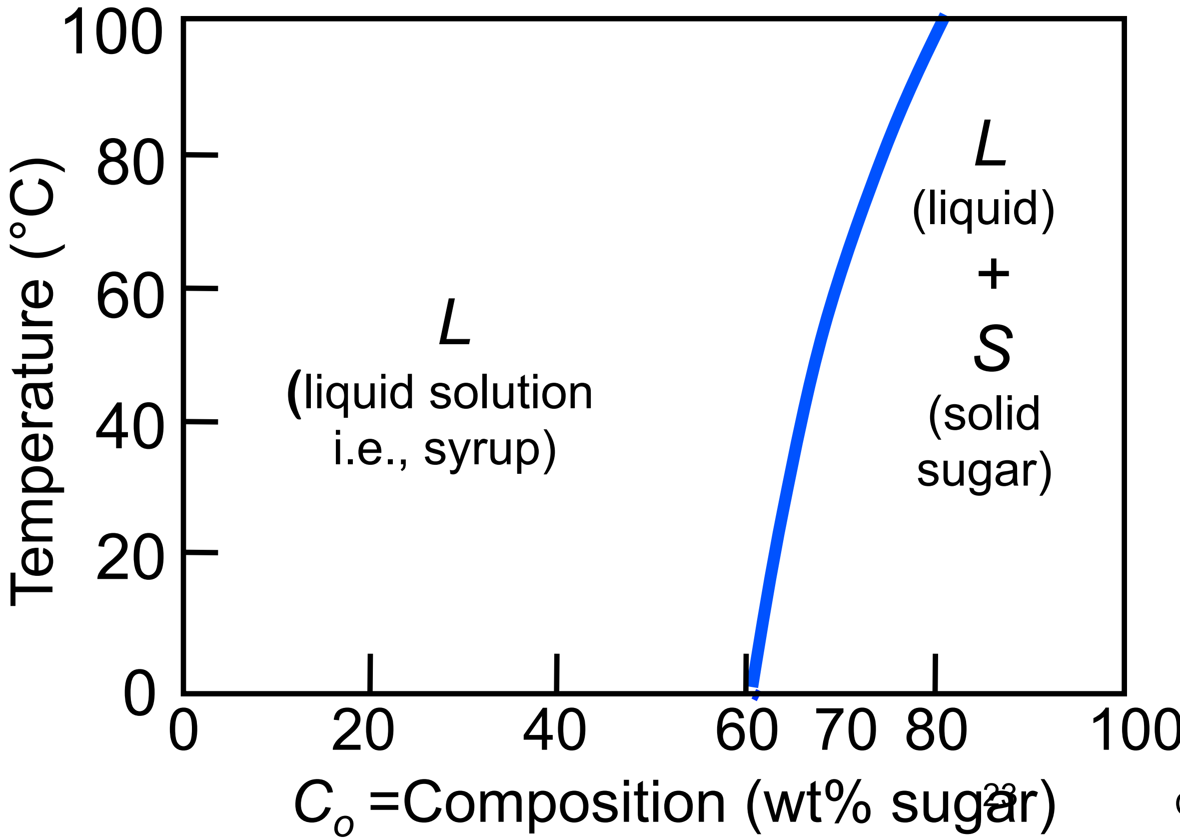
$$W_\alpha = \frac{R}{R+S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

Consider the sugar––water phase diagram.

(a) How much sugar will dissolve in 1500 g water at 90°C (363 K)?

(b) If the saturated liquid solution in part (a) is cooled to 20°C (293 K), some of the sugar will precipitate out as a solid. What will be the composition of the saturated liquid solution (in wt% sugar) at 20°C?

(c) How much of the solid sugar will come out of solution upon cooling to 20°C?



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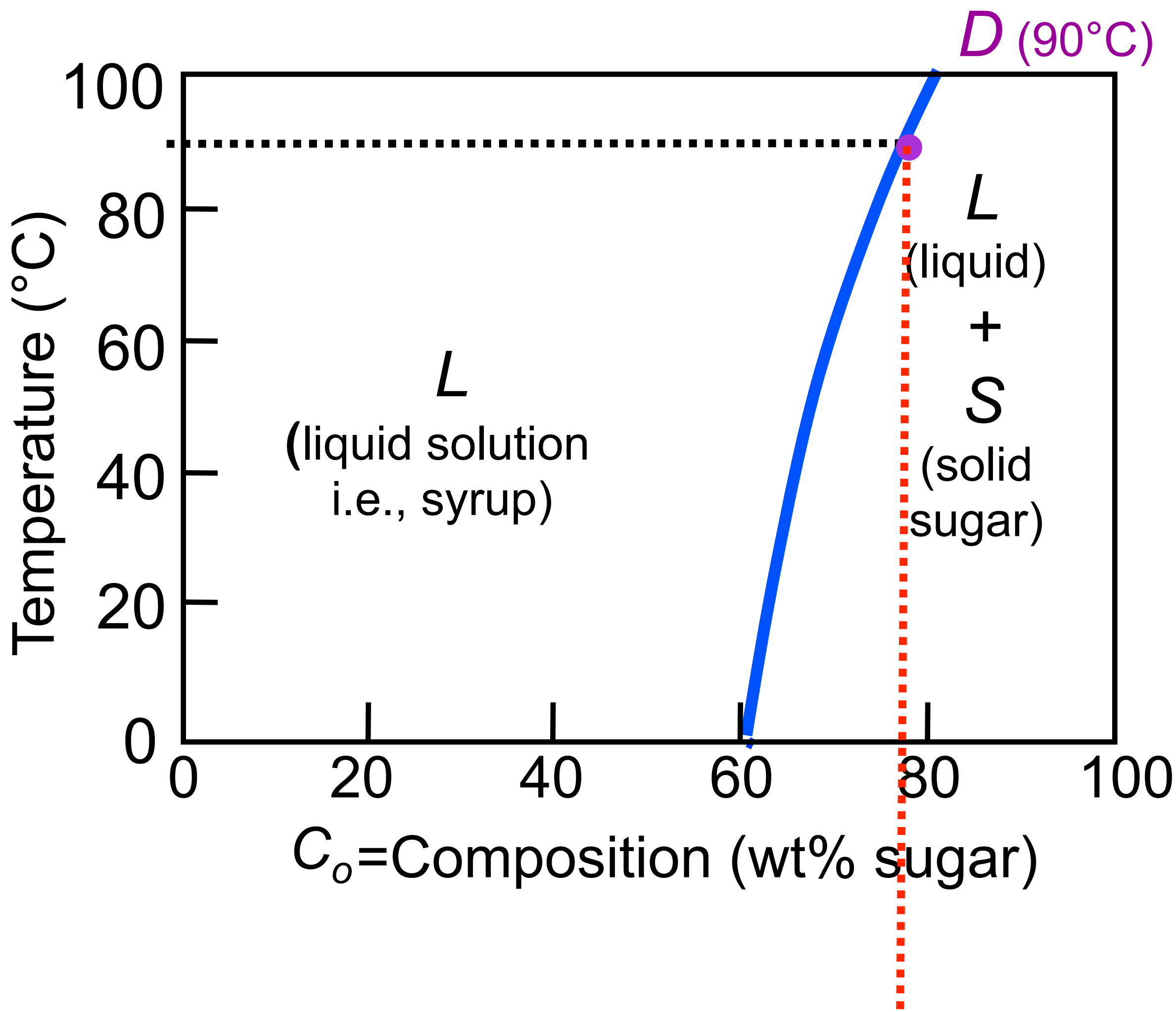

Consider the sugar––water phase diagram.

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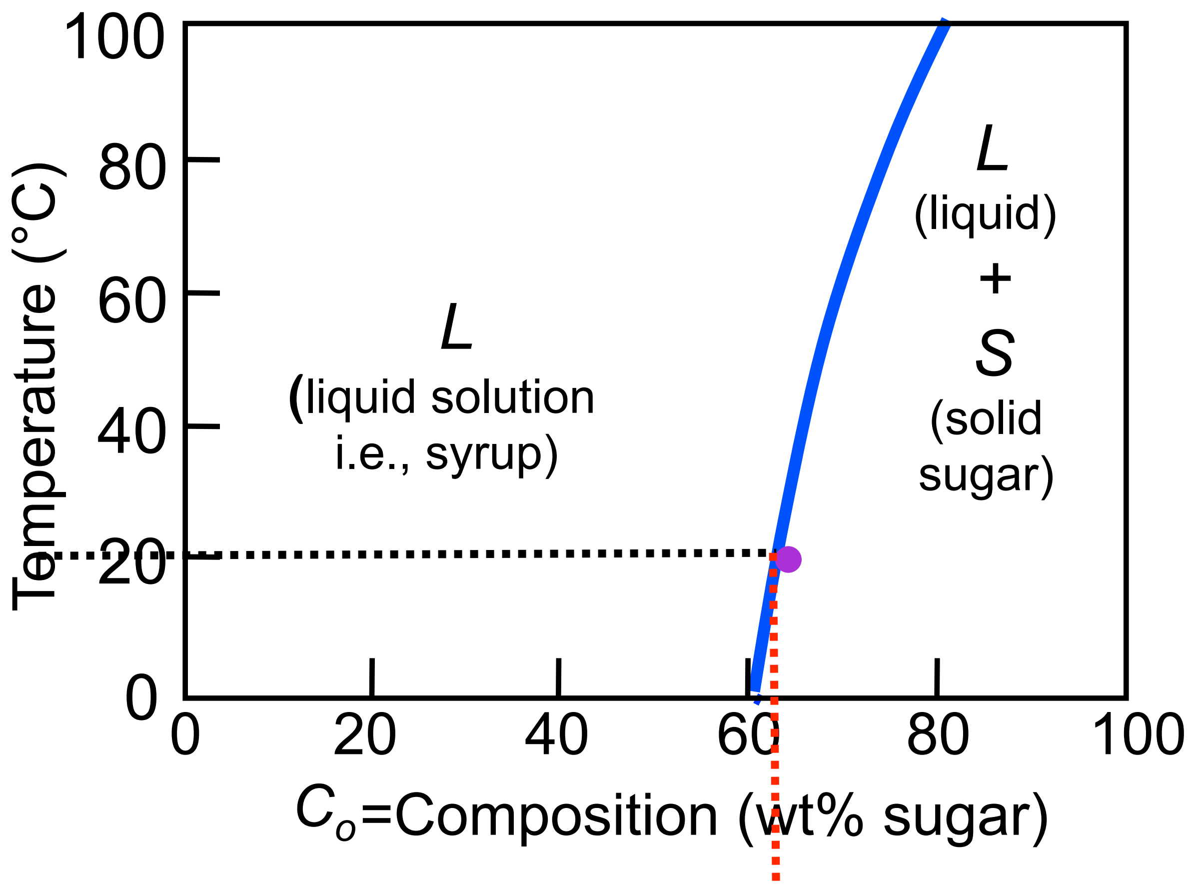
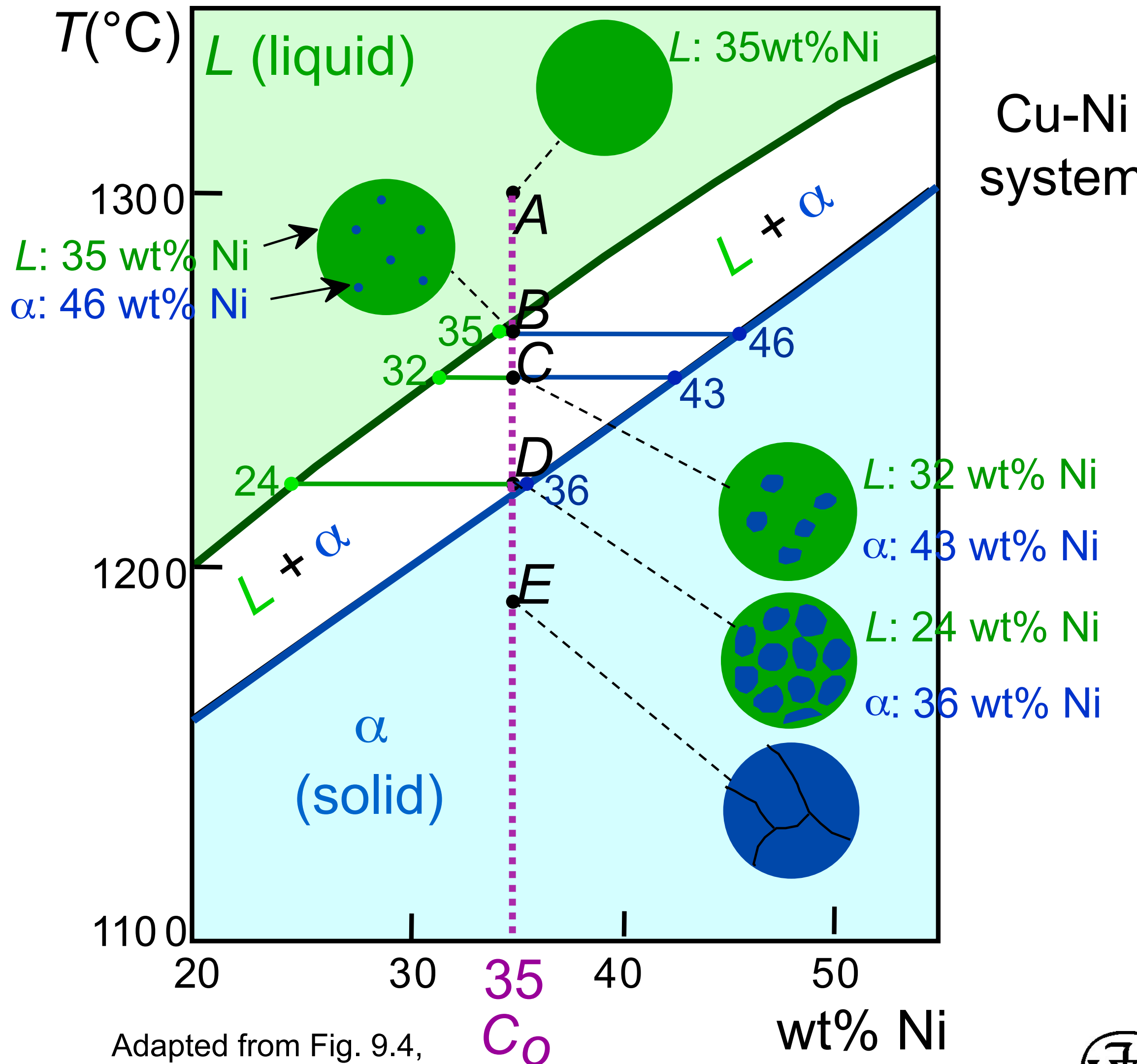


