Phase Diagrams
Binary Eutectoid Systems
and
Fe-C phase Diagram

What is 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

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

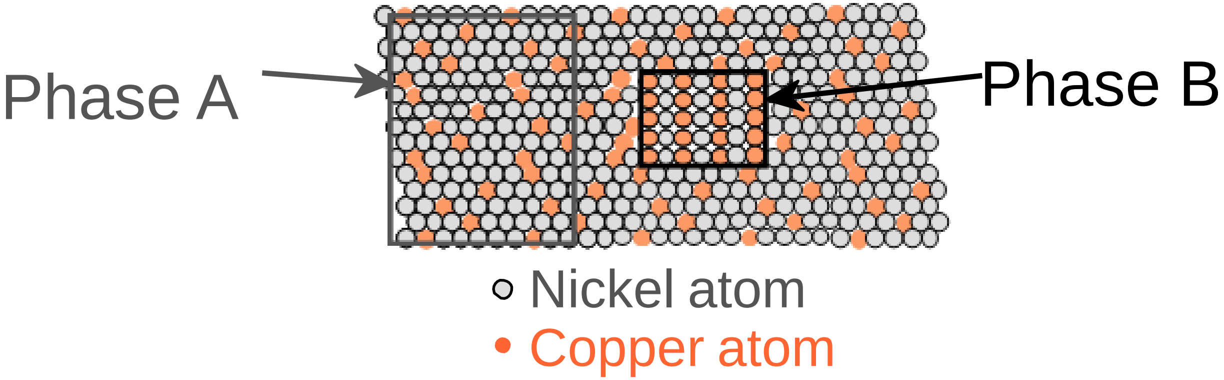
ISSUES TO ADDRESS...

- When we combine two elements...

  what equilibrium state do we get?

- In particular, if we specify...

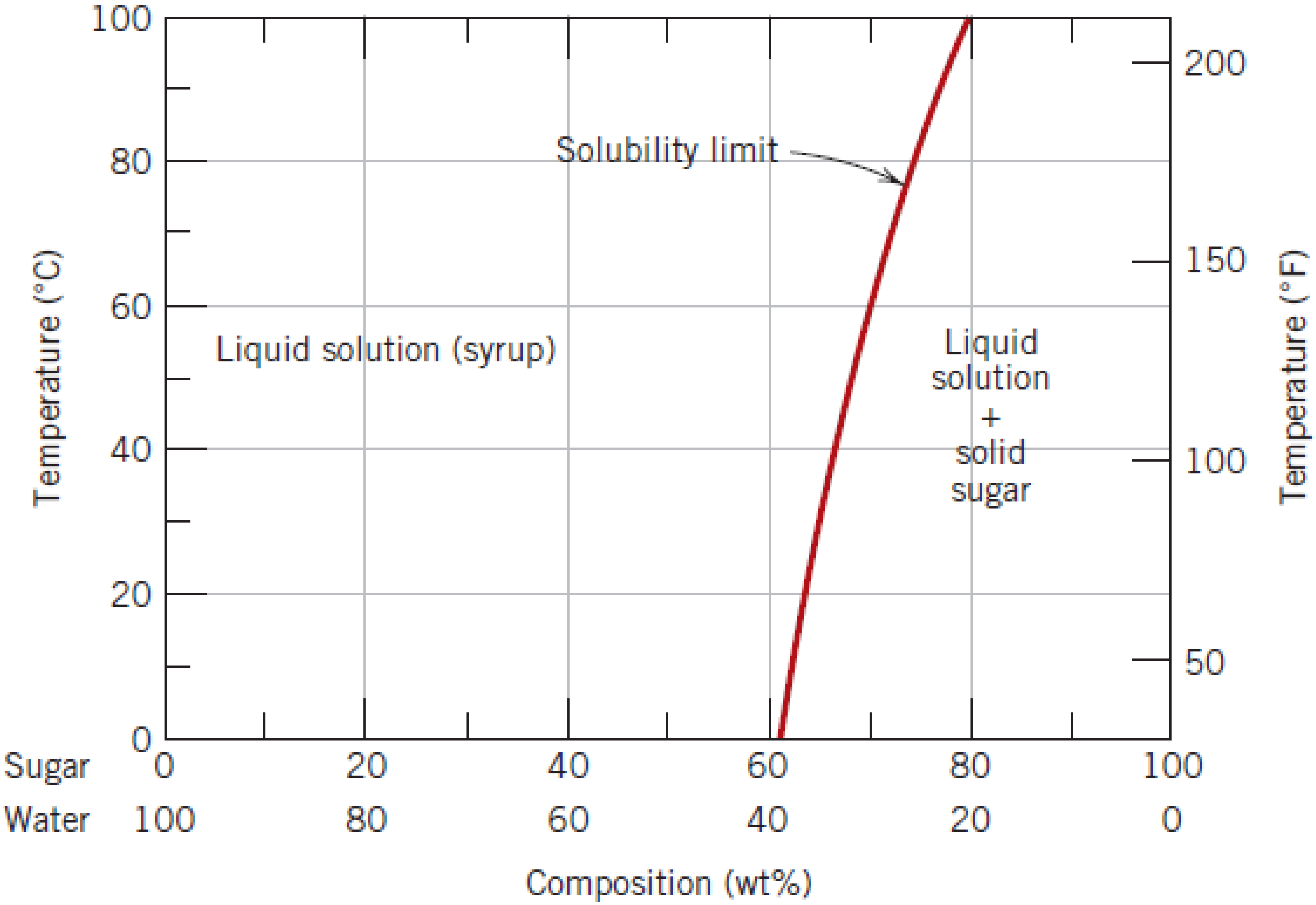
--a composition (e.g., wt% Cu - wt% Ni), and
--a temperature (*T*)
then...
How many phases do we get?
What is the composition of each phase? How much of each phase do we get?



Solubility Limit

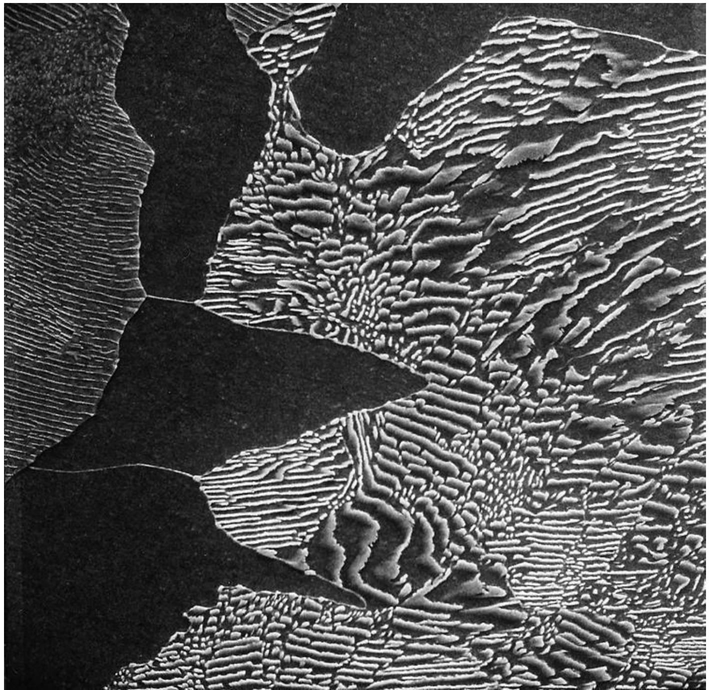
- At some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution, which is called as Solubility Limit
- The addition of solute in excess of this solubility limit results in the formation of another compound that has a distinctly different composition
- This solubility limit depends on the temperature

Solubility Limit Sugar-Water



Microstructure

- the structure of a prepared surface of material as revealed by a microscope above **25×** magnification
- The microstructure of a material can strongly influence properties such as strength, toughness, ductility, hardness, corrosion resistance, high/low temperature behavior, wear resistance, etc



Components and Phases

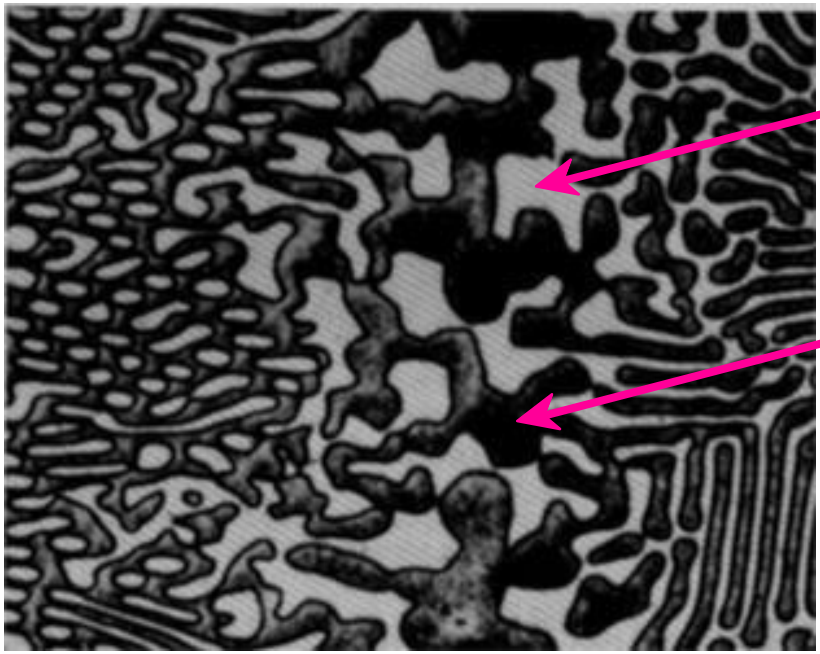
- **Components**:

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



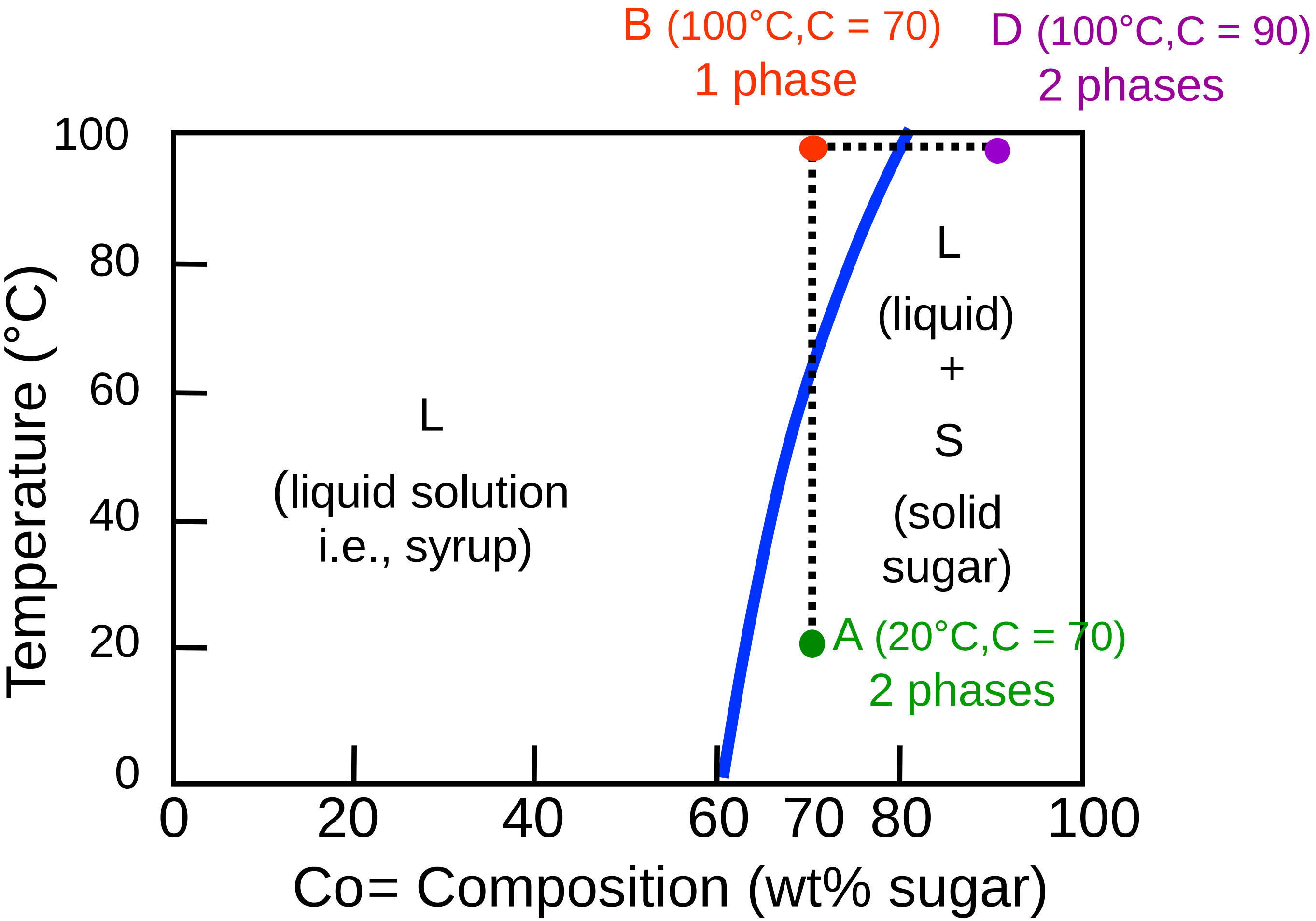
β (lighter phase)

α (darker phase)

Effect of Temperature T & Composition Co

- Altering T can change # of phases: path A to B.
- Altering C can change # of phases: path B to D.

water-
sugar
system



Binary Phase Diagrams

- A phase diagram in which temperature and composition are variable parameters, and pressure is held constant—normally 1atm
- Binary phase diagrams are maps that represent the relationships between temperature and the compositions and quantities of phases at equilibrium, which influence the microstructure of an alloy.
- Many microstructures develop from phase transformations, the changes that occur when the temperature is altered

Phase Equilibria

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

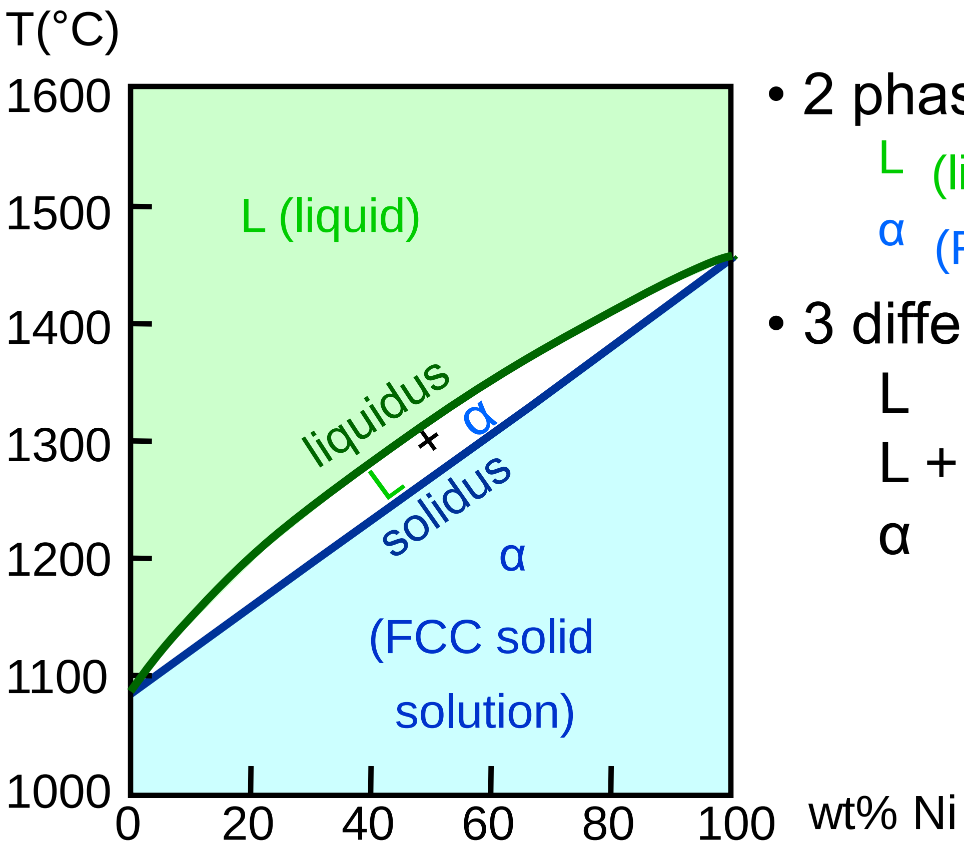
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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 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

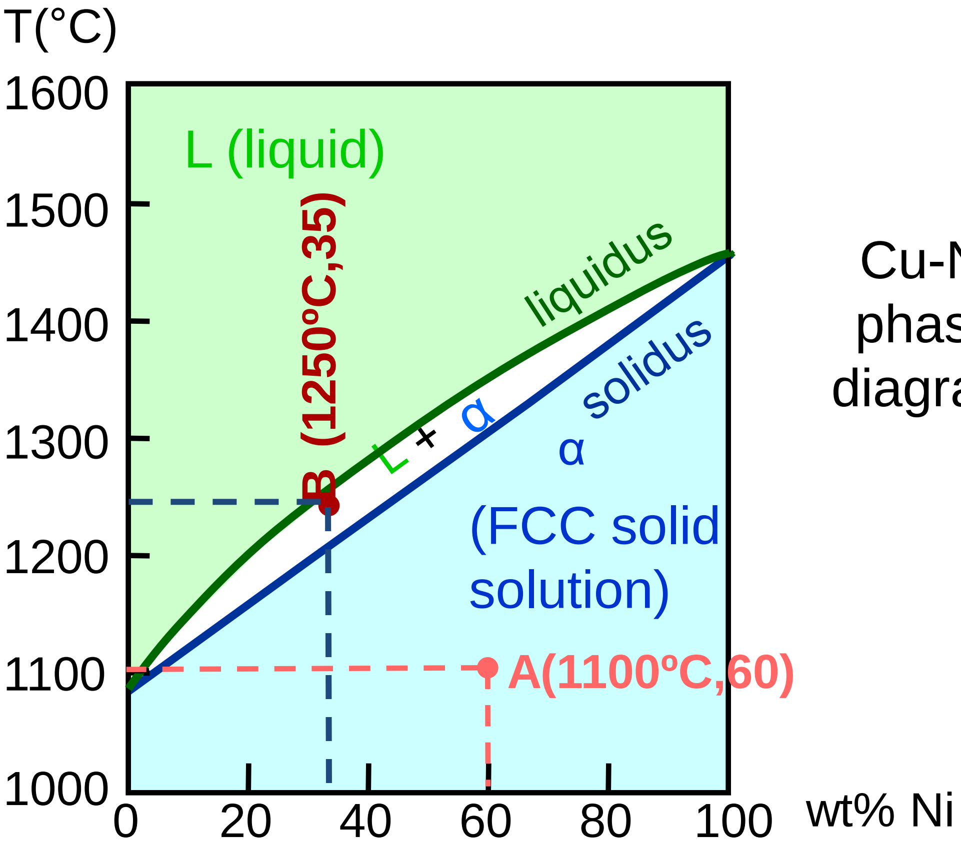
Phase Diagrams:
Determination of phase(s) present

- 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



Cu-Ni phase diagram

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

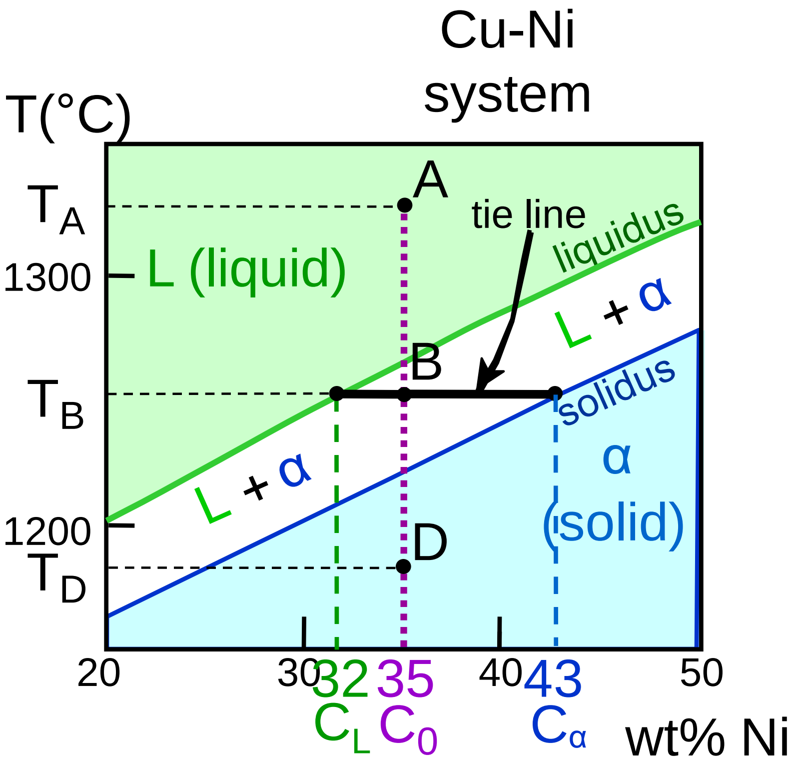
$C_\alpha = C_0$ (= 35 wt% Ni)

At T_B = 1250°C:

Both α and L present

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

$C_\alpha = C_{\text{solidus}}$ (= 43 wt% Ni)



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

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

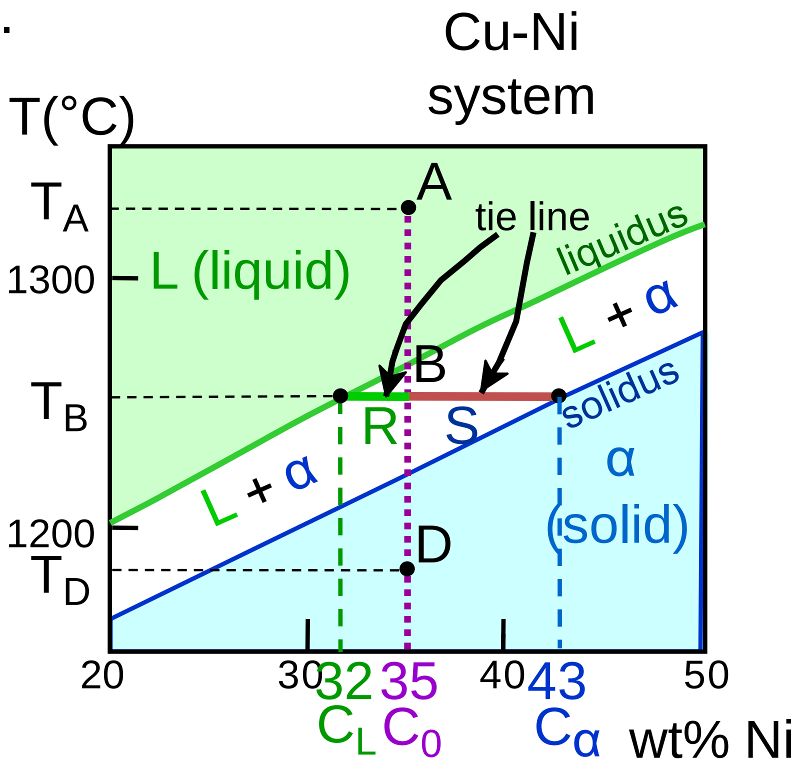
At T_D : Only Solid (α) present

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

At T_B : Both α and L present

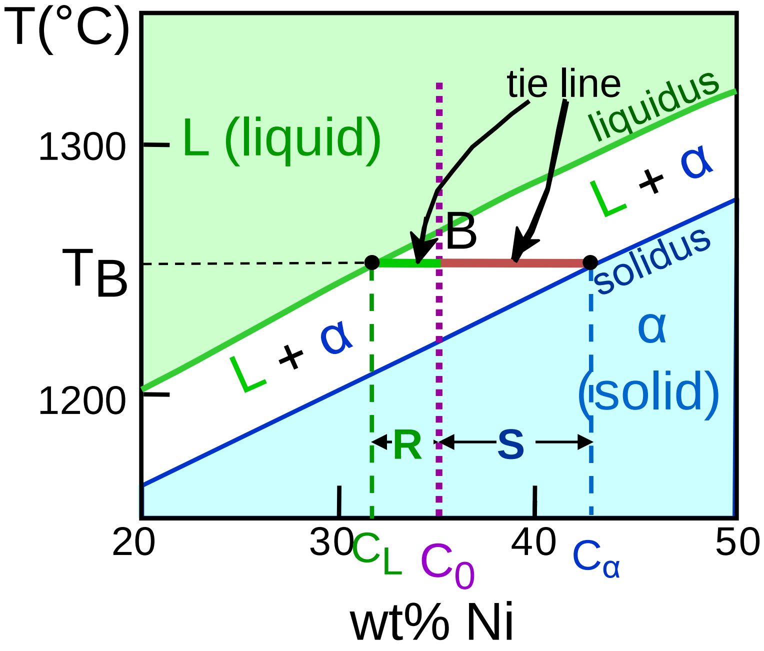
$$W_L = \frac{S}{R + S} = \frac{43 - 35}{43 - 32} = 0.73$$