(c) How much of the solid sugar will come out of solution upon cooling to 20°C?

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.*

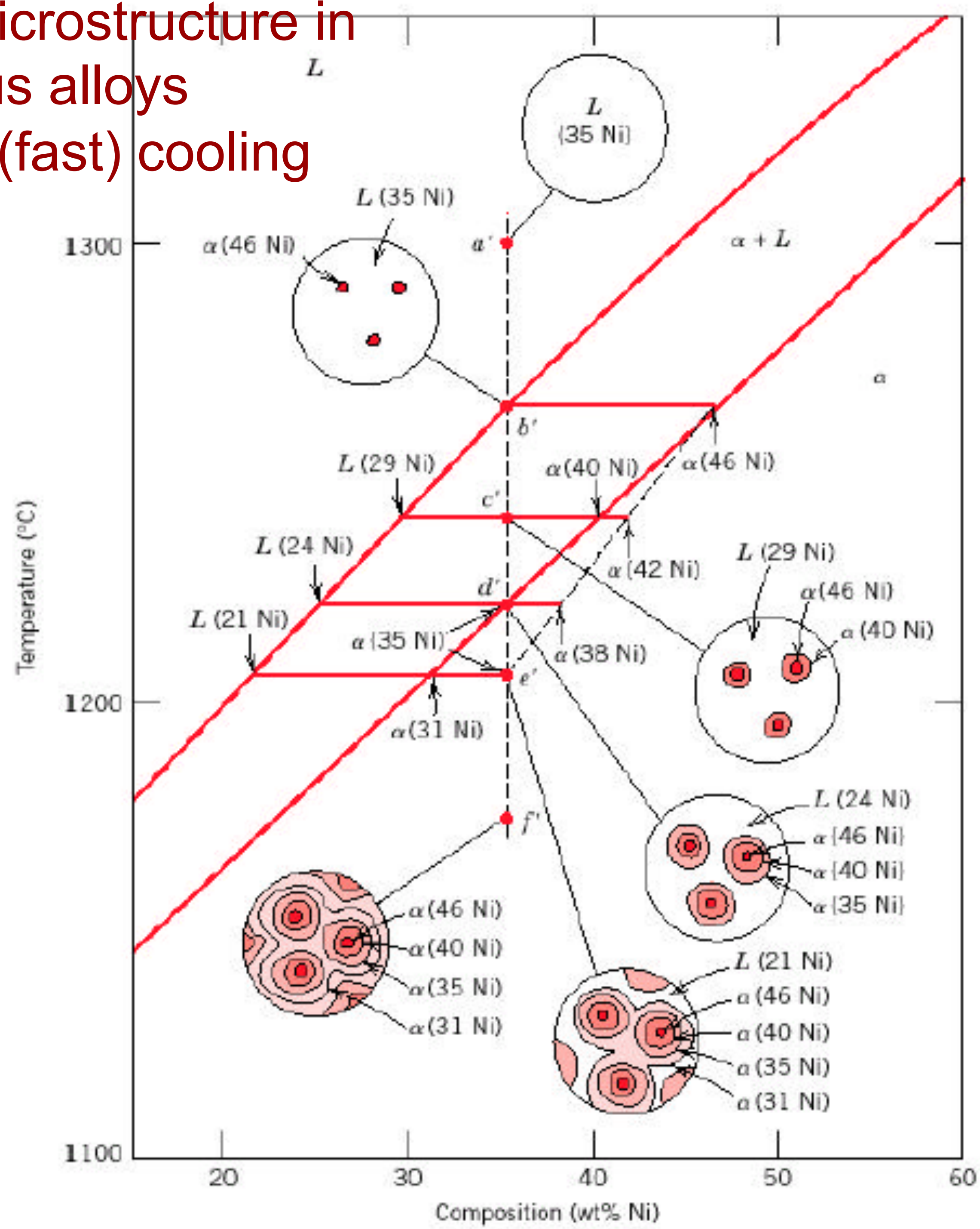
SUMMARY

- Development of microstructure in isomorphous alloys during equilibrium (very slow) cooling

1. **Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line.**
2. **The composition of the solid and the liquid change gradually during cooling (as can be determined by the tie-line method.) => DIFFUSION !**
3. **Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.**

Development of microstructure in isomorphous alloys
Non-equilibrium (fast) cooling

- ***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 & fast cooling



Adapted from Fig. 9.3, Callister 6e.

SUMMARY

Development of microstructure in <u>isomorphous</u> alloys during non-equilibrium (fast) cooling

Compositional changes require diffusion in solid and liquid phases

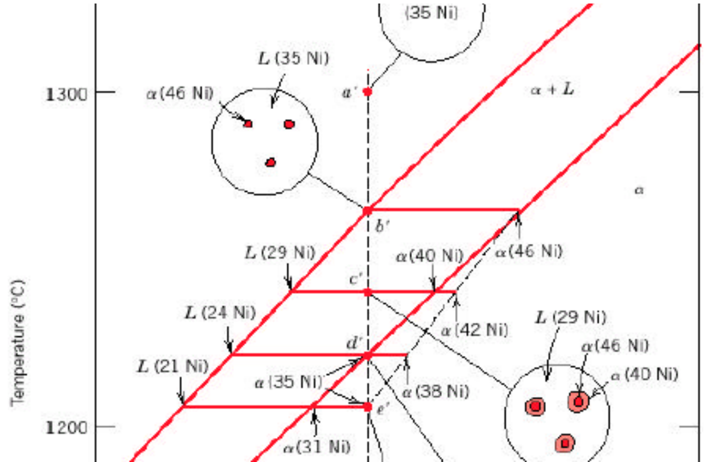
- **Diffusion in the solid state is very slow.**
- The new layers that solidify on top of the existing grains have the equilibrium composition at that temperature but once they are solid their composition does not change.
- Formation of layered (cored) grains and the invalidity of the tie-line method to determine the composition of the solid phase.

The tie-line method still works for the **liquid phase, where diffusion is fast.**

Average Ni content of solid grains is higher.

- Application of the lever rule gives us a greater proportion of liquid phase as compared to the one for equilibrium cooling at the same T.
- **<u>Solidus line is shifted to the right</u>** (higher Ni contents), **solidification is complete at lower T, <u>the outer part of the grains are richer in the low-melting component (Cu).</u>**

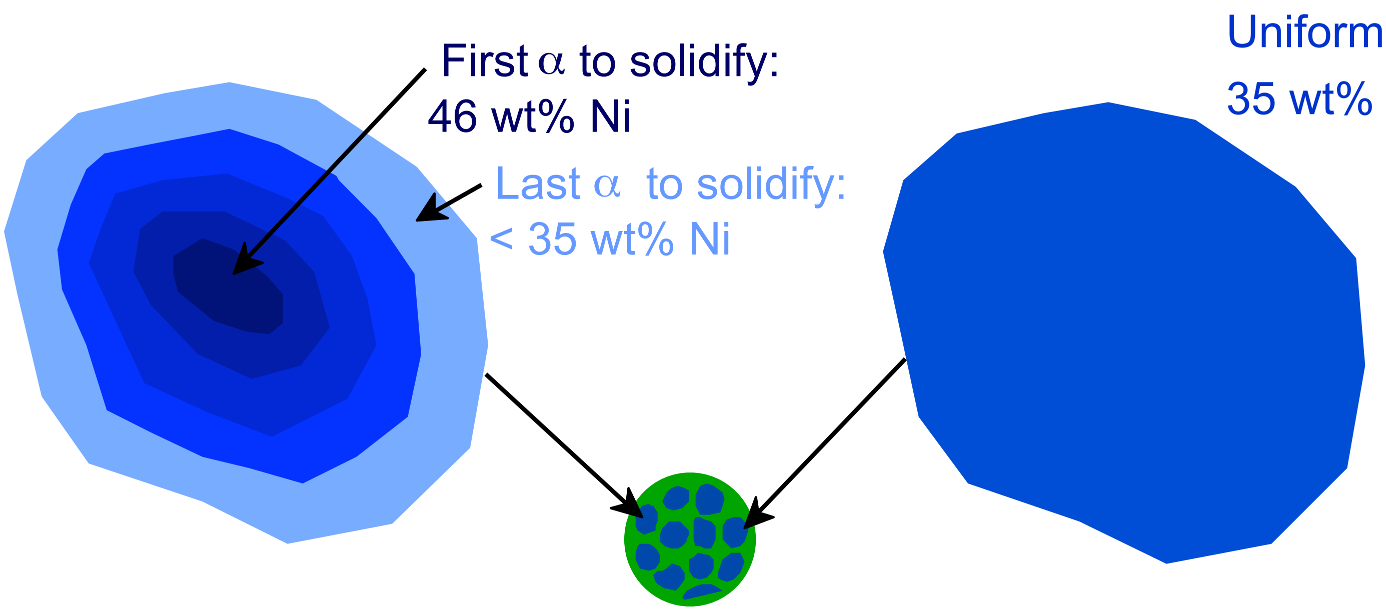
Upon heating **grain boundaries will melt first.** This can lead to premature mechanical failure at high temperatures.