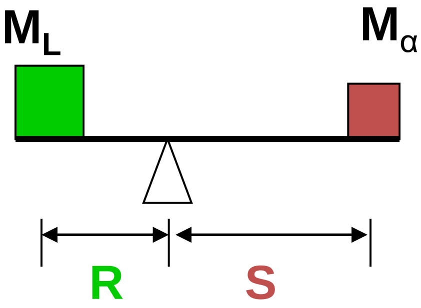
$$W_\alpha = \frac{R}{R + S} = 0.27$$



The Lever Rule

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





$$M_\alpha \text{ x } S = M_L \text{ x } R$$

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

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

Ex: Cooling of a Cu-Ni Alloy

- Phase diagram:
  Cu-Ni system.

System is:

--binary

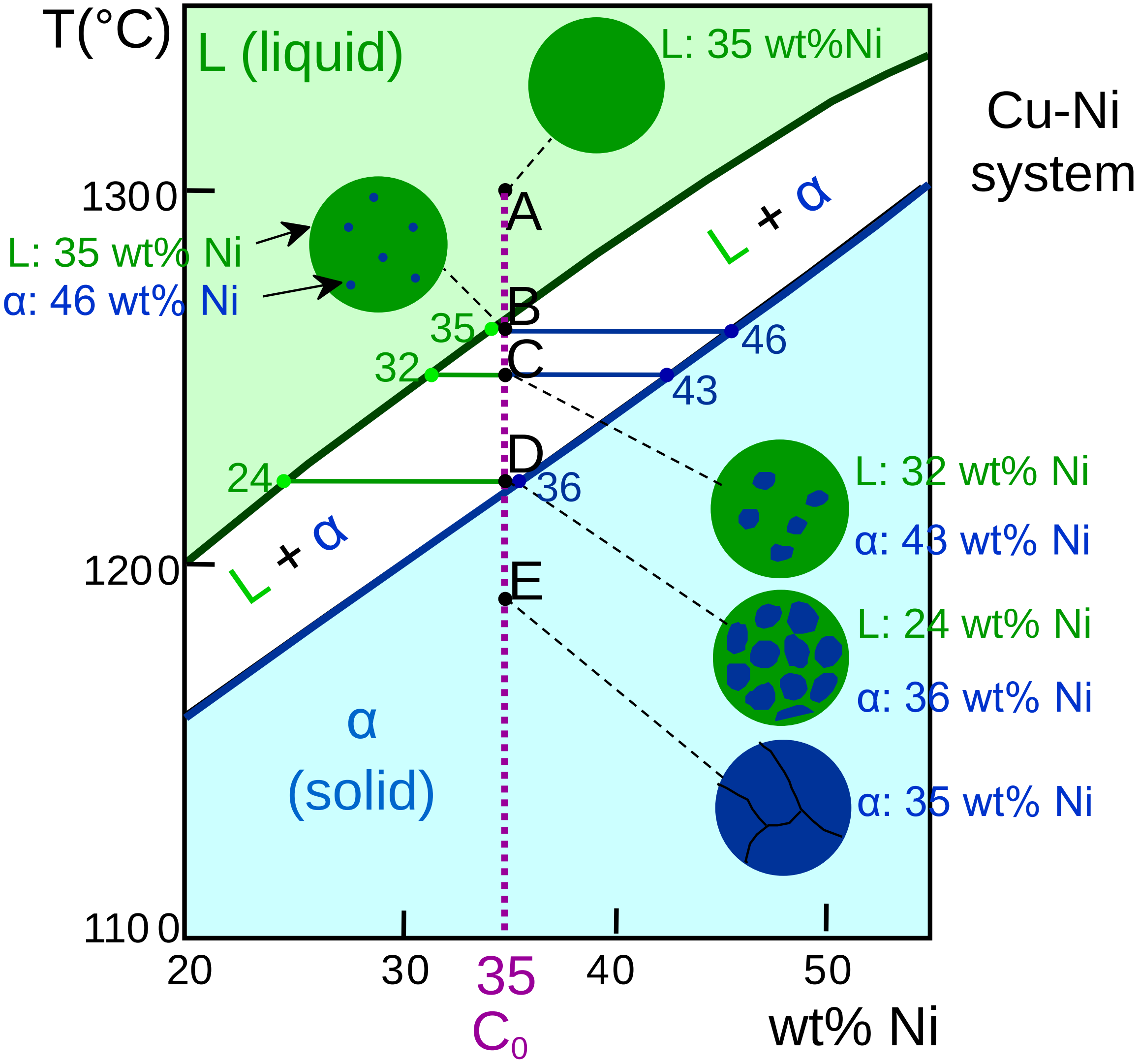
i.e., 2 components:

Cu and Ni.

-isomorphous

i.e., complete solubility of one component in another; a phase field extends from 0 to 100 wt% Ni.

Consider
microstuctural changes that accompany the cooling of a
C_0 = 35 wt% Ni alloy



Equilibrium Cooling

- (between the liquidus and solidus lines): With continued slow cooling, both compositions and relative amounts of each of the phases will change.
- The compositions of the liquid and α–phases will follow the liquidus and solidus lines, respectively.
- Furthermore, the fraction of the α–phase will increase with continued cooling.
- The overall alloy composition remains unchanged
- The final product (upon crossing the solidus line) has a uniform composition in a polycrystalline α–phase solid solution.
- Subsequent cooling will produce no microstructural or composition changes.

Nonequilibrium Cooling

- Slow cooling: readjustment in the compositions of the liquid and solid phases with changes in temperatures
  - Diffusion in both solid and liquid phases and also across the solid-liquid interface.
  - Diffusion is a time-dependent phenomenon
- In virtually all practical solidification situations, cooling rates are much too rapid to allow these compositional readjustments and maintenance of equilibrium.

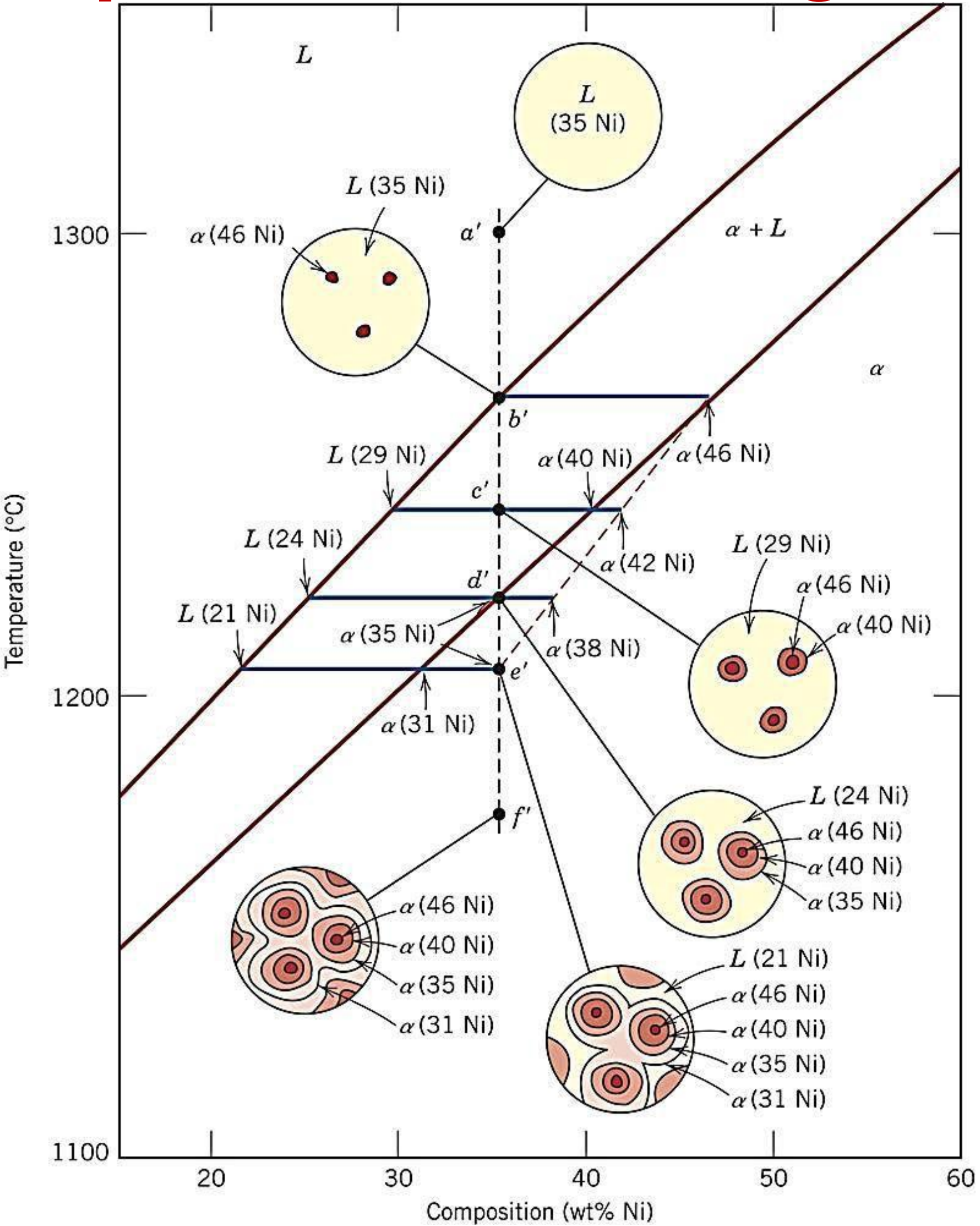
Nonequilibrium Cooling

- The average composition of the solid α–grains that have formed would be some volume weighted average composition.

- As a result, the distribution of the two elements within the grains is nonuniform: **Segregation**

- Segregation: concentration gradients are established across the grains.