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.

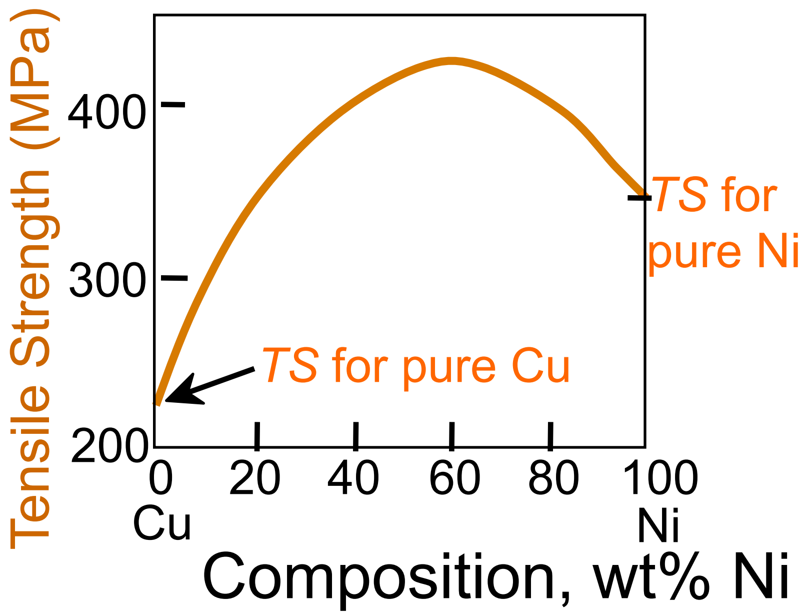
- Fast rate of cooling:
  Cored structure
- Slow rate of cooling:
  Equilibrium structure



Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

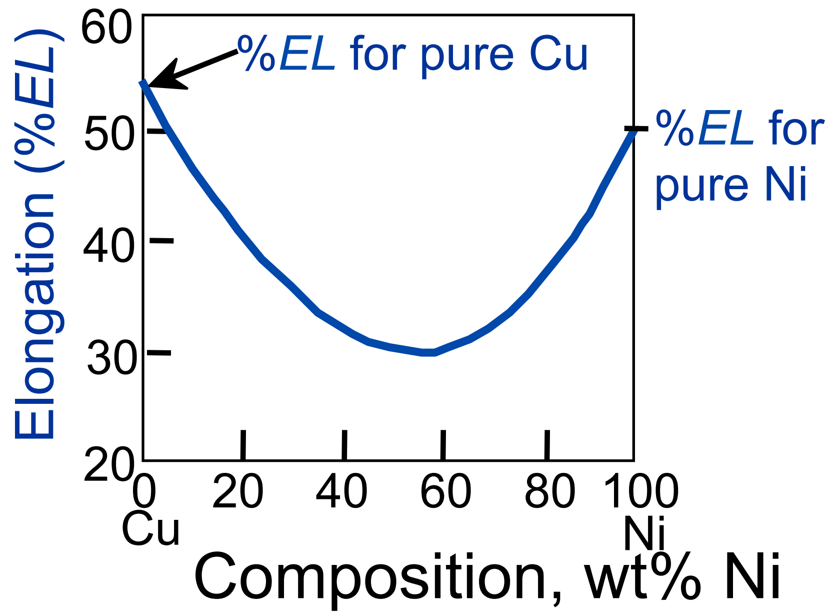
--Tensile strength (*TS*)



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

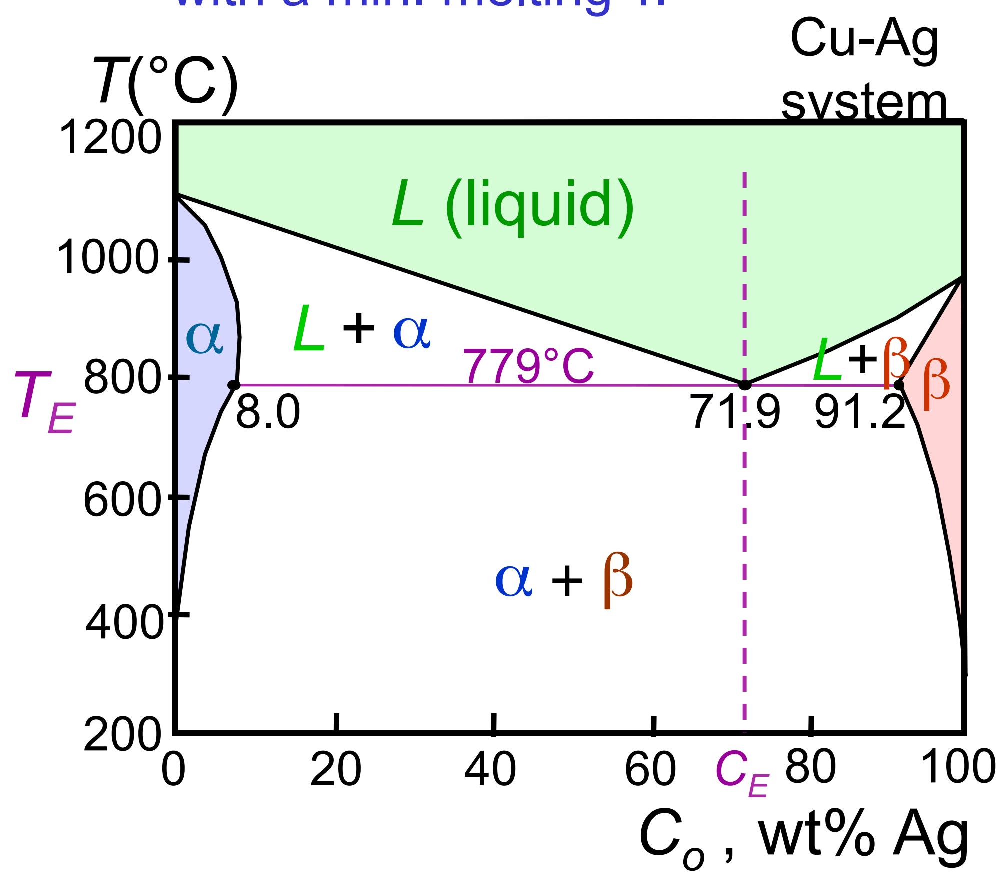
Binary-Eutectic Systems

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

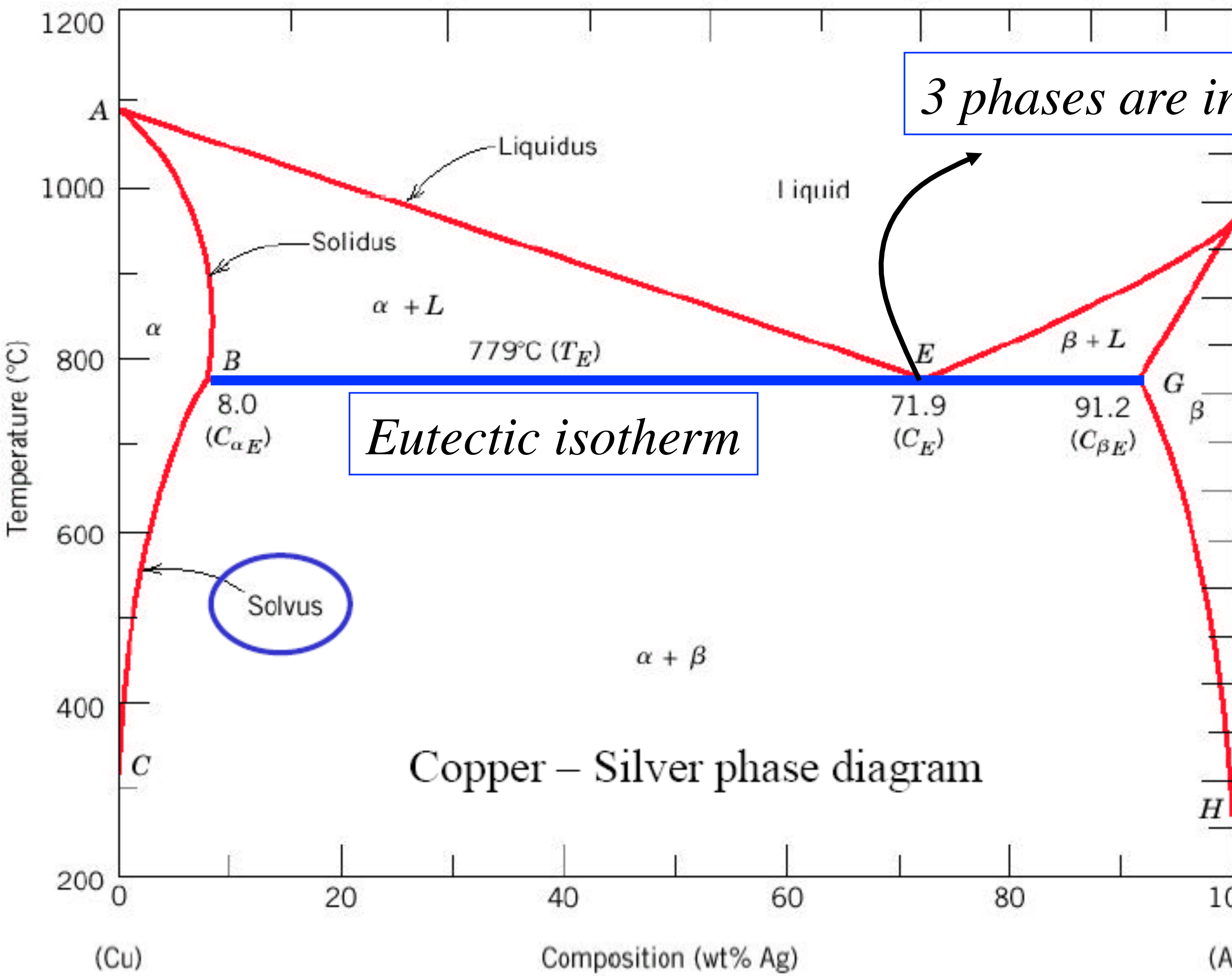


Adapted from Fig. 9.7, *Callister 7e.*

- **Eutectic transition**

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

More Information on Eutectic Systems (I)



More Information on Eutectic Systems (II)

- **Eutectic reaction – transition between liquid and mixture of two solid phases, α + β, at eutectic concentration C_E.**
  - **The melting point of the eutectic alloy is lower than that of the components (*eutectic = easy to melt in Greek*).**
- **At most two phases can be in equilibrium within a phase field. Three phases (L, α, β) may be in equilibrium only at a few points along the eutectic isotherm.**
- **Single phase regions are separated by 2-phase regions.**

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:

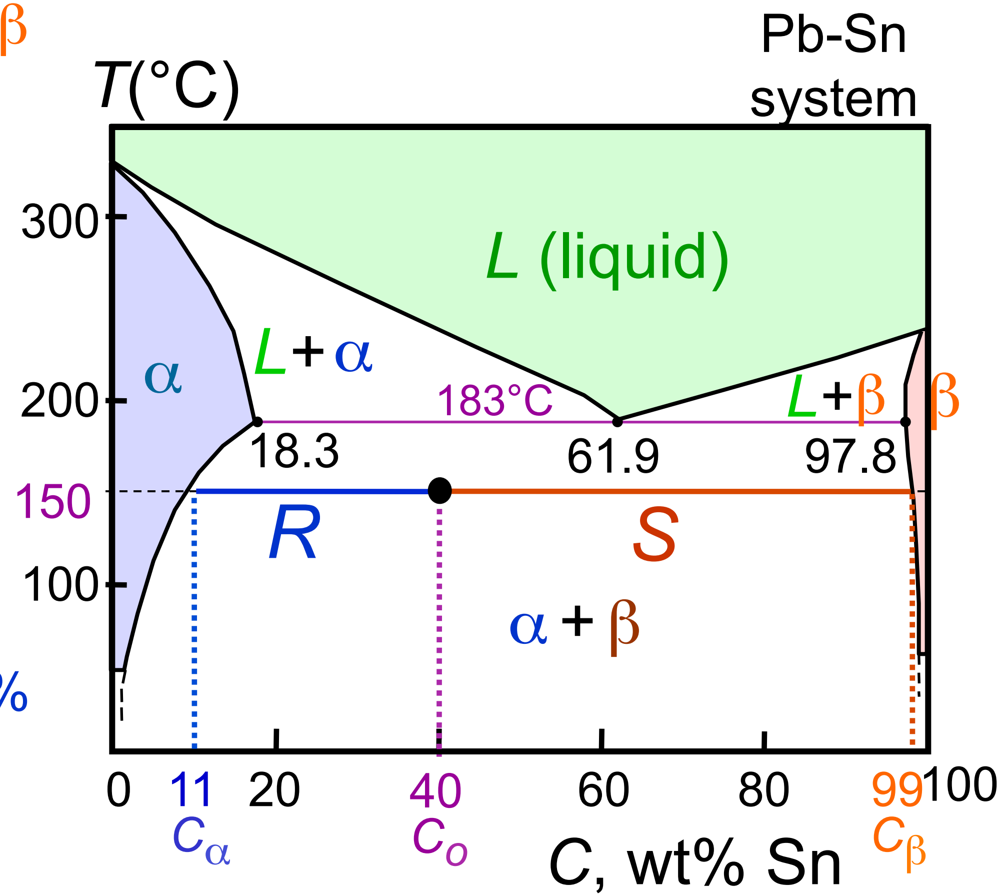
    C_O = 40 wt% Sn
    C_α = 11 wt% Sn
    C_β = 99 wt% Sn
  - --the relative amount of each phase:

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

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

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

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



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:

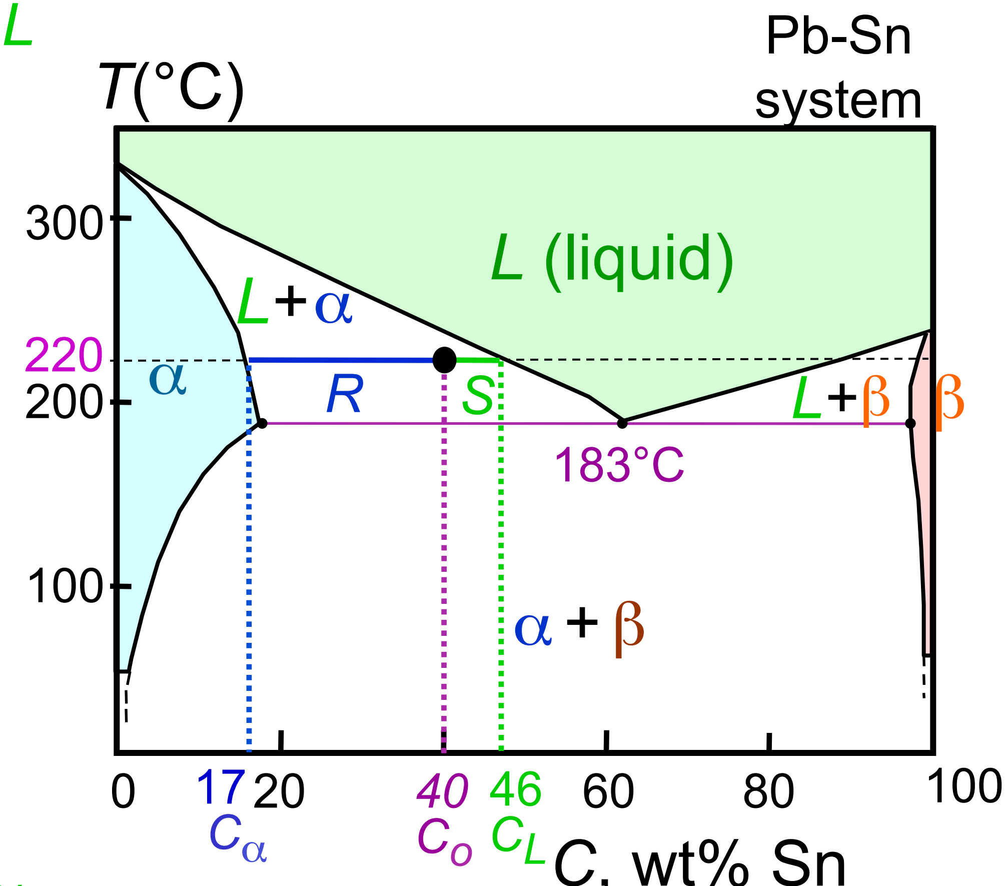
    C_O = 40 wt% Sn

    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.*

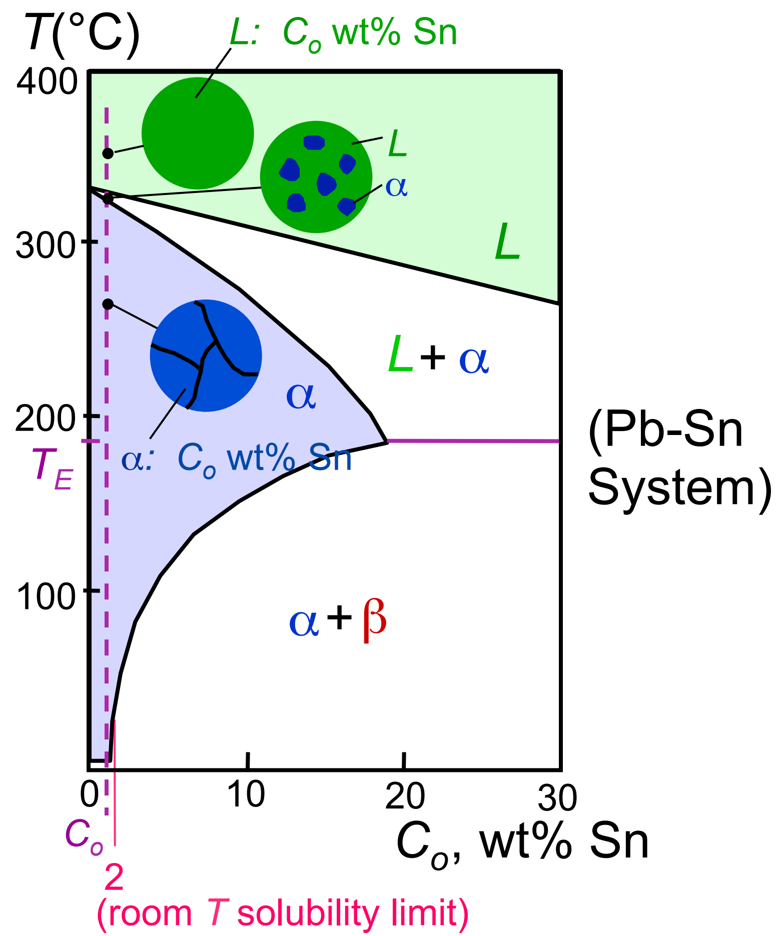
Microstructures in Eutectic Systems: I

- C_o < 2 wt% Sn
- Result:

  --at extreme ends

  --polycrystal of α grains

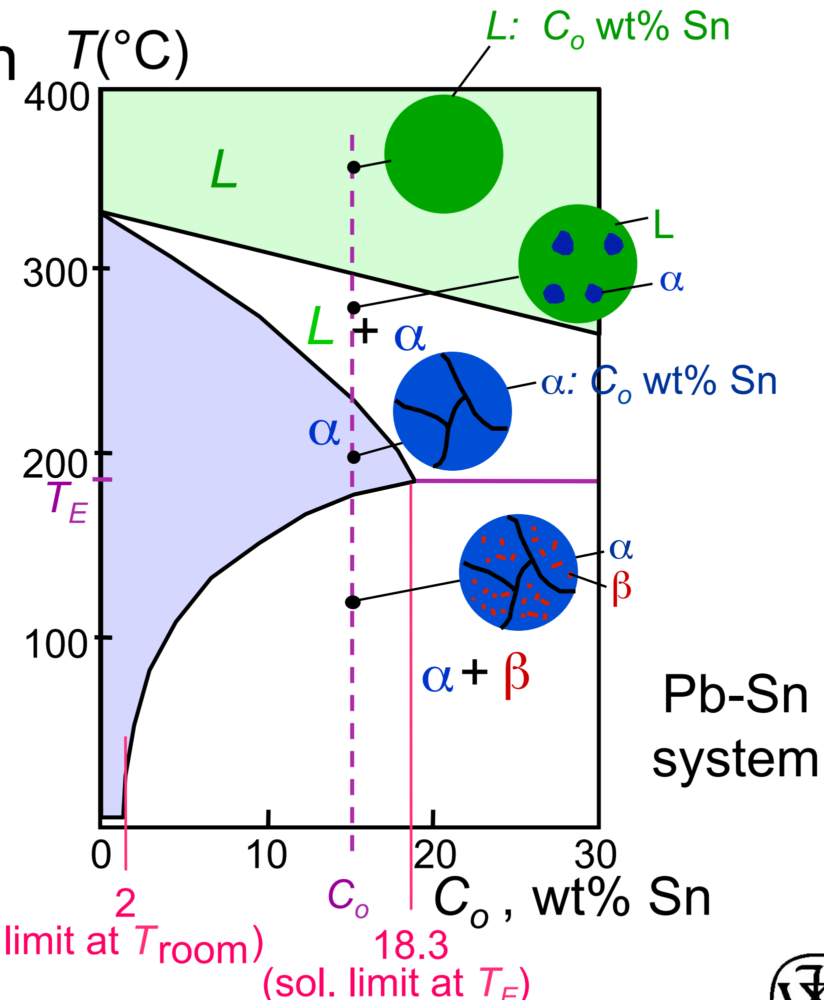
  i.e., only one solid phase.