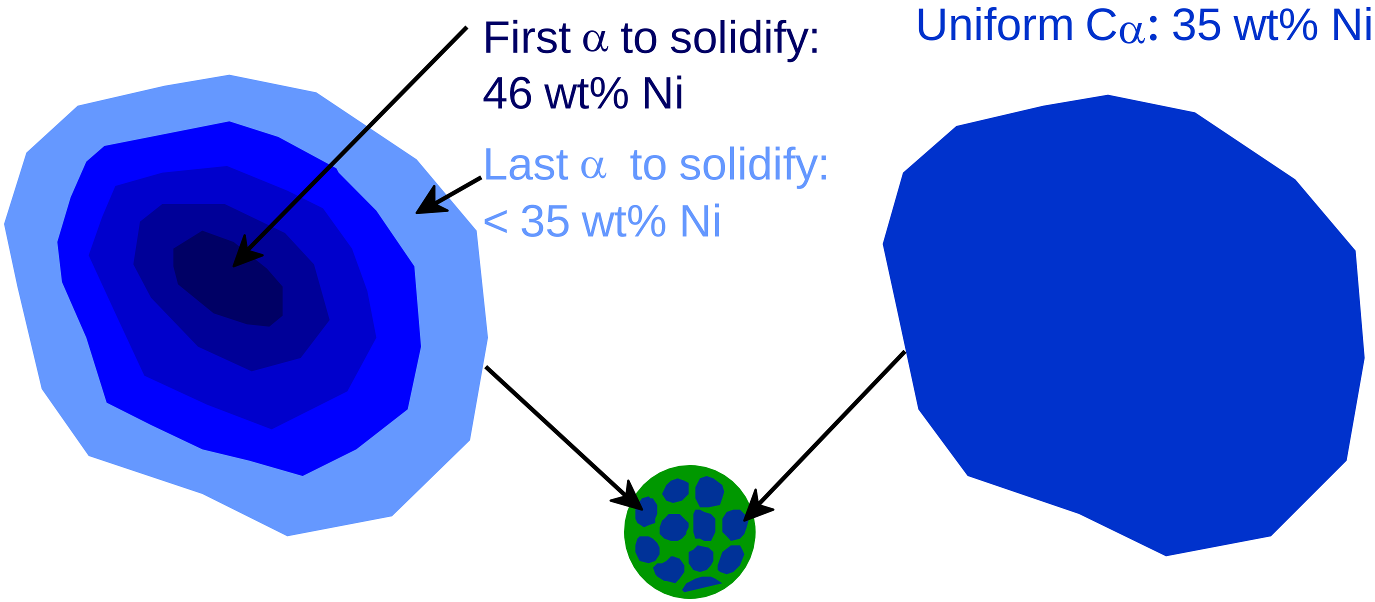
- **Cored Structure:** the centre of each grain, which is the first part to freeze, is rich in the high-melting element.



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



First α to solidify:
46 wt% Ni

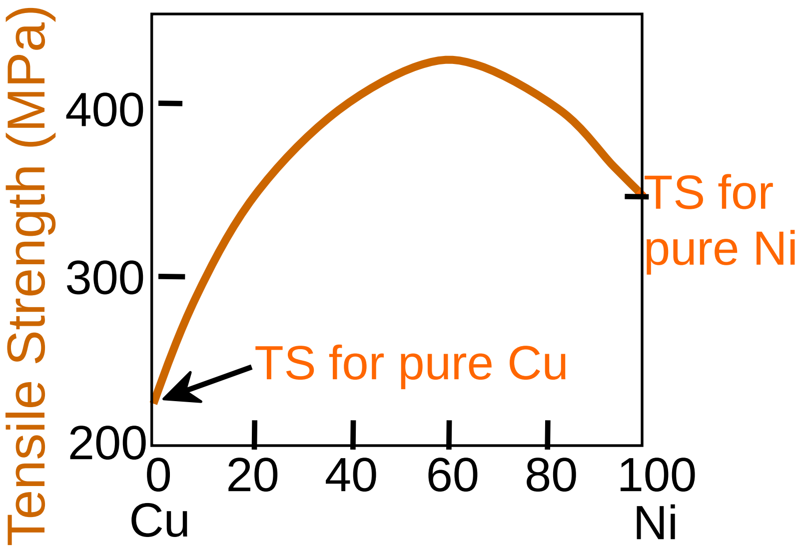
Last α to solidify:
< 35 wt% Ni

Uniform C_α: 35 wt% Ni

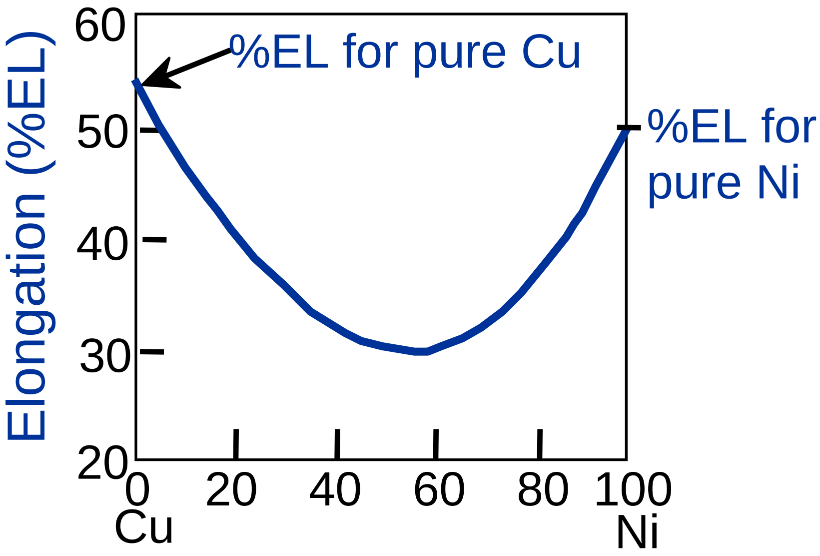
Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

-- Tensile strength (TS)

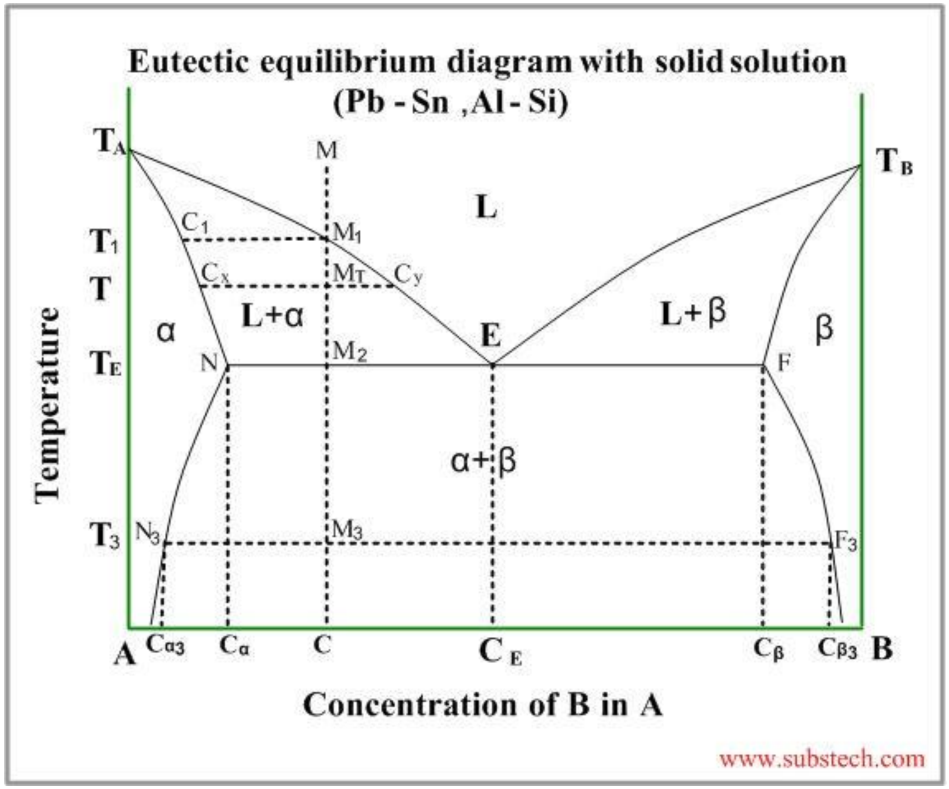


-- Ductility (%EL)



Eutectic System

A eutectic system is a mixture of chemical compounds or elements that has a single chemical composition that solidifies at a lower temperature than any other composition



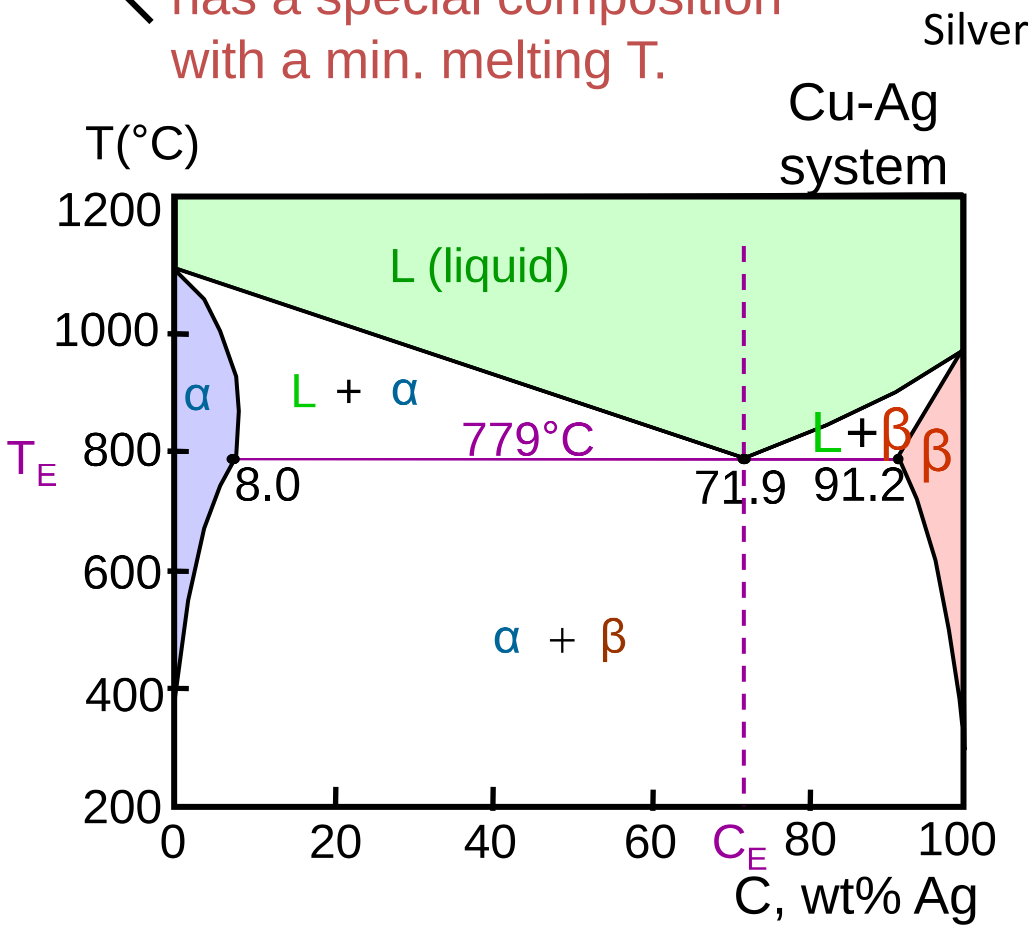
Binary-Eutectic Systems

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 : 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

Lead Tin

- For a **40** wt% Sn-**60** wt% Pb alloy at 150°C, determine:

-- the phases present

Answer: α + β

-- the phase compositions

Answer: $C_\alpha = 11$ wt% Sn

$C_\beta = 99$ wt% Sn

-- the relative amount of each phase

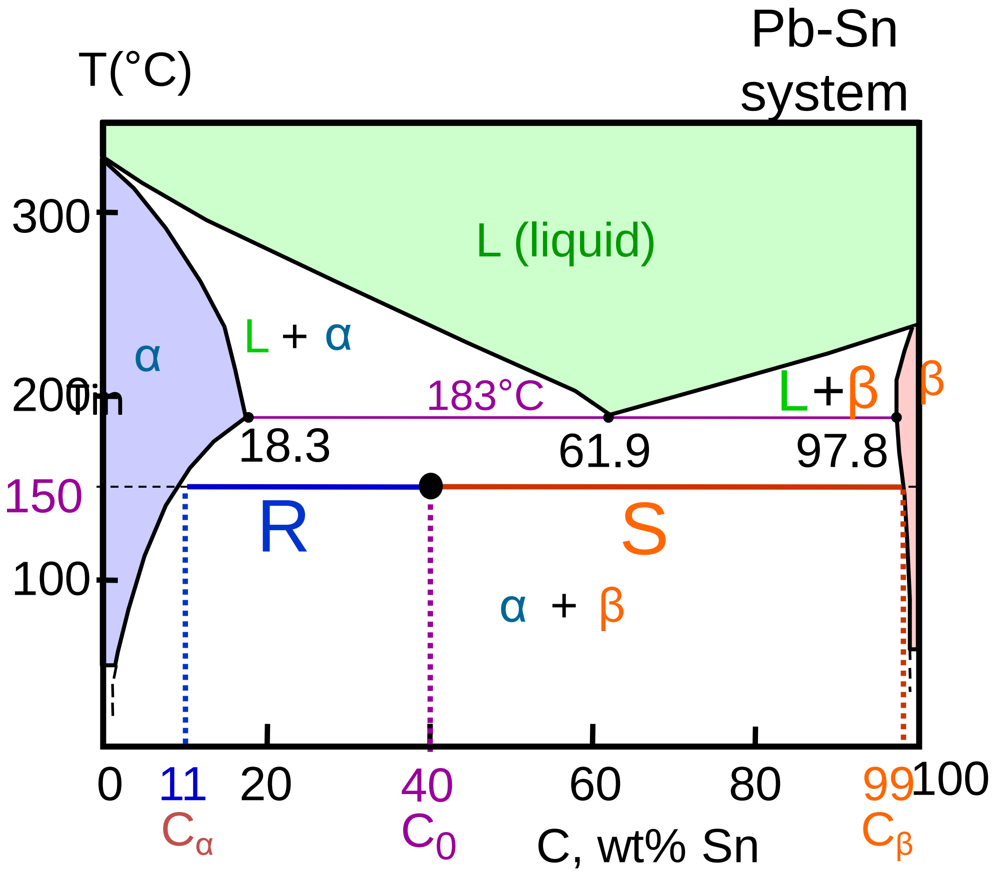
Answer:

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

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

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

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



EX 2: Pb-Sn Eutectic System

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

-- the phases present:

Answer: α + L

-- the phase compositions

Answer: C_α = 17 wt% Sn

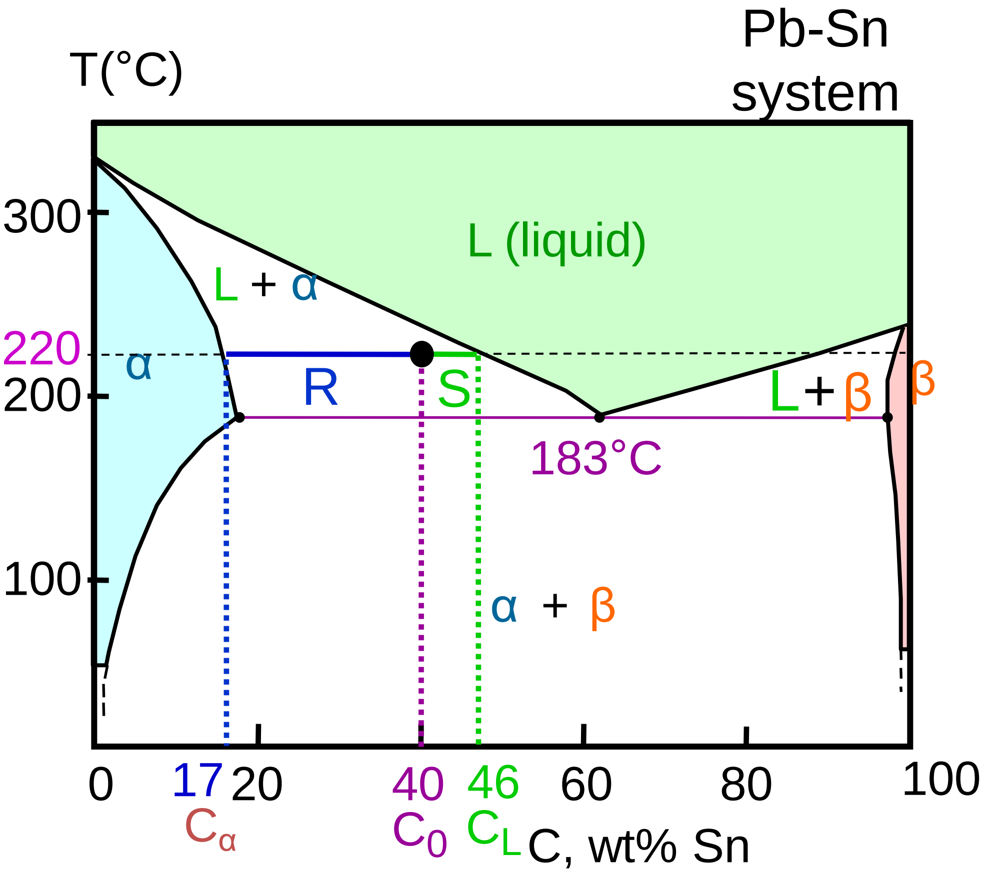
C_L = 46 wt% Sn

-- the relative amount of each phase

Answer:

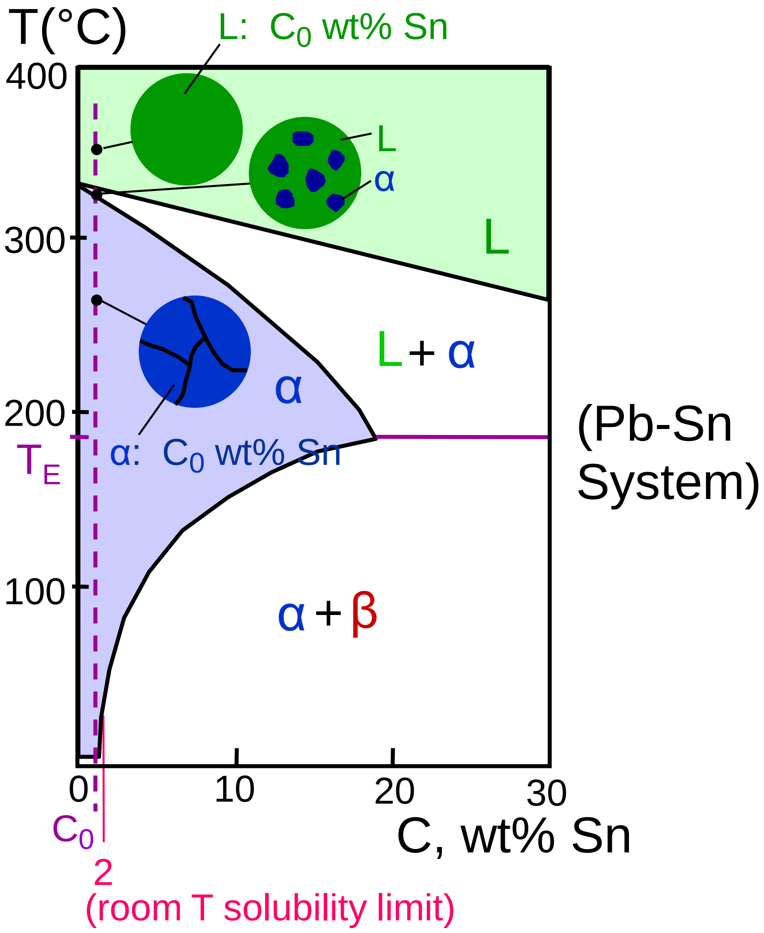
$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 0.21$$

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



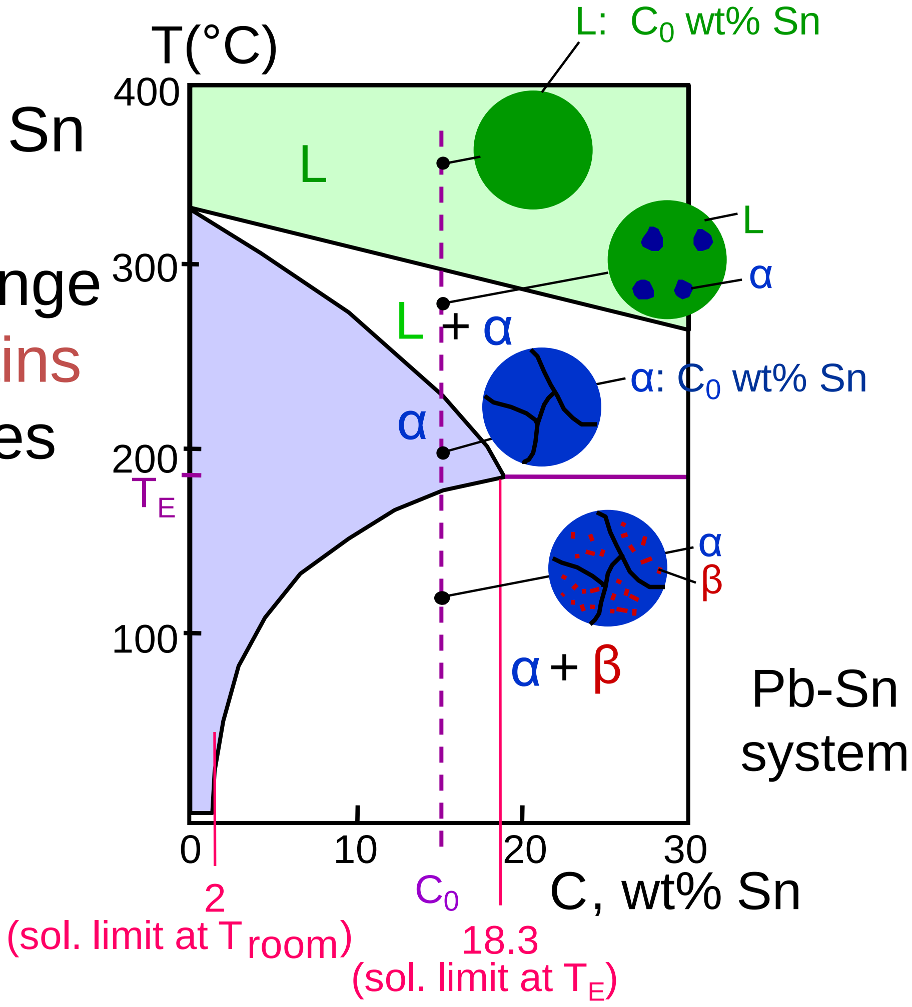
Microstructural Developments in Eutectic Systems I

- For alloys for which
  $C_0 < 2$ wt% Sn
- Result: at room temperature
  - -- polycrystalline with grains of α phase having composition C_0



Microstructural Developments in Eutectic Systems II

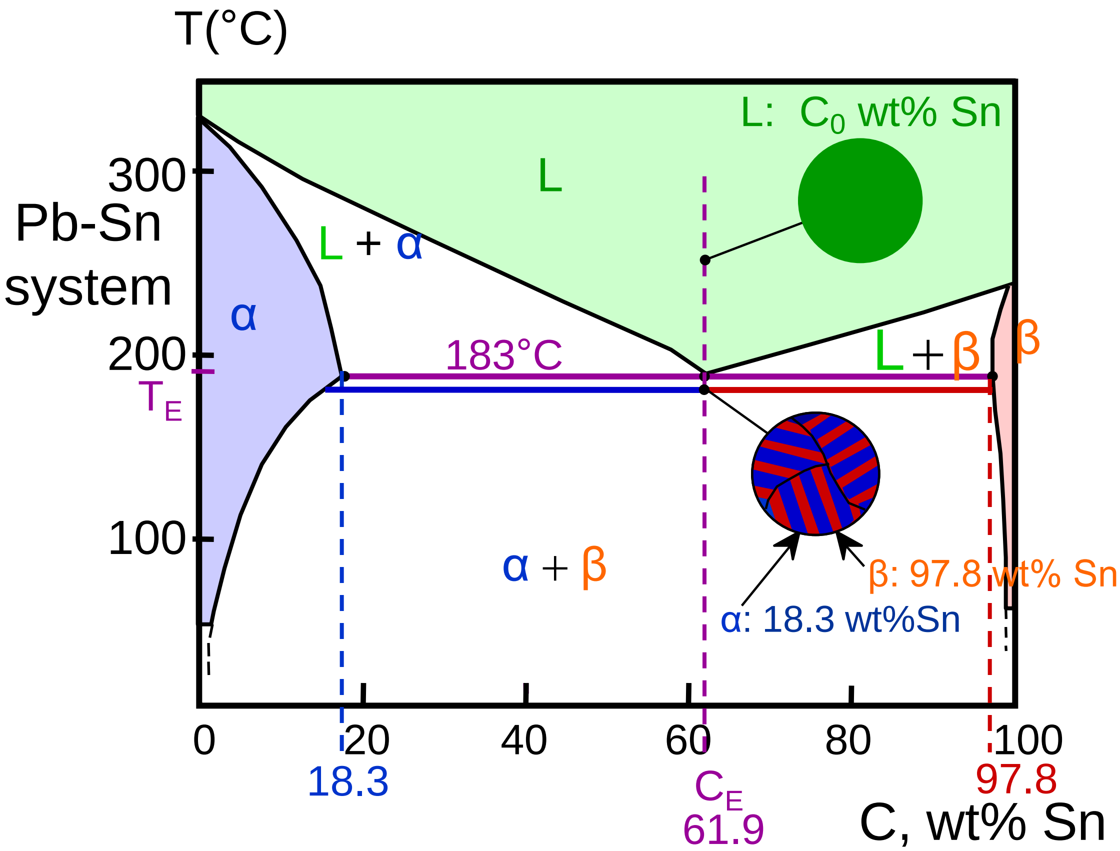
- For alloys for which
  2 wt% Sn < C_0 < 18.3 wt% Sn
- Result:
  at temperatures in α + β range
  -- polycrystalline with α grains
  and small β-phase particles



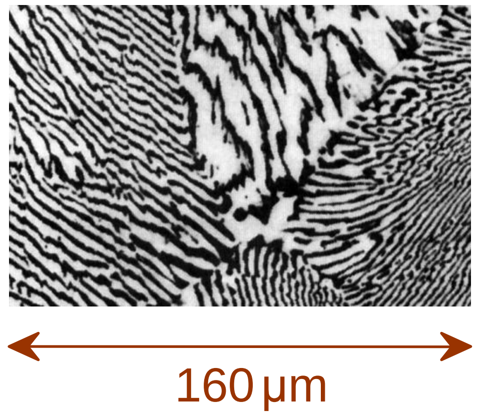
Microstructural Developments in Eutectic Systems III

- For alloy of composition $C_0 = C_E$
- Result: Eutectic microstructure (lamellar structure)

  -- alternating layers (lamellae) of α and β phases.



Micrograph of Pb-Sn eutectic microstructure



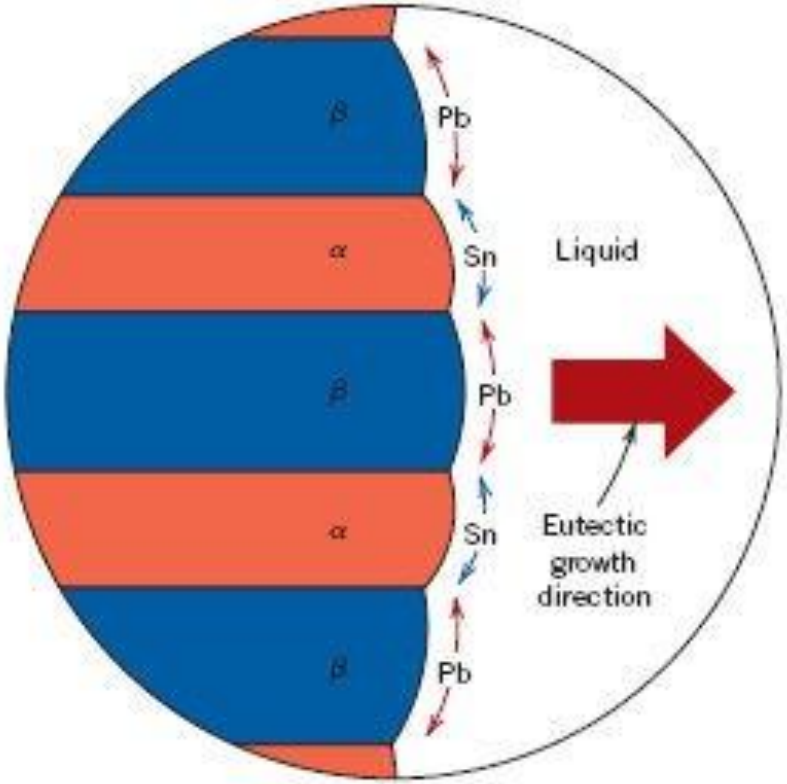
Microstructural Developments in Eutectic Systems III

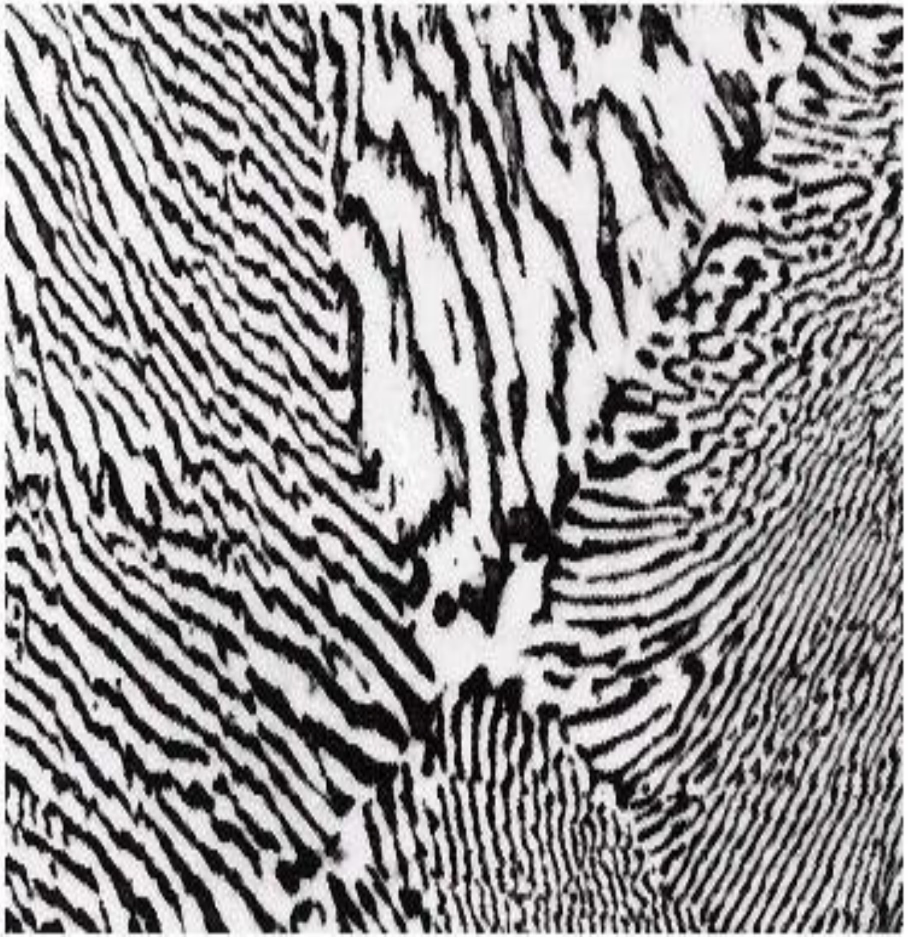
- The microstructure of the solid results from the Eutectic transformation consists of alternating layers (called lamellae) of the α and β phases that form simultaneously during the transformation.

- The microstructure at Eutectic point is called **EUTECTIC STRUCTURE**.

- Subsequent cooling of the alloy form just below the eutectic to room temperature will result in only minor microstructural alterations.

Lamellar Eutectic Structure





Microstructural Developments in Eutectic Systems III

- The α-β layered eutectic growing into and replacing the liquid phase
- The process of redistribution of lead and tin occurs by diffusion in the liquid just ahead of the eutectic-liquid interface.
- The arrows indicate the directions of diffusion of lead and tin atoms; lead atoms diffuse toward the α–phase layers because this α–phase is lead-rich.
- Similarly for the tin-rich phase

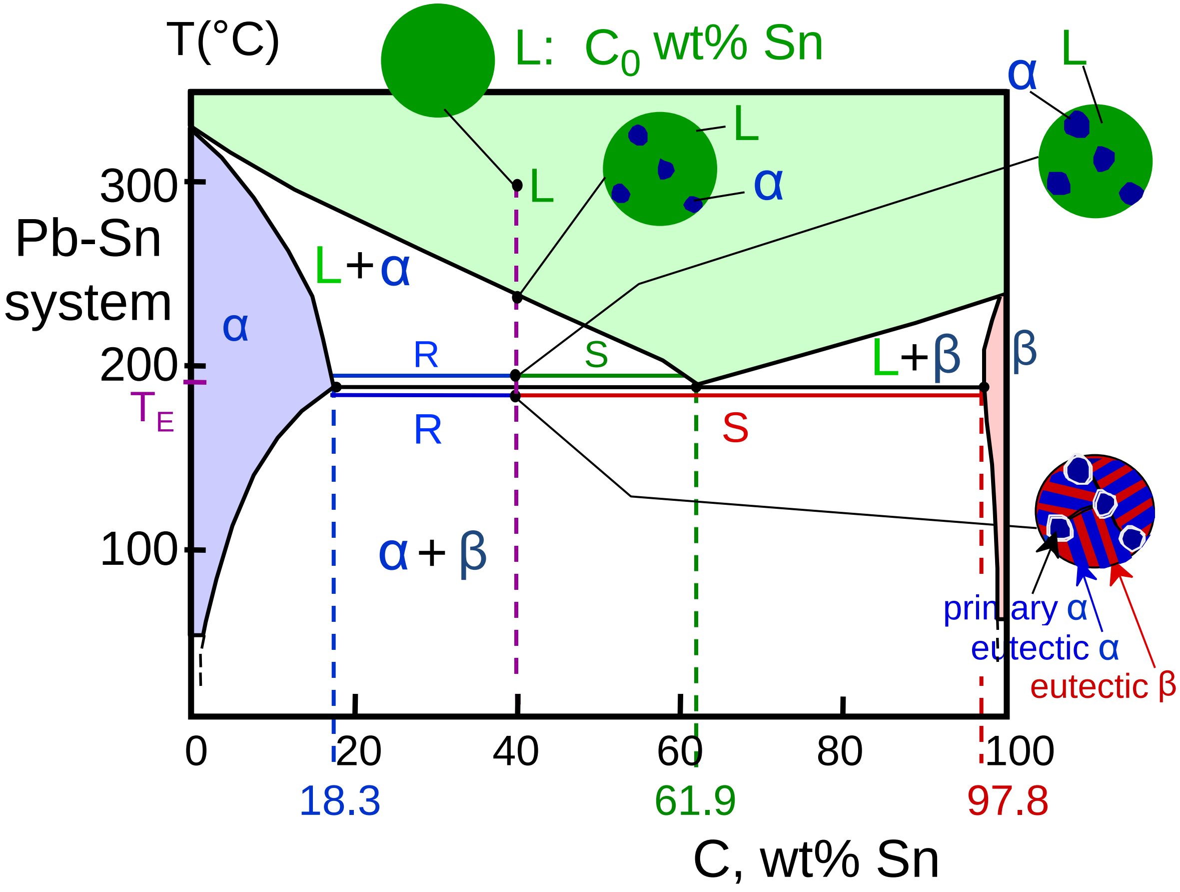
60/40 TIN-LEAD SOLDER

- A familiar example is the 60/40 solder, a low-melting temperature having near-Eutectic compositions.

- An alloy of this composition is completely molten about 185 C, which makes it especially attractive as a low- temperature solder.

Microstructures
in Eutectic Systems (Pb-Sn): IV

- For alloys for which 18.3 wt% Sn < C_0 < 61.9 wt% Sn
- Result: α phase particles and a eutectic microstructure



- Just above T_E :

$C_\alpha = 18.3$ wt% Sn

$C_L = 61.9$ wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.50$$

$$W_L = (1 - W_\alpha) = 0.50$$

- Just below T_E :

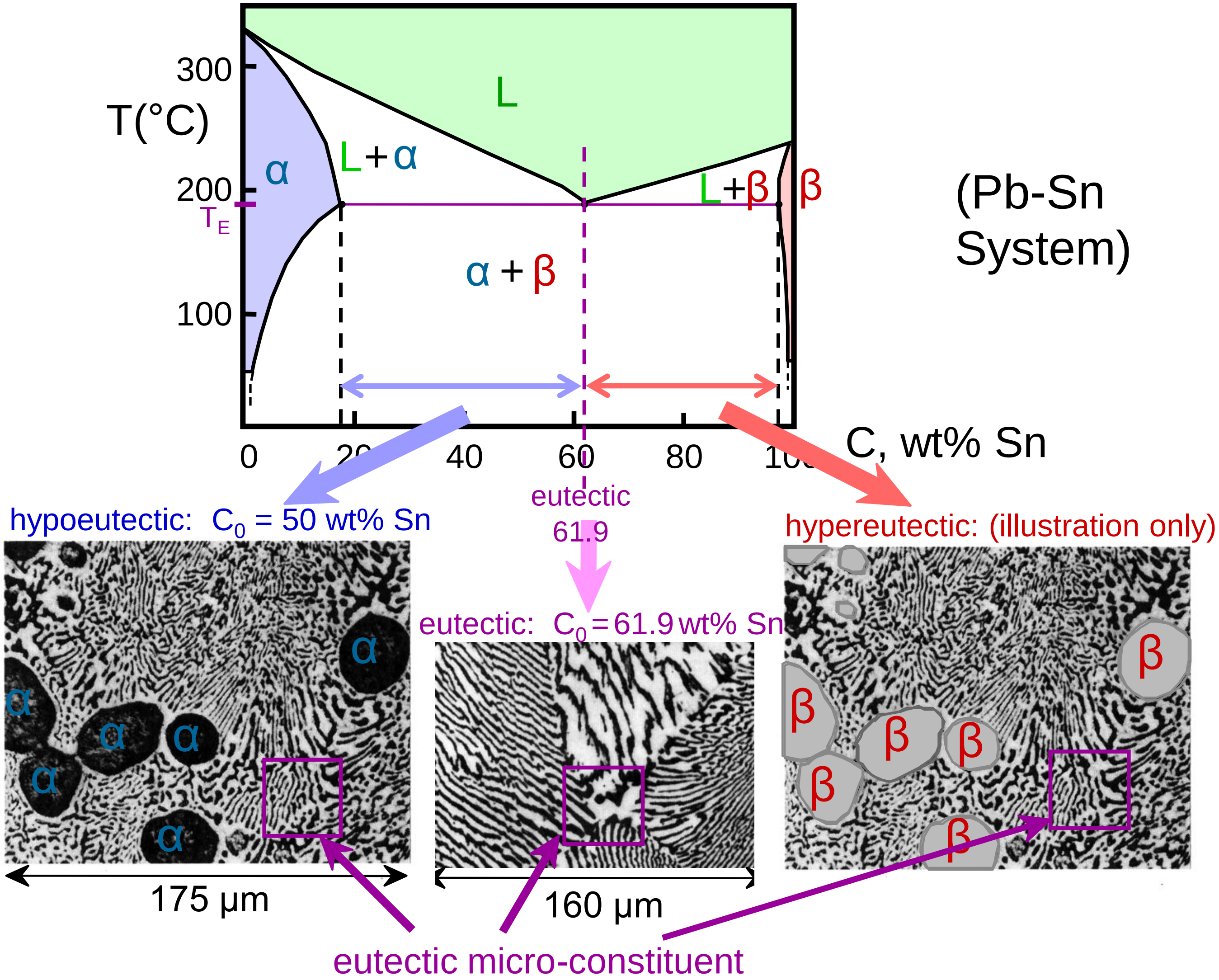
$C_\alpha = 18.3$ wt% Sn

$C_\beta = 97.8$ wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.73$$

$$W_\beta = 0.27$$

Hypoeutectic & Hypereutectic



(Pb-Sn System)

hypoeutectic: C_0 = 50 wt% Sn

eutectic: C_0 = 61.9 wt% Sn

hypereutectic: (illustration only)

eutectic micro-constituent

Microstructural Developments in Eutectic Systems IV

•Insignificant changes will occur with the phase that formed during cooling through the α + *L region.*

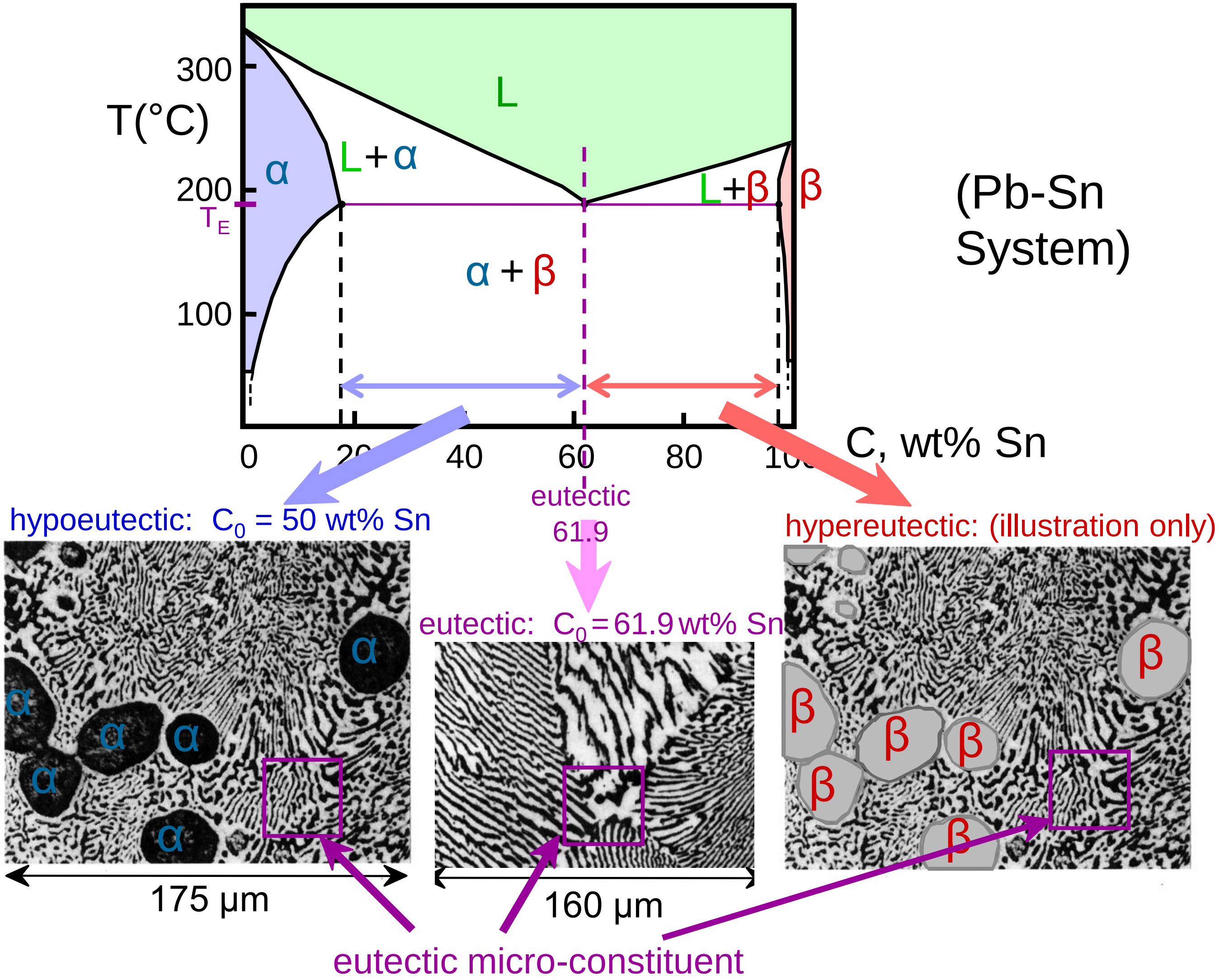
•So the –phase will be present in the eutectic structure and also as the phase that formed while cooling through the α + *L phase field.*

•So there are two **microconstituents**: α and eutectic structures.

•Microconstituent is an element of the microstructure having an identifiable and characteristic structure.

•It is possible to compute the relative amounts of both eutectic and primary microconstituents.

Hypoeutectic & Hypereutectic



(Pb-Sn System)

hypoeutectic: C_0 = 50 wt% Sn

eutectic 61.9

eutectic: C_0 = 61.9 wt% Sn

hypereutectic: (illustration only)

175 μm

160 μm

eutectic micro-constituent

Eutectic, Eutectoid, & Peritectic

- **Eutectic - liquid transforms to two solid phases**

  $L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + \beta$ **(For Pb-Sn, 183^{o}C, 61.9 wt%**

- 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^{o}C, 0.76 wt%C)

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

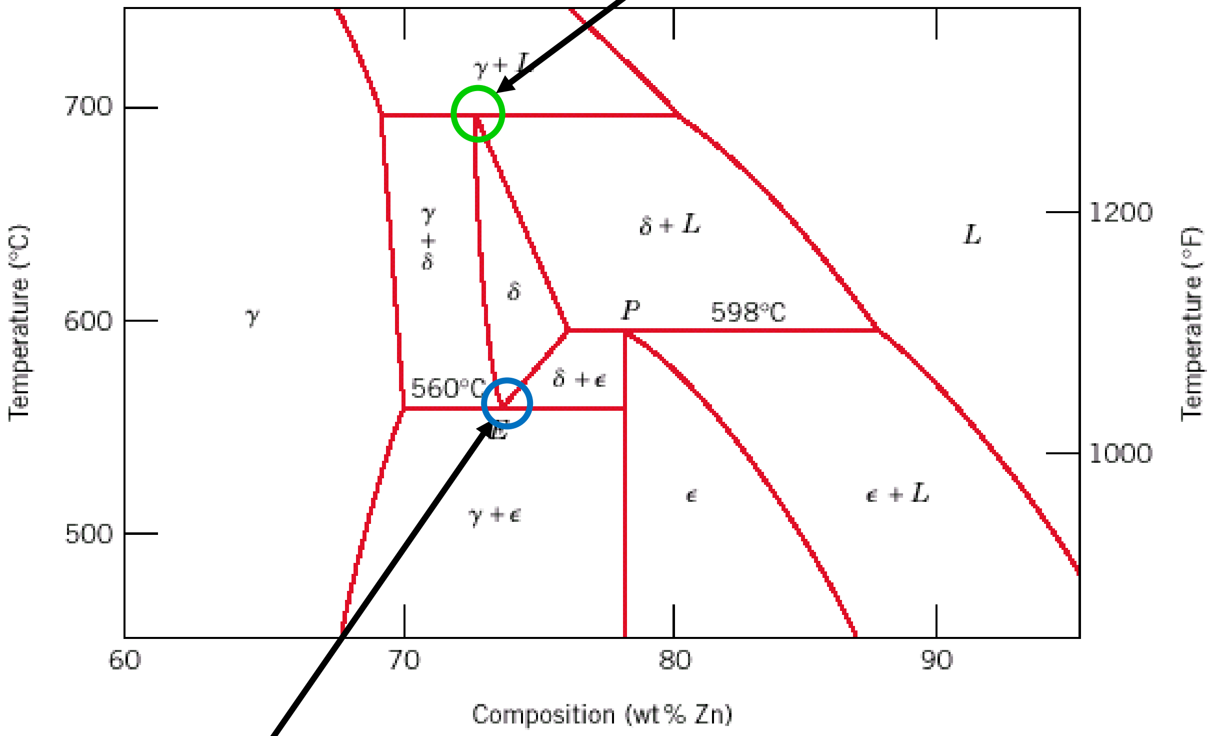
  $S_1 + L \rightleftharpoons S_2$

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

Eutectoid & Peritectic

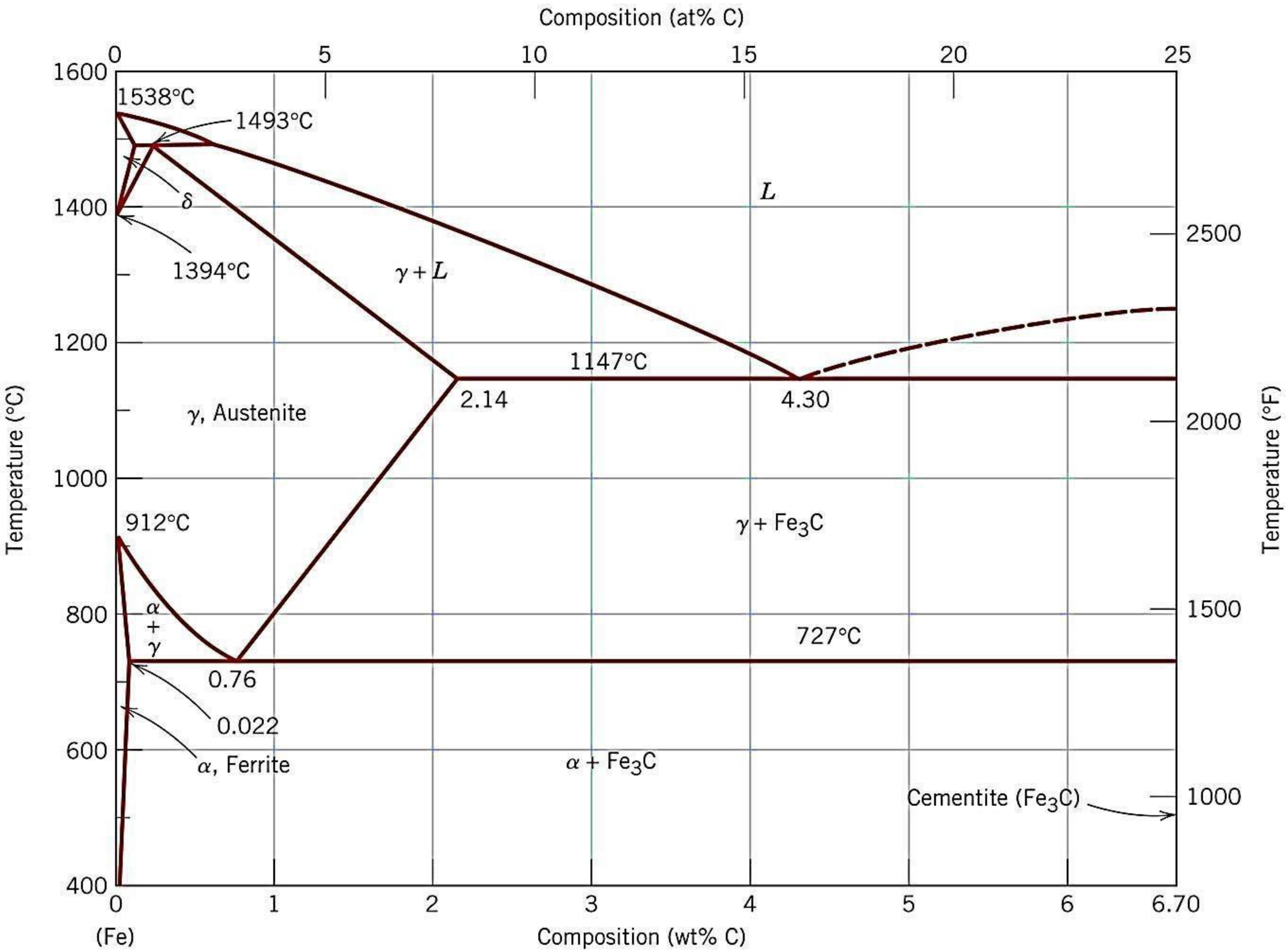
Cu-Zn Phase diagram

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



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

IRON-CARBON (Fe-C) PHASE DIAGRAM



Adapted from Fig. 9.24, *Callister & Rethwisch 8e.*

FERRITE

- **Ferrite** or α-iron has a BCC crystal structure.
- Only a small concentrations of carbon are soluble in α-ferrite (0.022 wt% at 727 ºC).
- Carbon significantly influences the mechanical properties of ferrite even at small concentrations of carbon
- This particular iron-carbon phase is relatively soft, may be magnetic at temperatures below 768 ºC

AUSTENITE

- At 912 ºC, ferrite experiences a polymorphic transformation to FCC **austenite** (or γ–iron).
- γ–phase of iron alloyed with carbon is not stable below 727 ºC.
- The maximum solubility of carbon in austenite is 2.14 wt%, occurs at 1147 ºC.

- This solubility is approximately 100 times greater than the maximum for BCC ferrite, because the FCC interstitial positions are larger.

- Austenite is nonmagnetic.

δ–FERRITE

- At 1394 ºC, the austenite reverts back to a BCC phase known as δ–ferrite, which finally melts at 1538 ºC.

- δ–ferrite is virtually the same as α–ferrite, except for the range of temperatures over which each exists.

- Because δ–ferrite is stable only at relatively high temperatures, it will not be discussed further.

CEMENTITE

- The composition axis in Figure (Fe- Fe_3C phase diagram) extends only to 6.70 wt% C: the intermediate compound iron carbide or **cementite** (Fe_3C): represented by a vertical line on the phase diagram.

- In practice, all steels and cast irons have carbon contents less than 6.7 wt% C.

- Cementite forms when the solubility limit of carbon in α–ferrite is exceeded below 727 ºC (α coexists with Fe_3C).

- Fe_3C also coexists with γ–phase between 727 and 1147 ºC.

- Cementite is very hard and brittle.

FERROUS ALLOYS

•Are those in which iron is the prime component, but carbon as well as other alloying elements may be present.

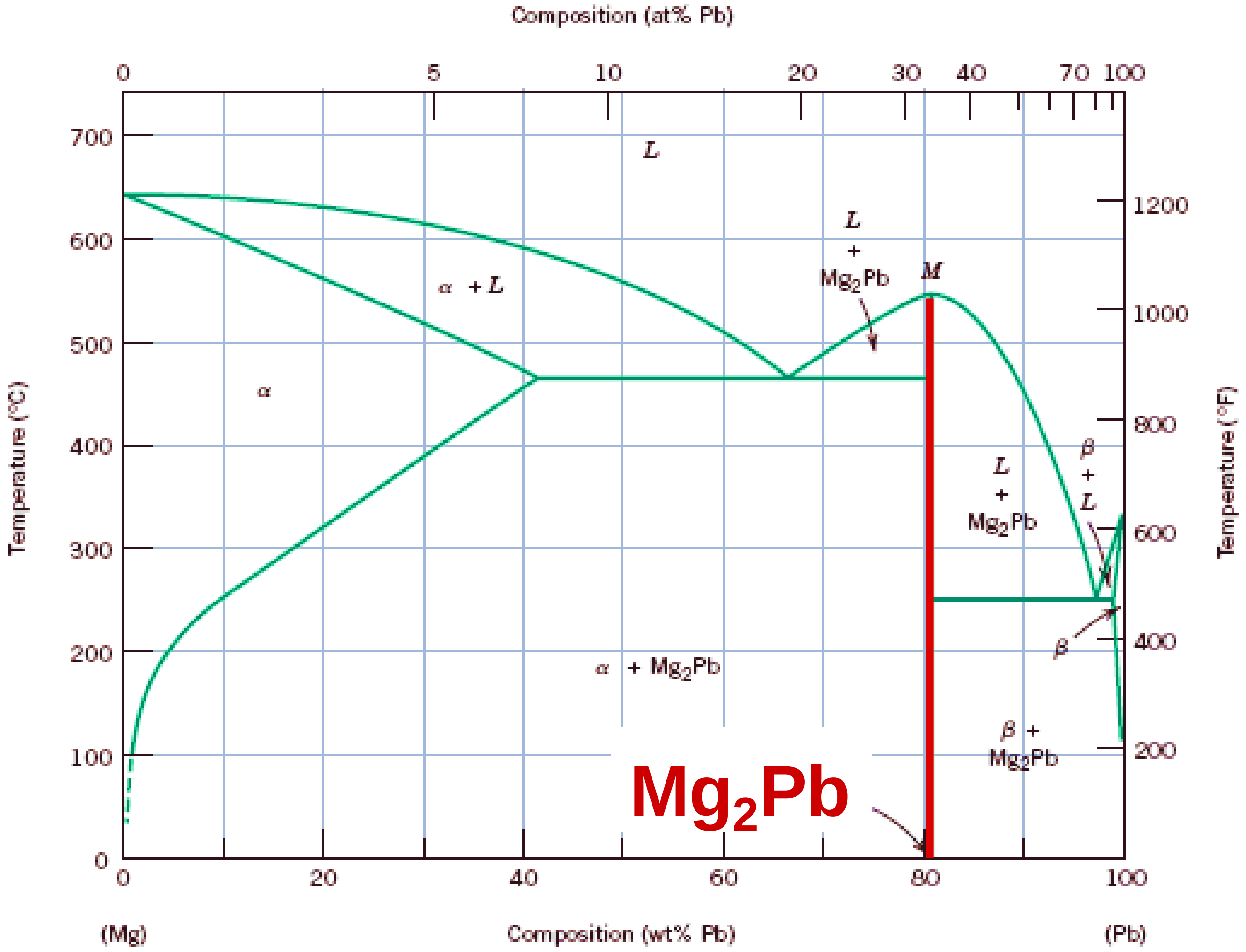
•Three classification of ferrous alloys based on carbon content: iron, steel, and cast iron.

•Commercially, pure iron contains less than 0.008 wt% (almost exclusively α -phase at room temperature).

•Iron-carbon alloys that contain 0.008-2.14 wt% C are classified as steels (mostly α+ Fe_3C)

•Cast iron contain 2.14-6.70 wt% C (commercially less than 4.5 wt%

Intermetallic Compounds



Adapted from
Fig. 9.20, *Callister &*
Rethwisch 8e.

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).

Intermetallic Compounds

- That means that **Mg_2Pb** can exist by itself only at the precise composition of 19 wt% Mg-81 wt% Pb.
- In other words, discrete intermediate compounds rather than solid solutions may be found on the phase diagram.
- These compounds have distinct chemical formulas; for metal-metal systems (**intermetallic compounds)**.

OTHER CHARACTERISTICS OF Mg-Pb SYSTEM

- Mg_2Pb melts at approximately 550 ºC.
- The solubility of lead in magnesium is rather extensive.
- The solubility of magnesium in lead is extremely limited.
- There are two eutectic reactions.

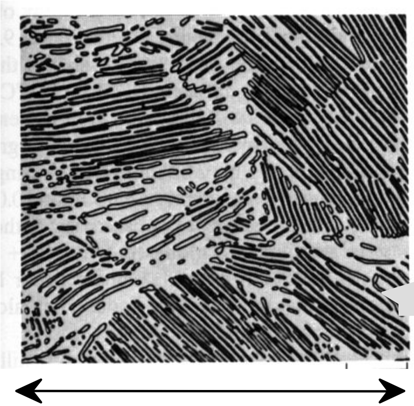
Iron-Carbon (Fe-C) Phase Diagram

- 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