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

Microstructures in Eutectic Systems: II

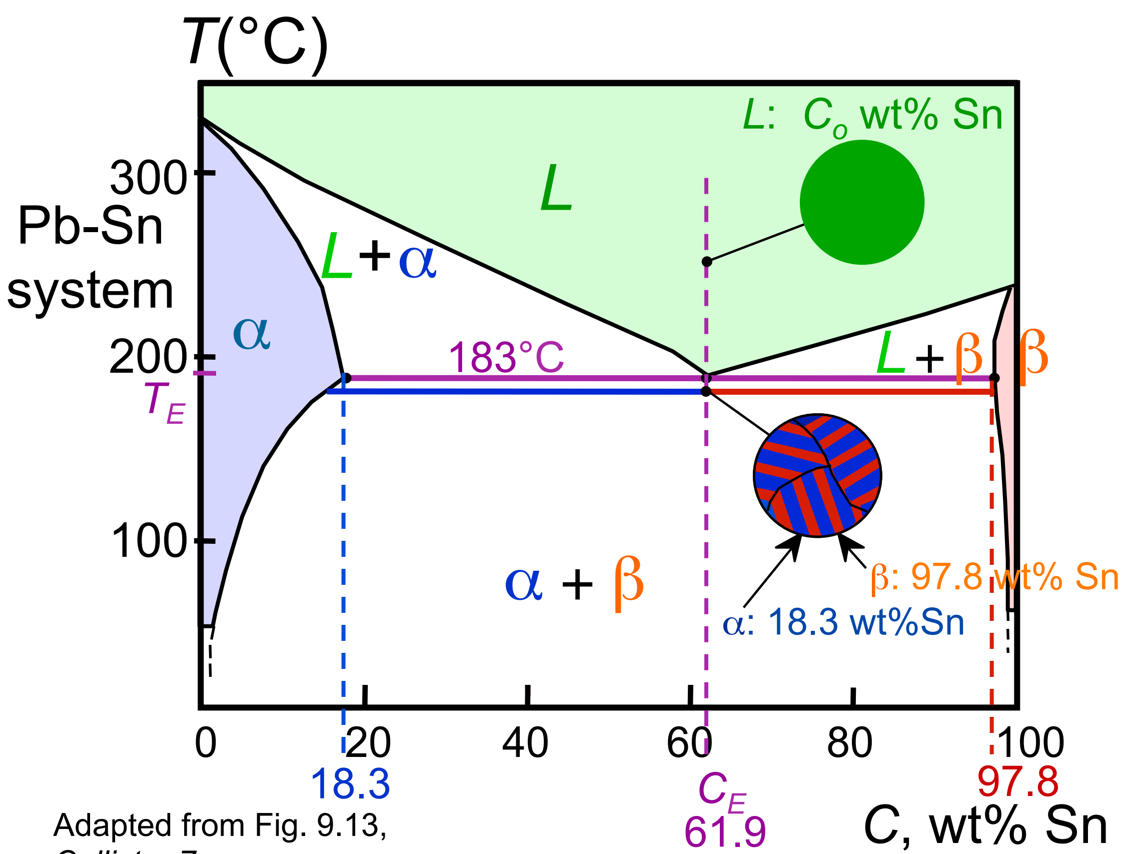
- 2 wt% Sn < C_o < 18.3 wt% Sn
- Result:
  - Initially liquid + α
  - then α alone
  - finally two phases
    - α polycrystal
    - fine β-phase inclusions



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

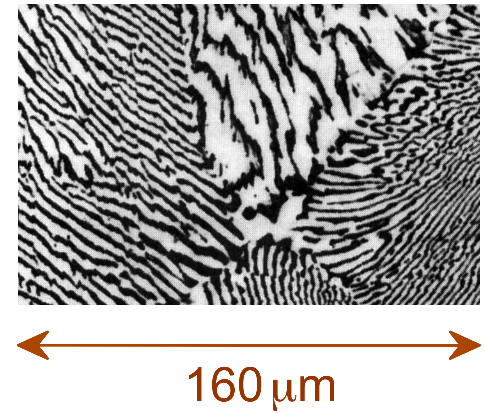
Microstructures in Eutectic Systems: III

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



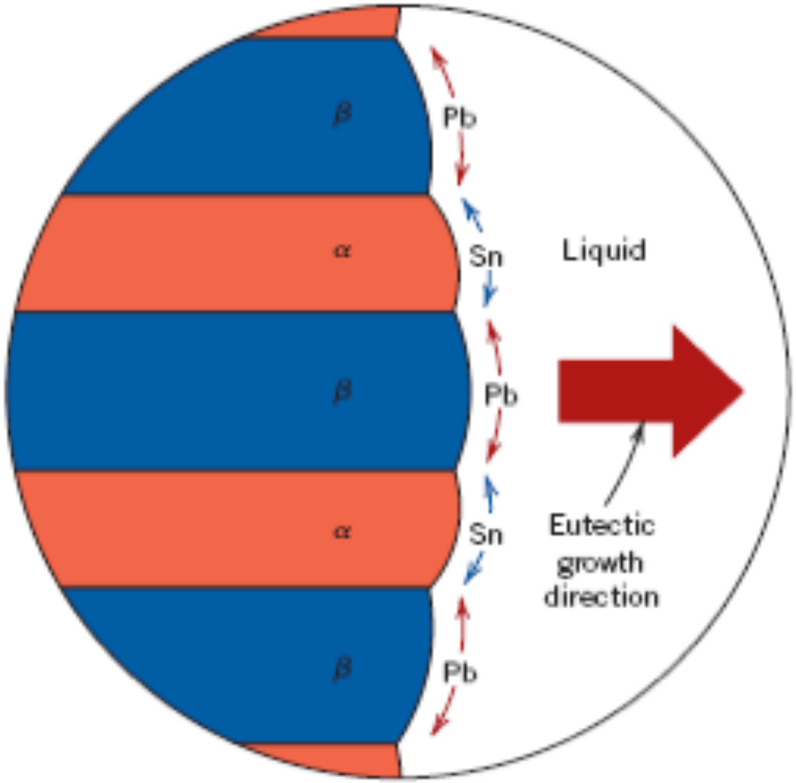
Adapted from Fig. 9.13, *Callister 7e.*

Micrograph of Pb-Sn eutectic microstructure

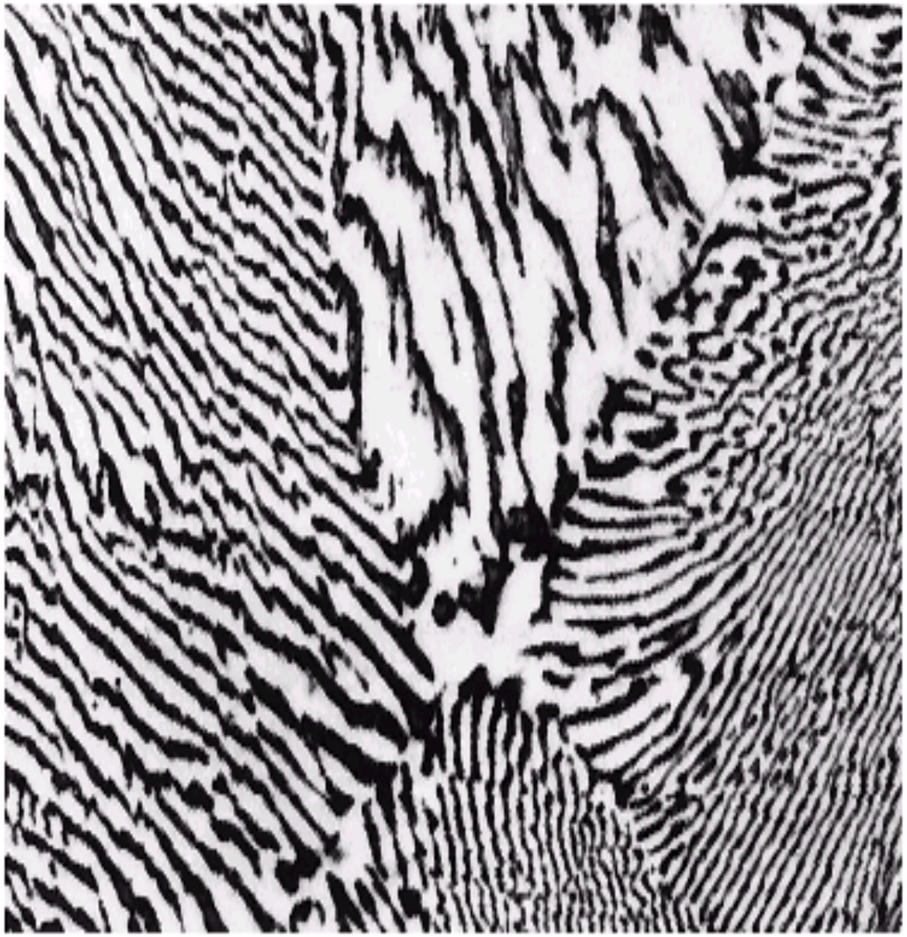


Adapted from Fig. 9.14, *Callister 7e.*

Lamellar Eutectic Structure

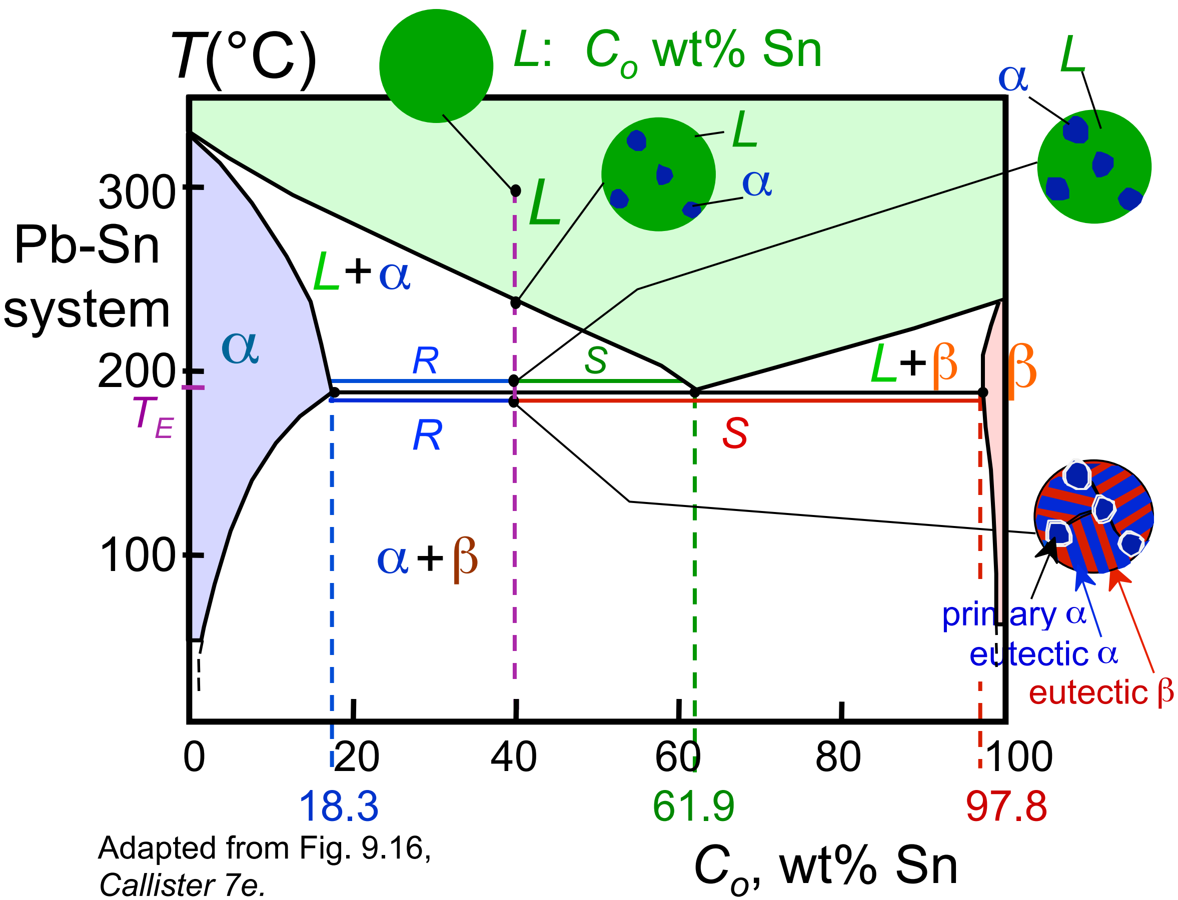


Adapted from Figs. 9.14 & 9.15, *Callister 7e.*



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 wt%

- Just below T_E:

  C_α = 18.3 wt% Sn

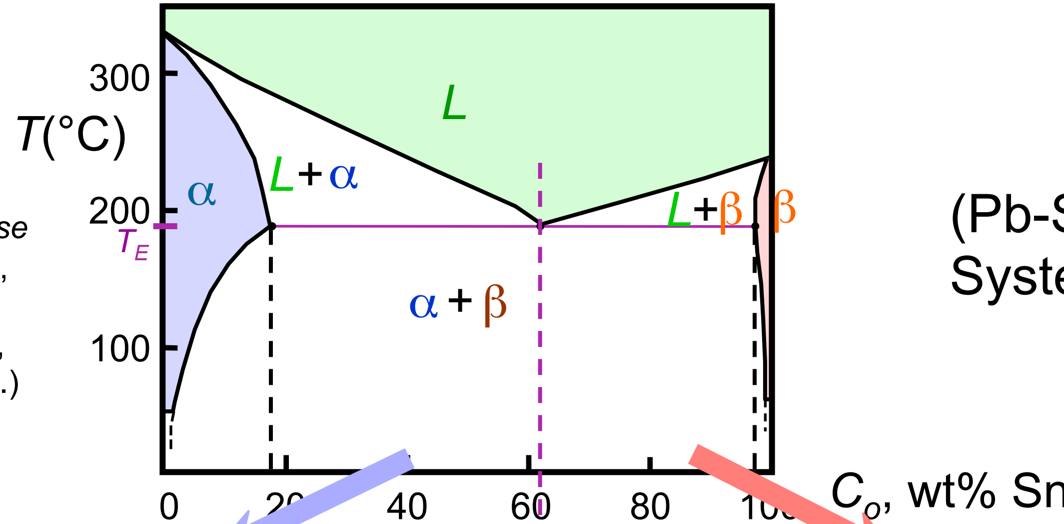
  C_β = 97.8 wt% Sn

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

  W_β = 27 wt%

Hypoeutectic & Hypereutectic

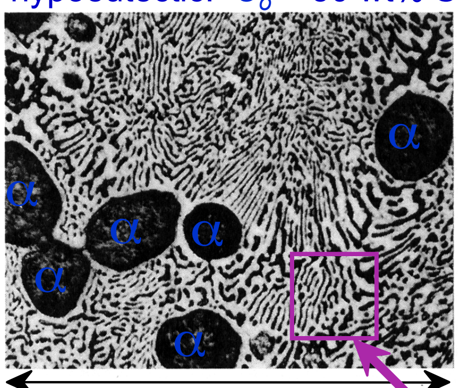
Adapted from Fig. 9.8, *Callister 7e.* (Fig. 9.8 adapted from *Binary Phase Diagrams*, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)



(Pb-Sn System)

eutectic
61.9

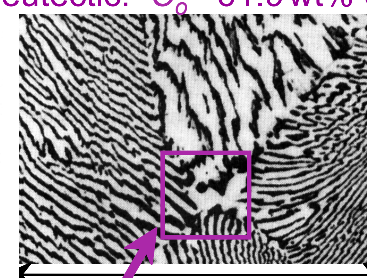
hypoeutectic: C_o = 50 wt% Sn



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

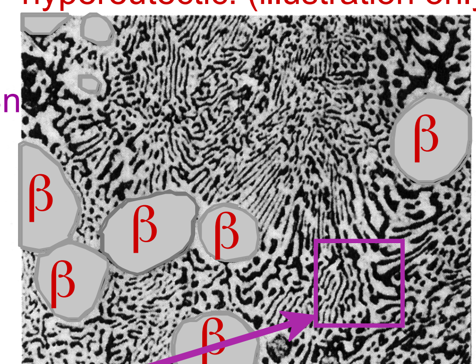
Adapted from Fig. 9.17, *Callister 7e.*

eutectic: C_o = 61.9 wt% Sn



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

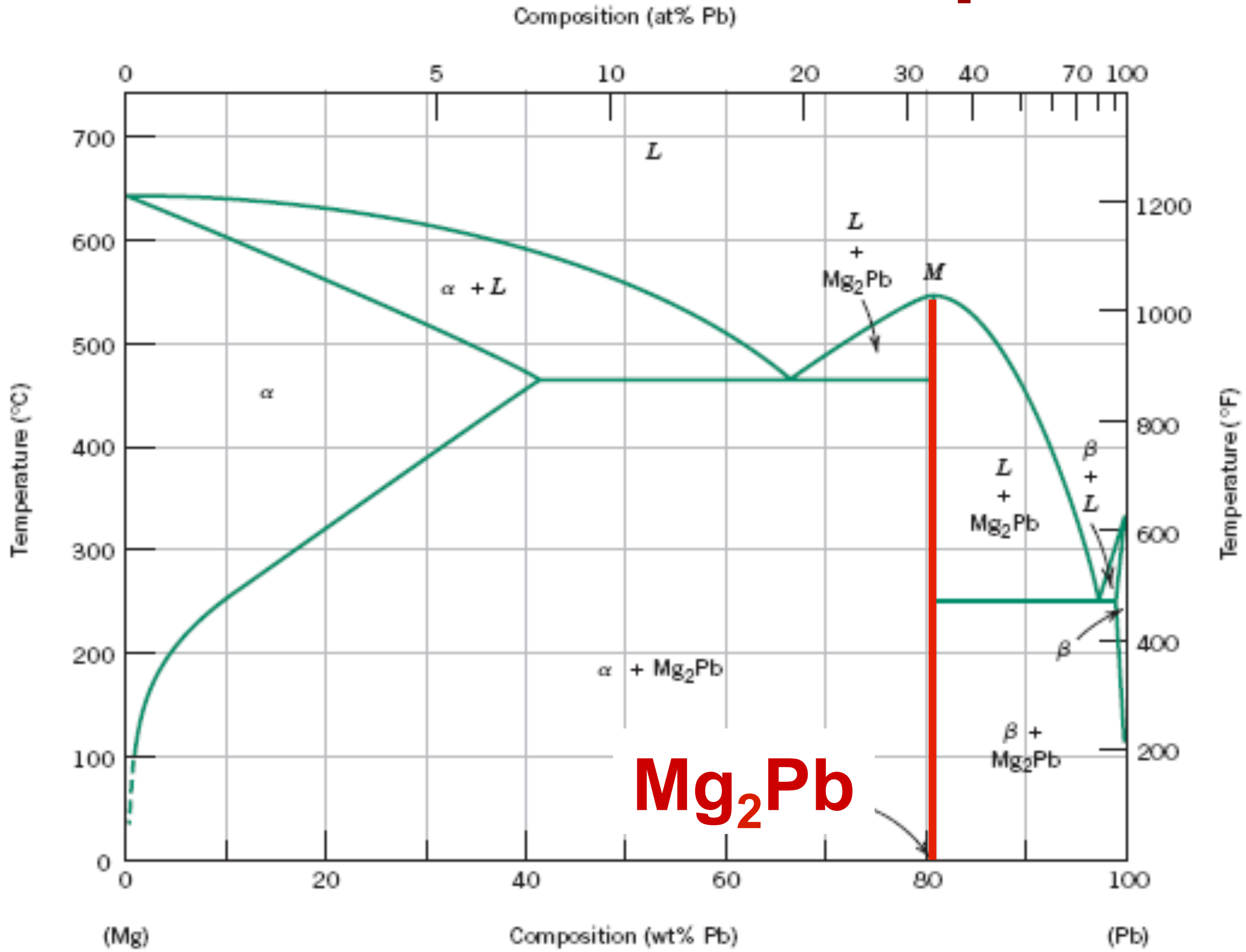
hypereutectic: (illustration only)



Adapted from Fig. 9.17, *Callister 7e.* (Illustration only)

eutectic micro-constituent

Intermetallic Compounds



Adapted from
Fig. 9.20, *Callister 7e.*

Note: intermetallic compound forms a line - not an area - because stoichiometry (i.e. composition) is exact.

Eutectoid & Peritectic

- Eutectic - liquid in equilibrium with two solids

$$L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + \beta$$

- Eutectoid - solid phase in equation with two solid phases

$$S_2 \rightleftharpoons S_1 + S_3$$

intermetallic compound - cementite

$$\gamma \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + Fe_3C \qquad (727^\circ C)$$

- Peritectic - liquid + solid 1 → solid 2 (Fig 9.21)

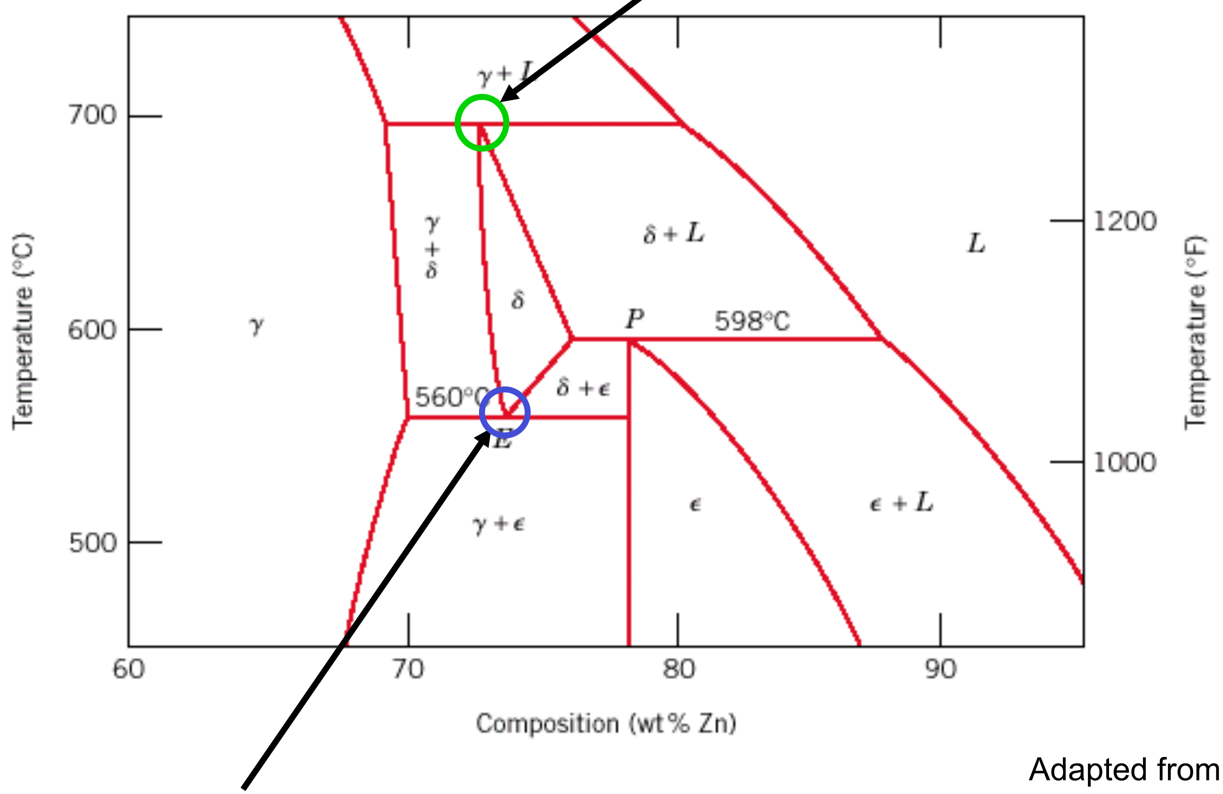
$$S_1 + L \rightleftharpoons S_2$$

$$\delta + L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \gamma \qquad (1493^\circ C)$$

Eutectoid & Peritectic

Cu-Zn Phase diagram

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



Adapted from
Fig. 9.21, *Callister 7e.*

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

Iron-Carbon (Fe-C) Phase Diagram

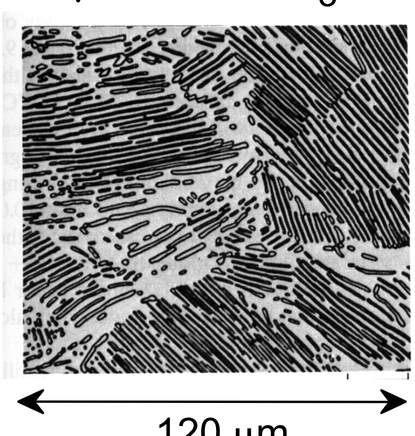
- 2 important points

  -Eutectic (*A*):

  $L \Rightarrow \gamma + Fe_3C$

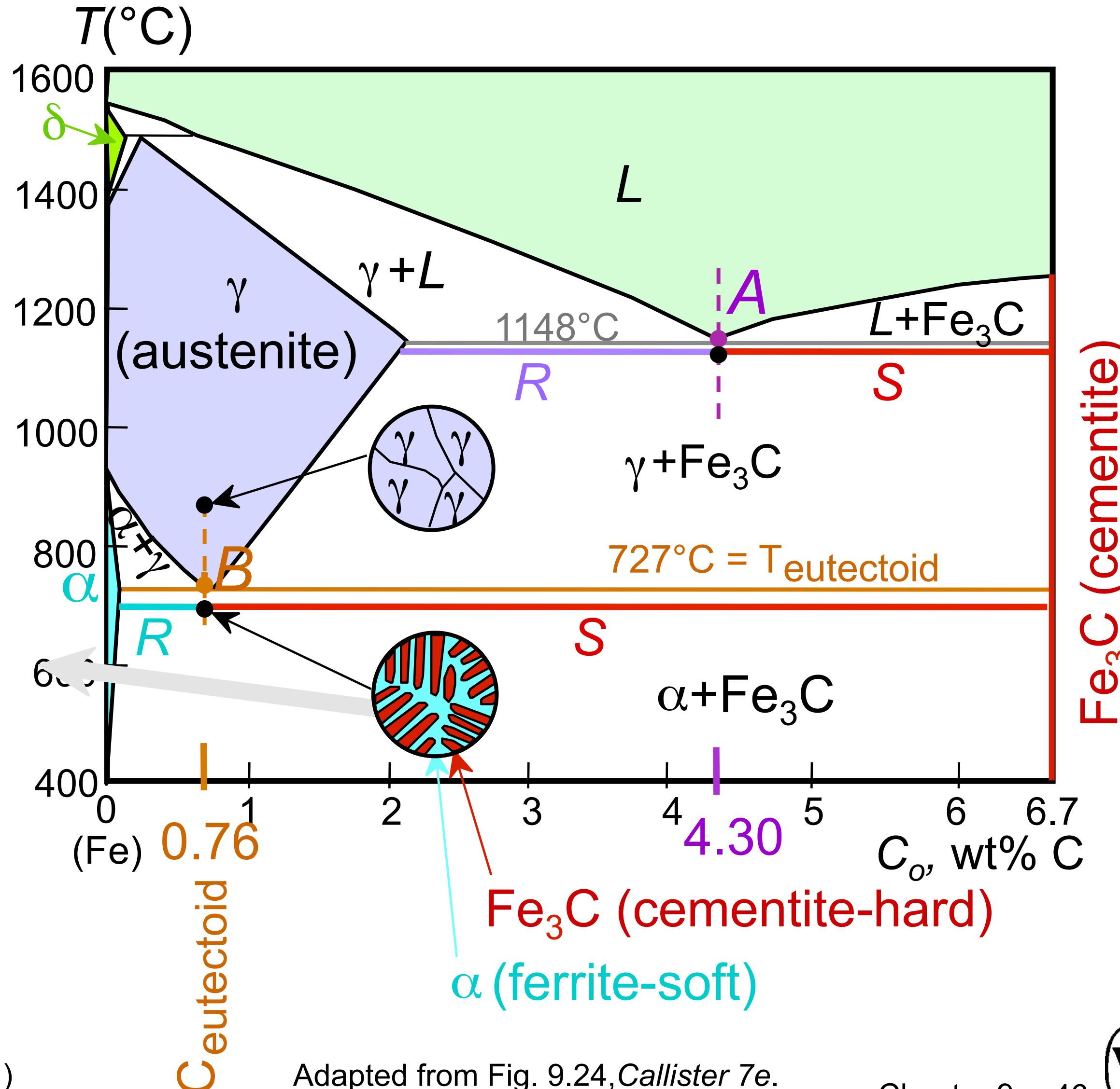
  -Eutectoid (*B*):

  $\gamma \Rightarrow \alpha + Fe_3C$



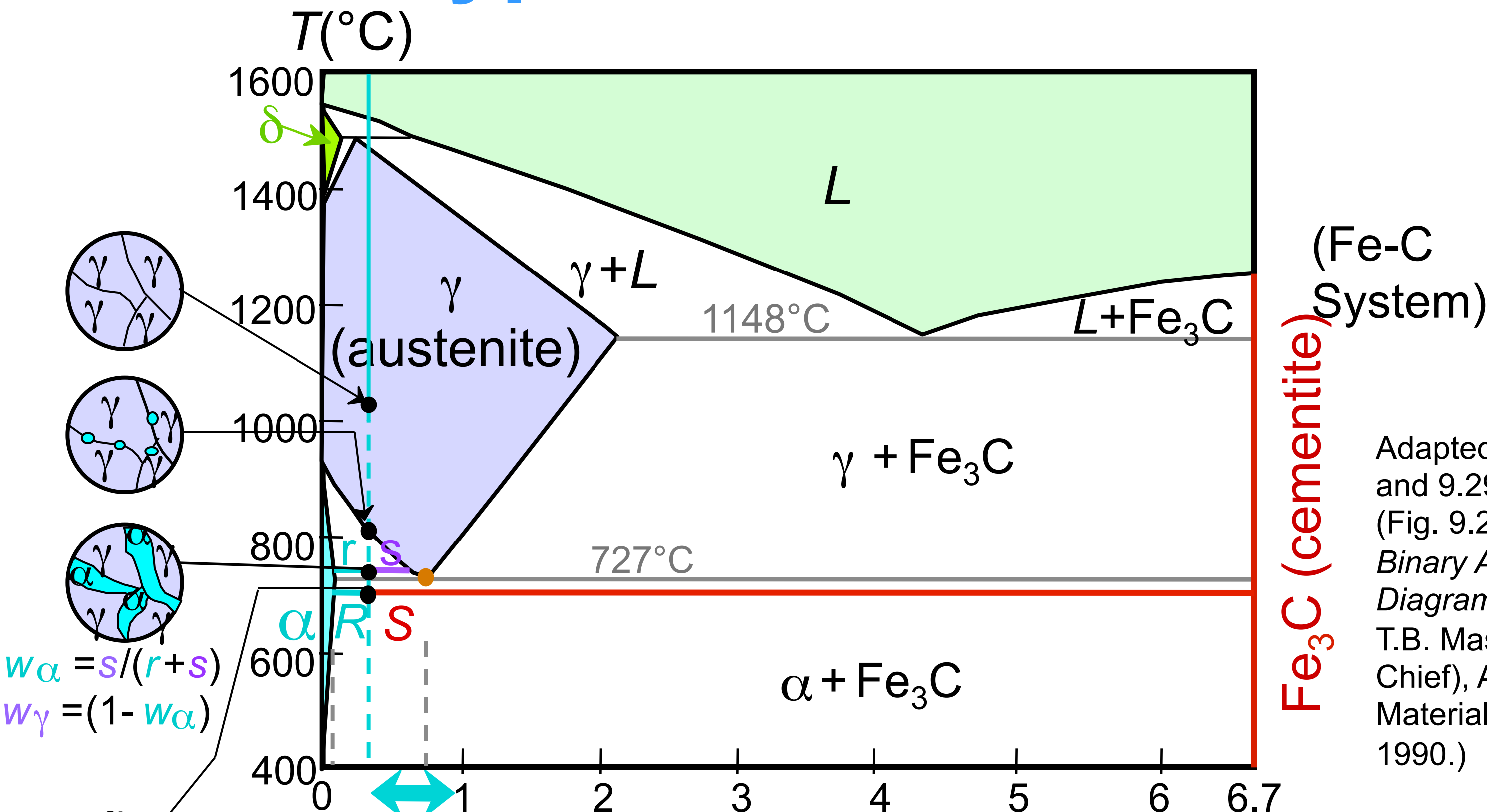
Result: Pearlite = alternating layers of α and Fe_3C phases

(Adapted from Fig. 9.27, *Callister 7e*.)



Adapted from Fig. 9.24, *Callister 7e*.

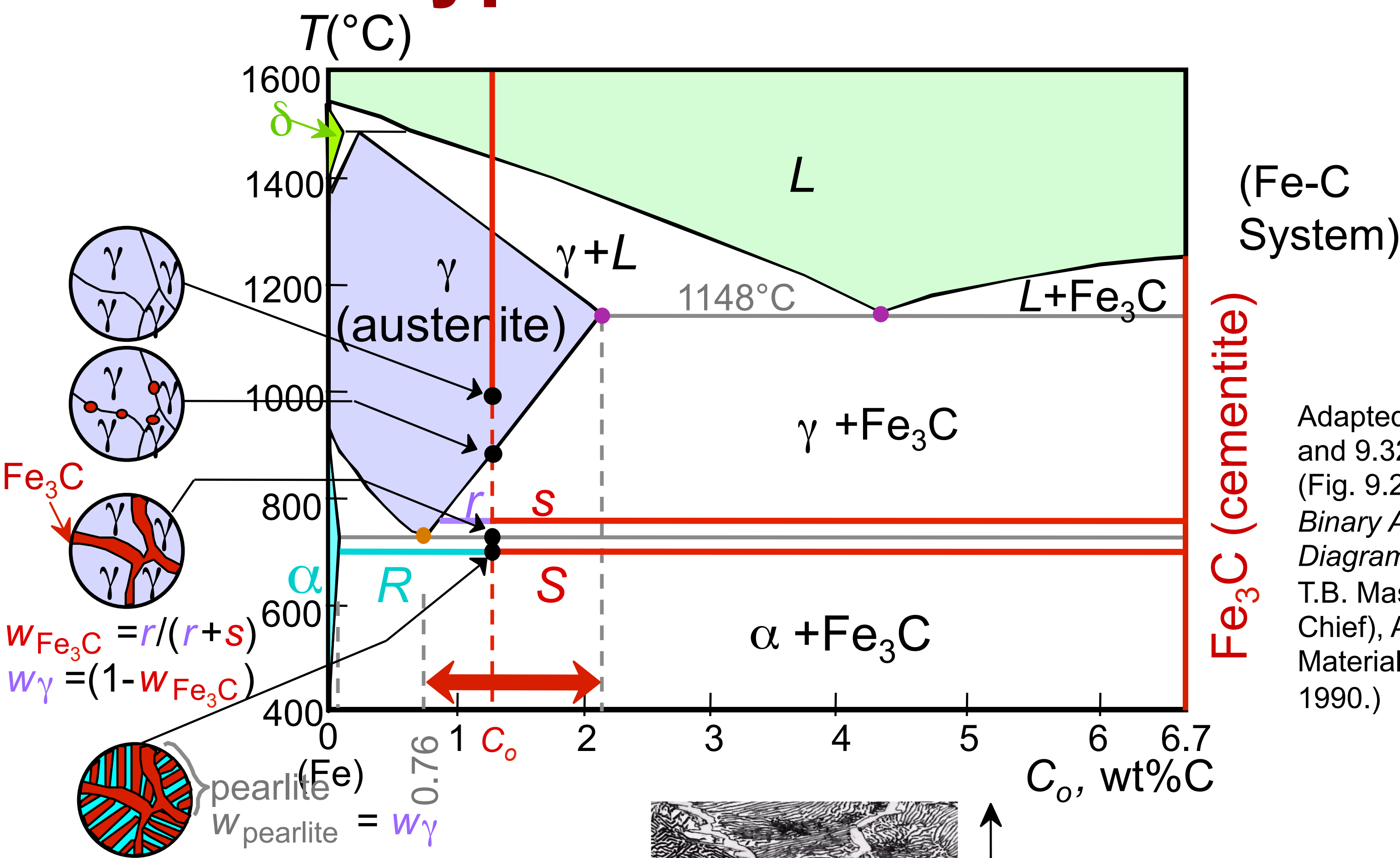
Hypoeutectoid Steel



Adapted from Figs. 9.24 and 9.29, *Callister 7e*. (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 7e*.

Hypereutectoid Steel



Adapted from Figs. 9.24 and 9.32, *Callister 7e*. (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 7e*.

Example: Phase Equilibria

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

a) composition of Fe_3C and ferrite (α)

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

c) the amount of pearlite and proeutectoid ferrite (α)

Chapter 9 – Phase Equilibria

Solution: a) composition of Fe_3C and ferrite (α)

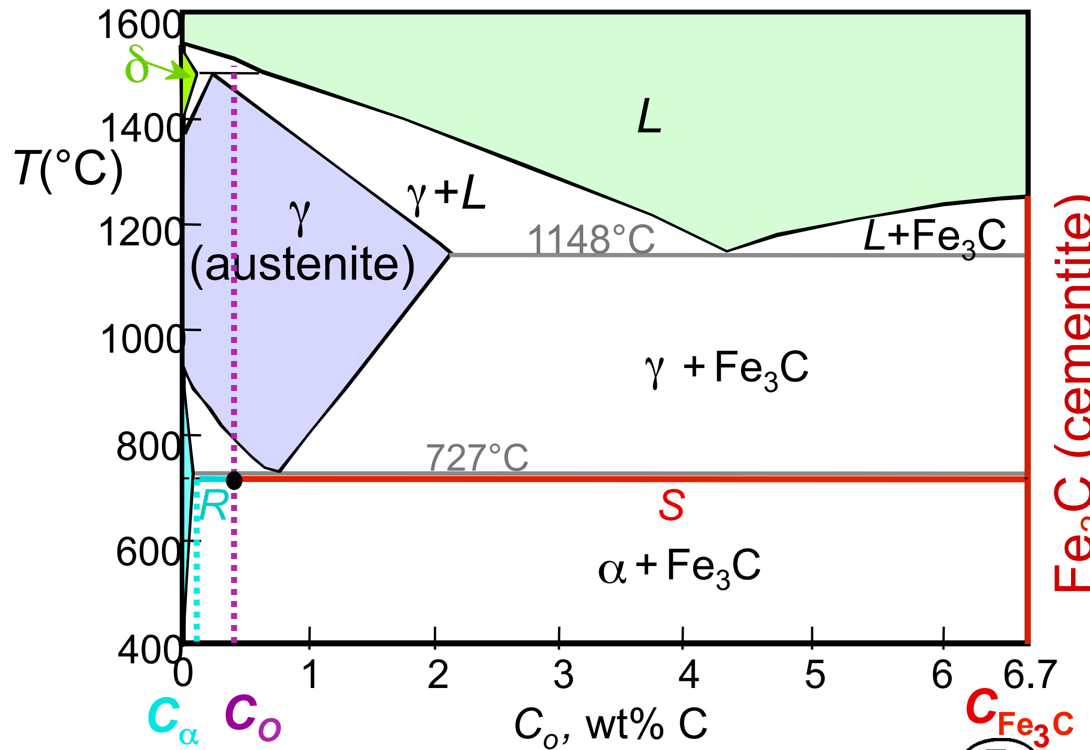
b) the amount of carbide (cementite) in grams that forms per 100 g of steel

$C_O = 0.40$ wt% C
$C_\alpha = 0.022$ wt% C
$C_{Fe_3C} = 6.70$ wt% C

$$\frac{Fe_3C}{Fe_3C + \alpha} = \frac{C_o - C_\alpha}{C_{Fe_3C} - C_\alpha} x100$$

$$= \frac{0.4 - 0.022}{6.7 - 0.022} x\,100 = 5.7g$$

$Fe_3C = 5.7$ g
$\alpha = 94.3$ g



Chapter 9 – Phase Equilibria

c. the amount of pearlite and proeutectoid ferrite (α)

note: amount of pearlite = amount of γ just above T_E

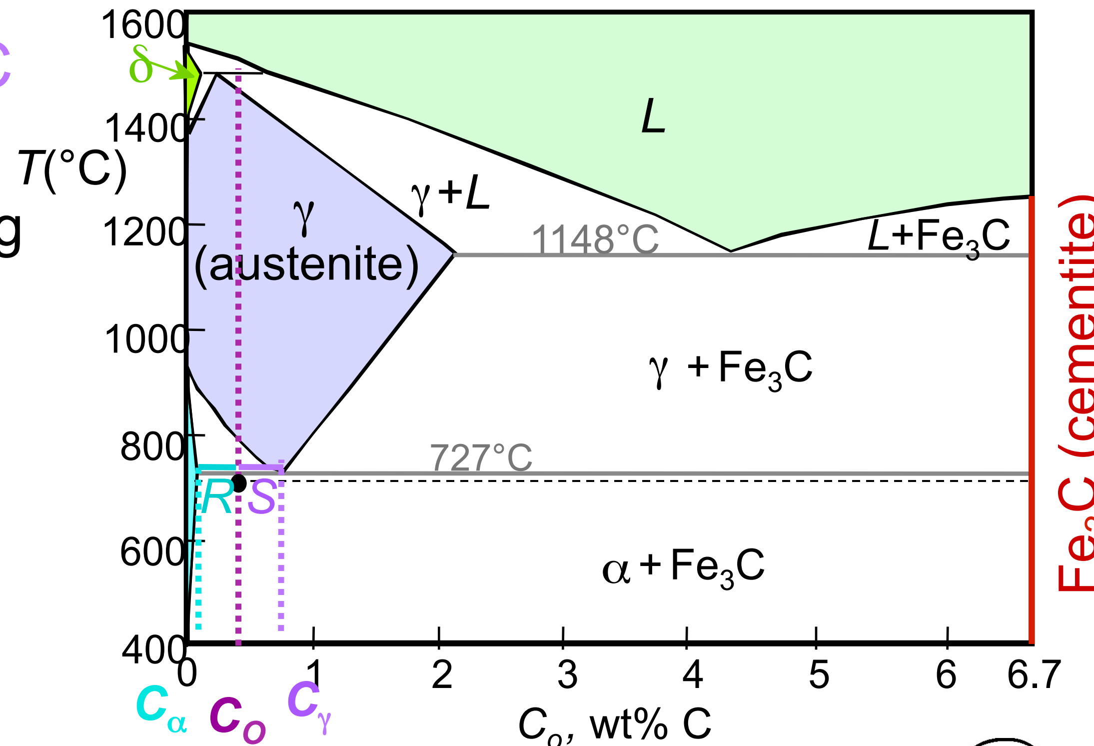
C_o = 0.40 wt% C

C_α = 0.022 wt% C

$C_{pearlite}$ = C_γ = 0.76 wt% C

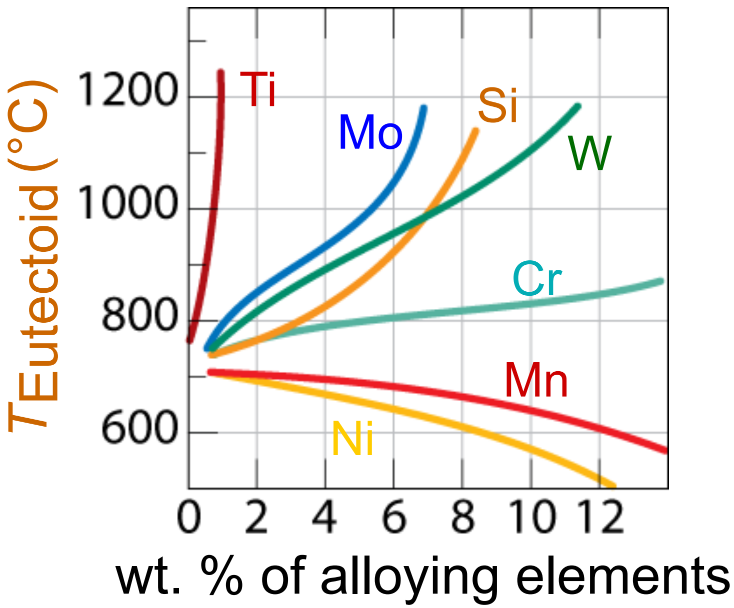
$$\frac{\gamma}{\gamma + \alpha} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha} \times 100 = 51.2 \text{ g}$$

pearlite = 51.2 g
proeutectoid α = 48.8 g



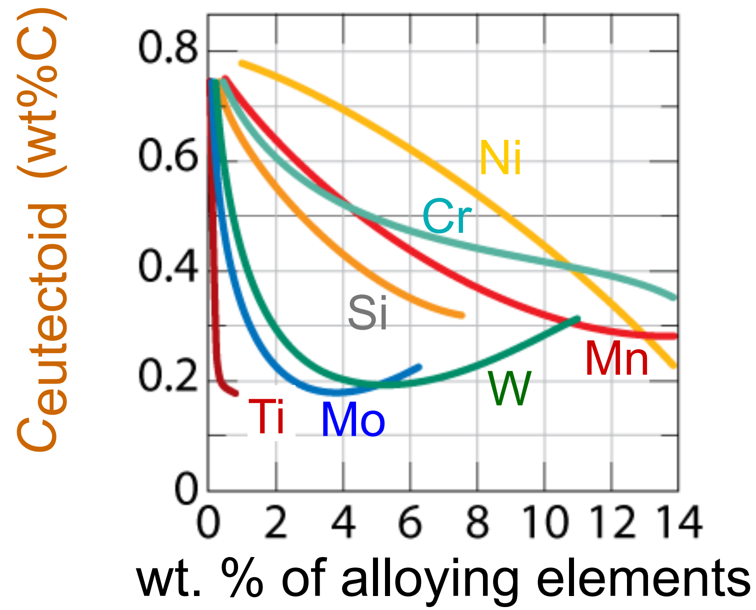
Alloying Steel with More Elements

- $T_{eutectoid}$ 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.)

- $C_{eutectoid}$ changes:



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.)

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: