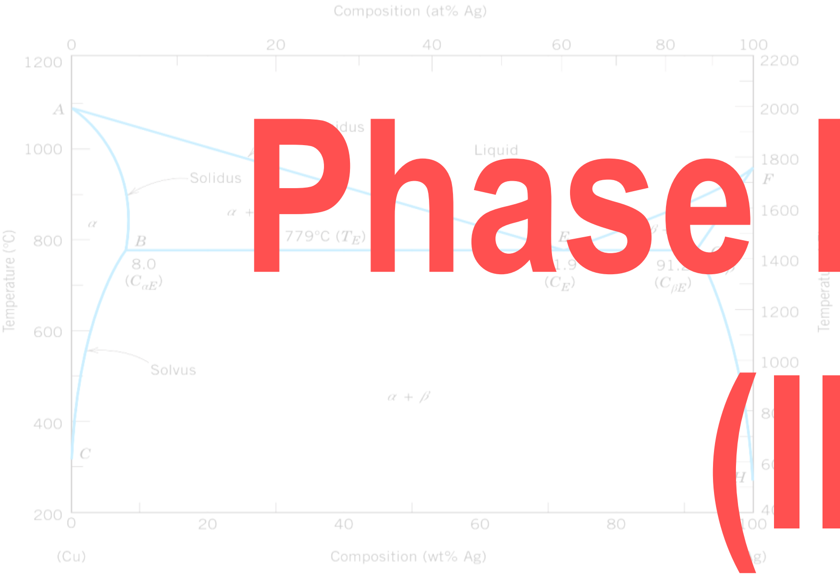
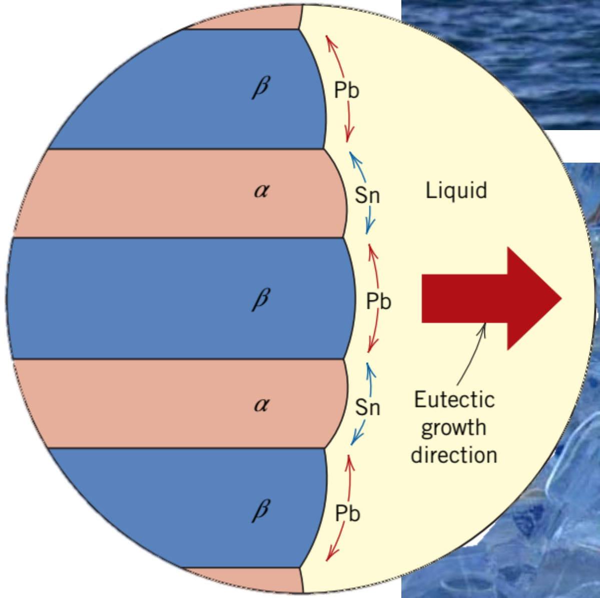
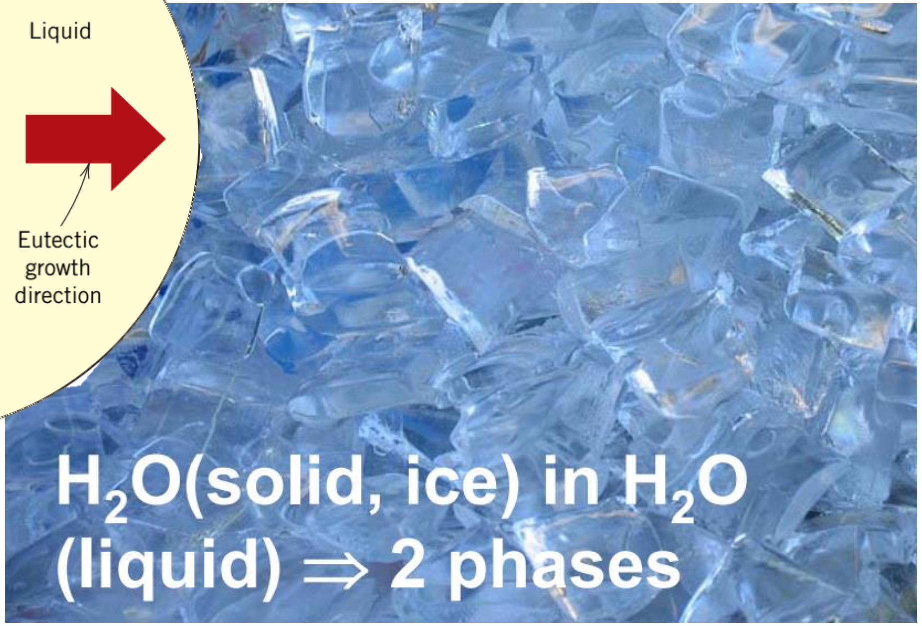
MS31007: Chapter 7

Phase Diagrams (III-IV)







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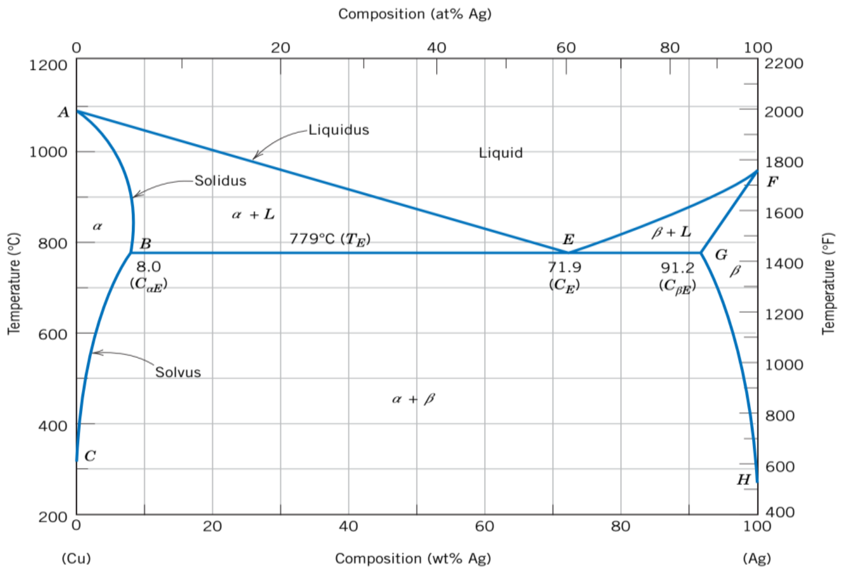
Phase diagram

- Solubility Limits
- Phases
- Phase Equilibrium
- Interpretation of Phase Diagrams
- Binary Isomorphous Systems (Cu-Ni)
- Development of Microstructure
- Mechanical Properties
- Binary Eutectic Systems
- Development of Eutectic Alloy Microstructure
- The Kinetics Of Phase Transformations

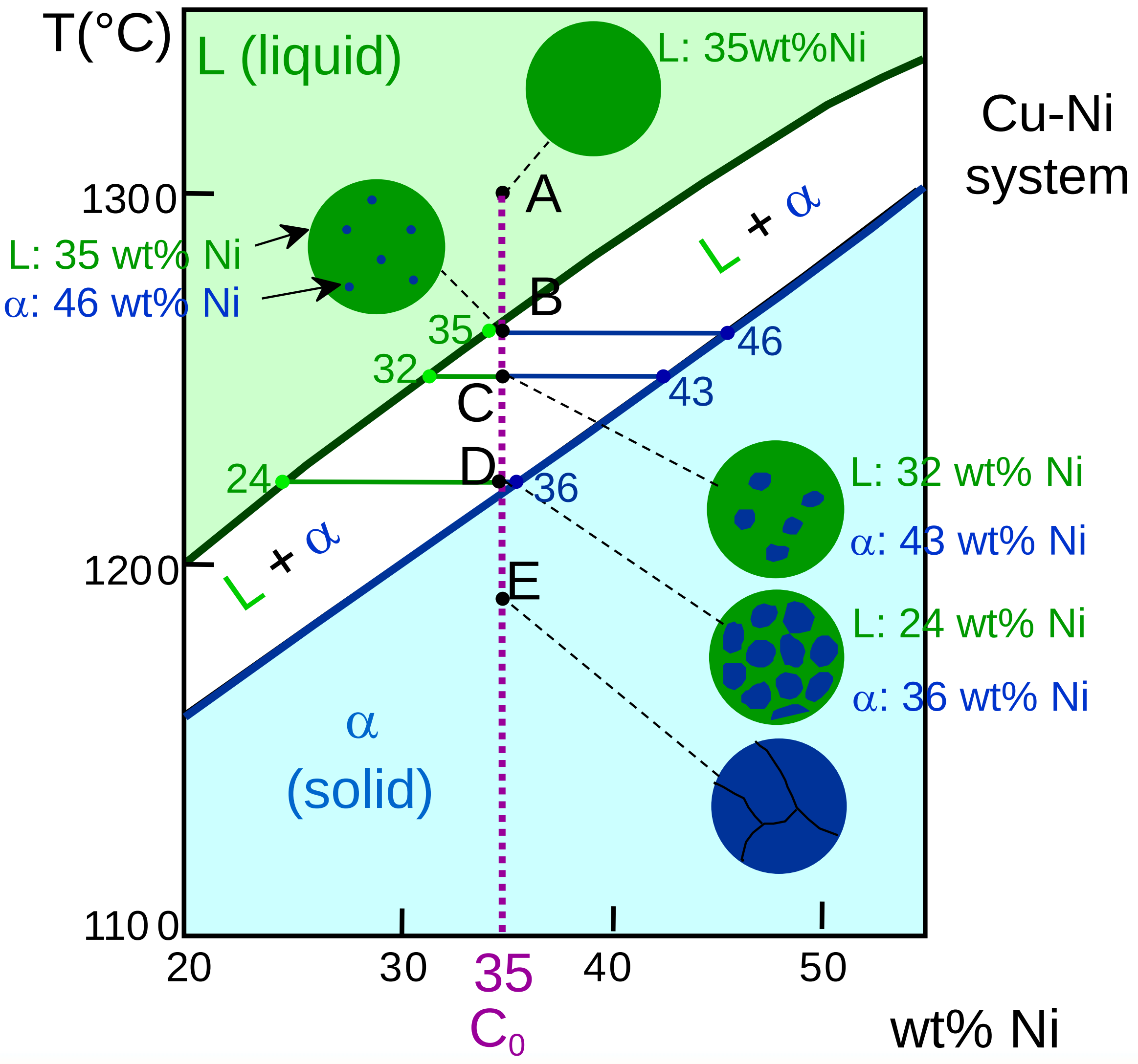


Equilibrium Cooling of a Cu-Ni Alloy : Solidification

Condition: The cooling occurs very slowly, in that phase equilibrium is continuously maintained

- Phase diagram:
  Cu-Ni system.

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

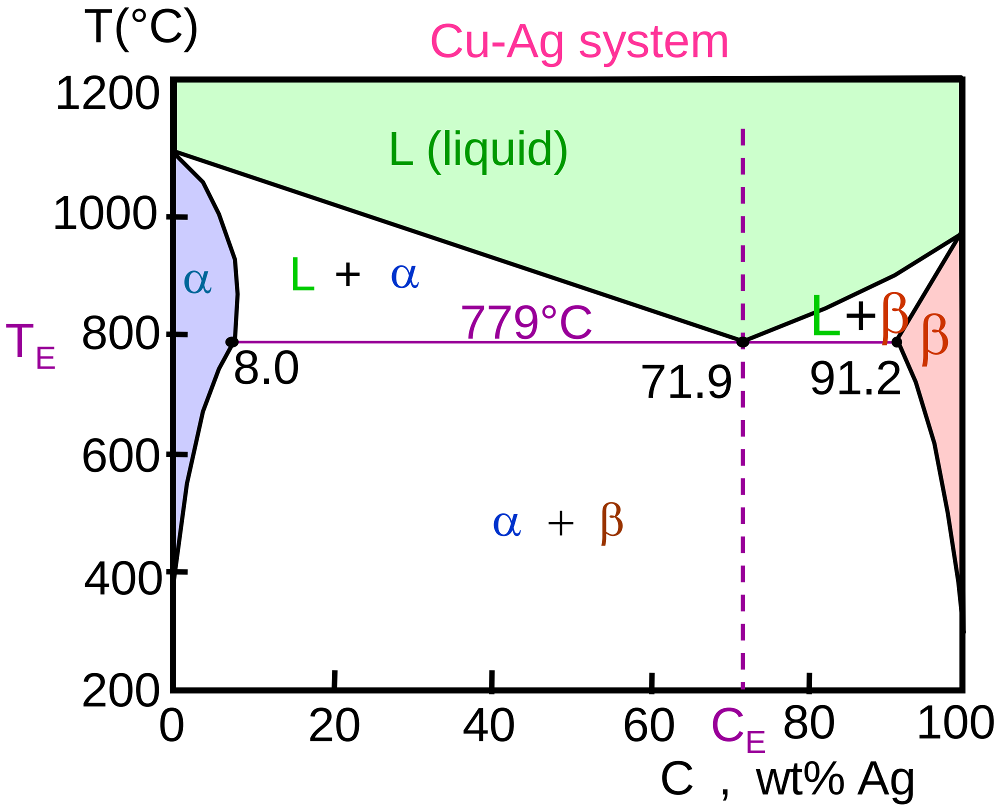


Binary-Eutectic Systems

Upon cooling, a liquid phase is transformed into the two solid α and β phases at T_E ; the opposite reaction occurs upon heating. This is called a

Eutectic reaction = $L(C_E) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$

$$L(71.9\text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(8.0\text{ wt\% Ag}) + \beta(91.2\text{ wt\% Ag})$$

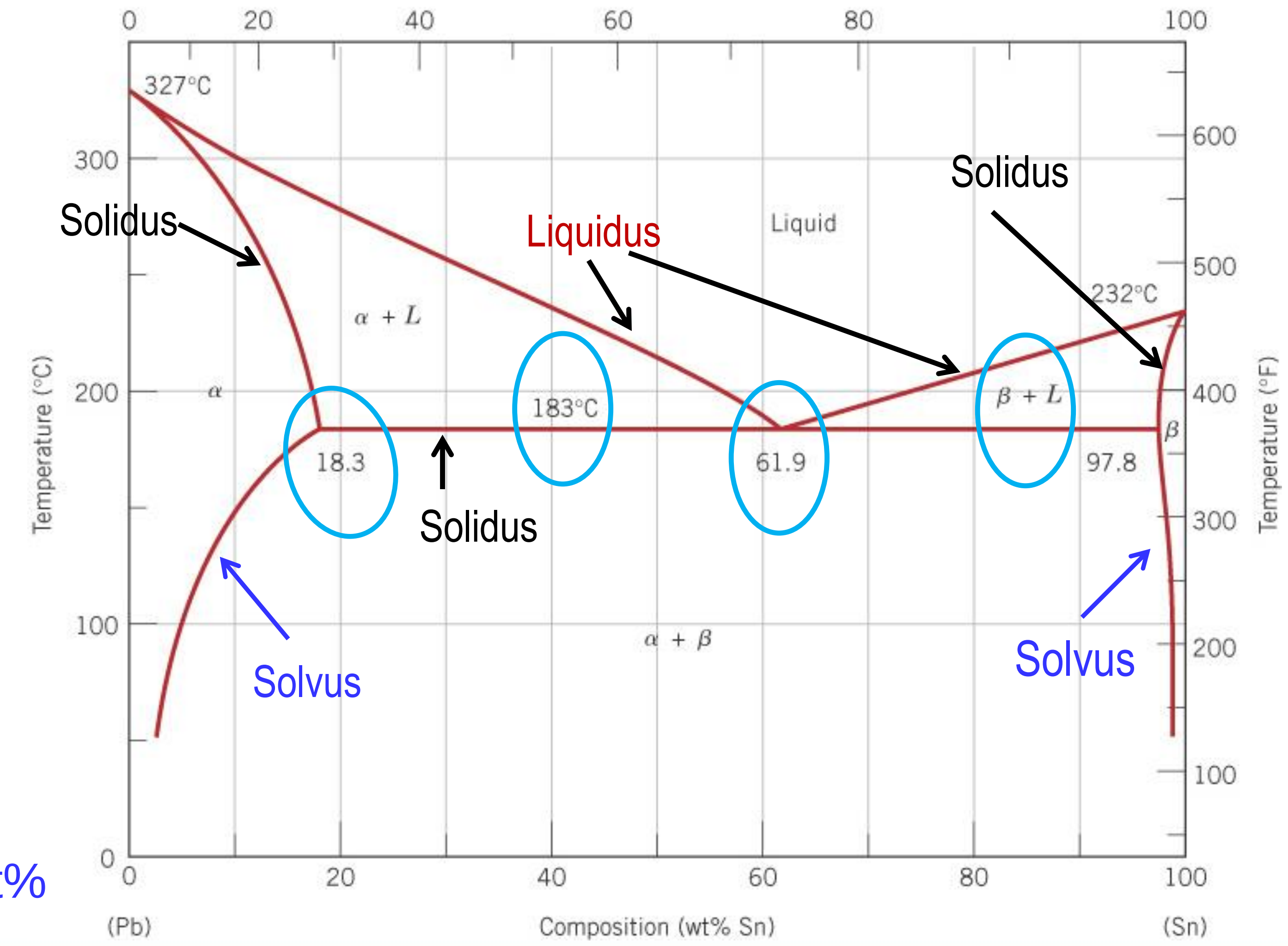


- The horizontal solidus line at T_E is called the ***eutectic isotherm***
- The solid product of eutectic solidification is always two solid phases
- For a eutectic system, three phases may be in equilibrium, but only at points along the eutectic isotherm.
- Another general rule is that single-phase regions are always separated from each other by a two-phase region that consists of the two single phases that it separates

Solidification of Eutectic Mixtures

Mixtures of some metals, such as Cu & Ni, are completely soluble in both liquid and solid states for all concentrations of both metals. Cu & Ni have the same crystal structure (FCC) and have nearly the same atomic radii. The solid formed by cooling can have any proportion of Cu & Ni. Such completely miscible mixtures of metals are called **isomorphous**.

- By contrast, a mixture of lead & tin that is **eutectic** is only partially soluble when in the solid state. Pb & Sn have different crystal structures (FCC versus BCC) and Pb atoms are much larger.
- No more than 18.3 weight % solid Sn can dissolve in solid Pb
- No more than 2.2% of solid Pb can dissolve in solid Sn
- The solid lead-tin alloy consists of a mixture of two solid phases, one consisting of a maximum of 18.3 wt% Sn (the **alpha** phase) and one consisting of a maximum of 2.2 wt% Pb (the **beta** phase).

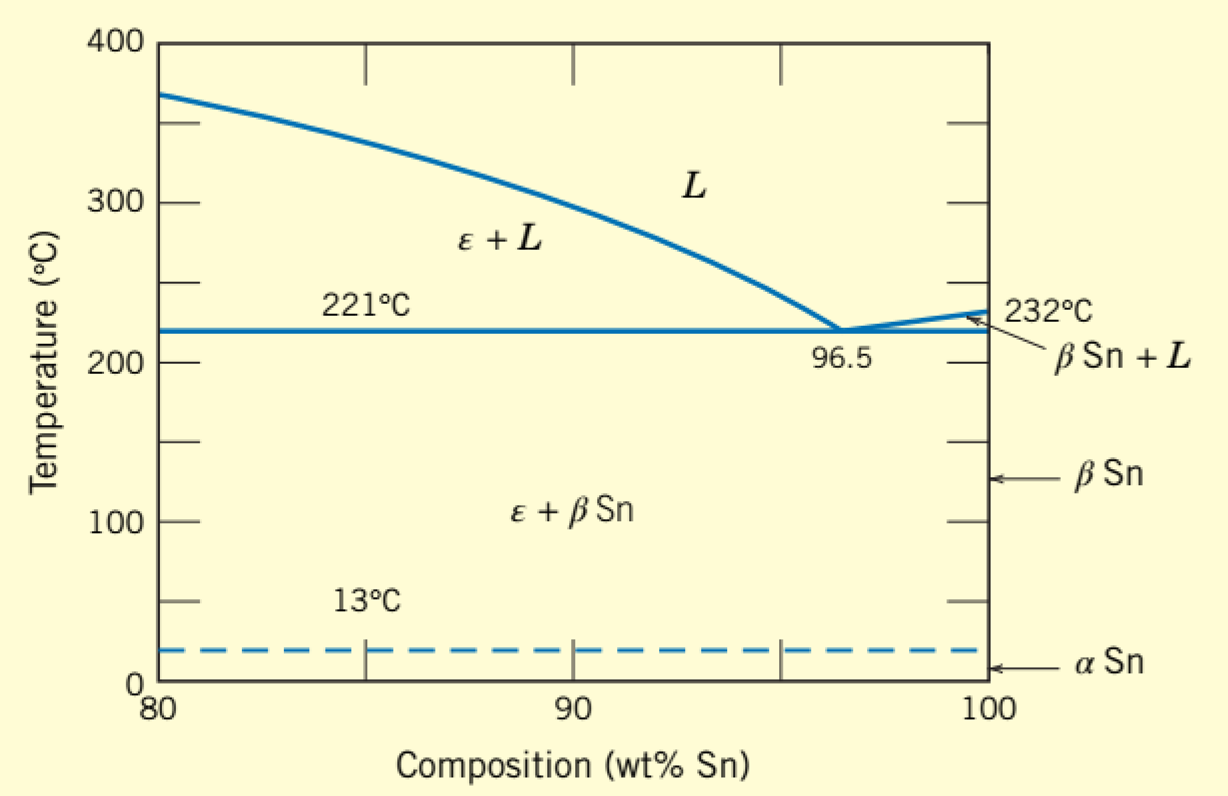


The eutectic invariant point is located at 61.9 wt% Sn and 183°C

Eutectic lead–tin solder

- For lead & tin the eutectic composition is 61.9 wt% tin and the eutectic temperature is 183ºC -- which makes this mixture useful as **solder**.
- At 183ºC, compositions of greater than 61.9 wt% tin result in precipitation of a tin-rich solid in the liquid mixture, whereas compositions of less than 61.9 wt% tin result in precipitation of lead-rich solid.

The tin-rich side of the silver–tin phase diagram.



Composition (wt%)	*Solidus Temperature (°C)*	*Liquidus Temperature (°C)*
Solders Containing Lead		
63 Sn–37 Pb[a]	183	183
50 Sn–50 Pb	183	214
Lead-Free Solders		
99.3 Sn–0.7 Cu[a]	227	227
96.5 Sn–3.5 Ag[a]	221	221
95.5 Sn–3.8 Ag–0.7 Cu	217	220
91.8 Sn–3.4 Ag–4.8 Bi	211	213
97.0 Sn–2.0 Cu–0.85 Sb–0.2 Ag	219	235

Pb-Sn Eutectic System

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

-- the phases present at B

Answer: $\alpha + \beta$

-- the phase compositions

Answer: C_α = 11 wt% Sn
C_β = 99 wt% Sn

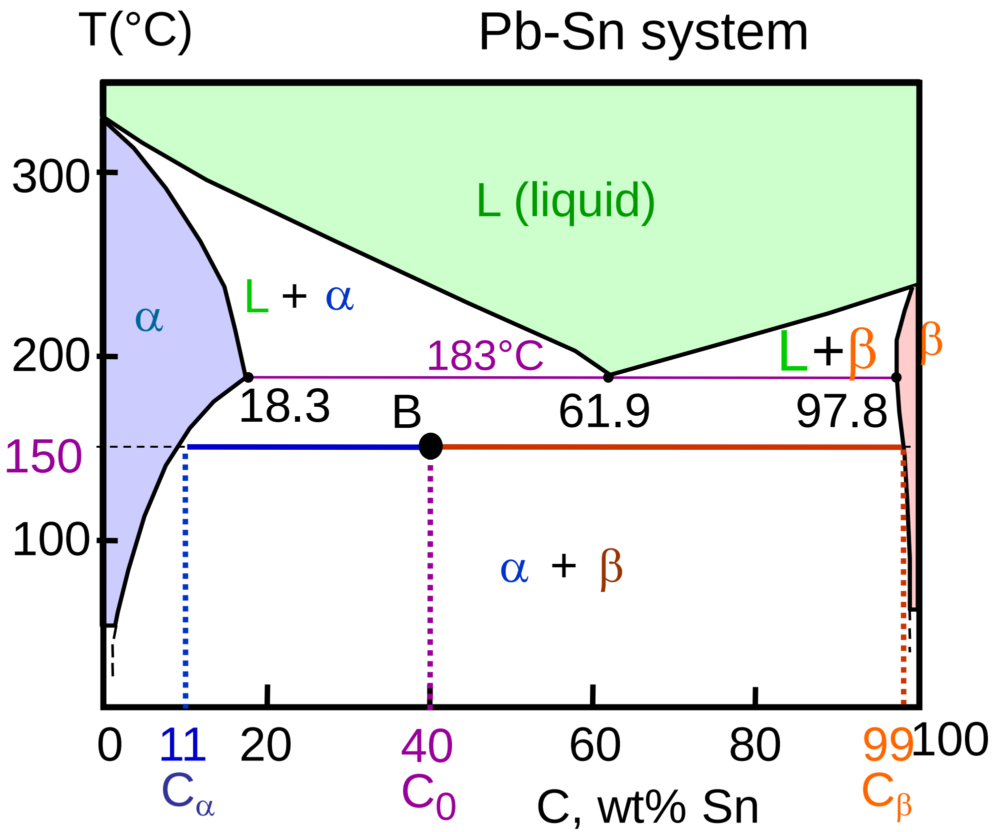
-- the relative amount of each phase

Answer: $$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha}$$

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

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

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



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

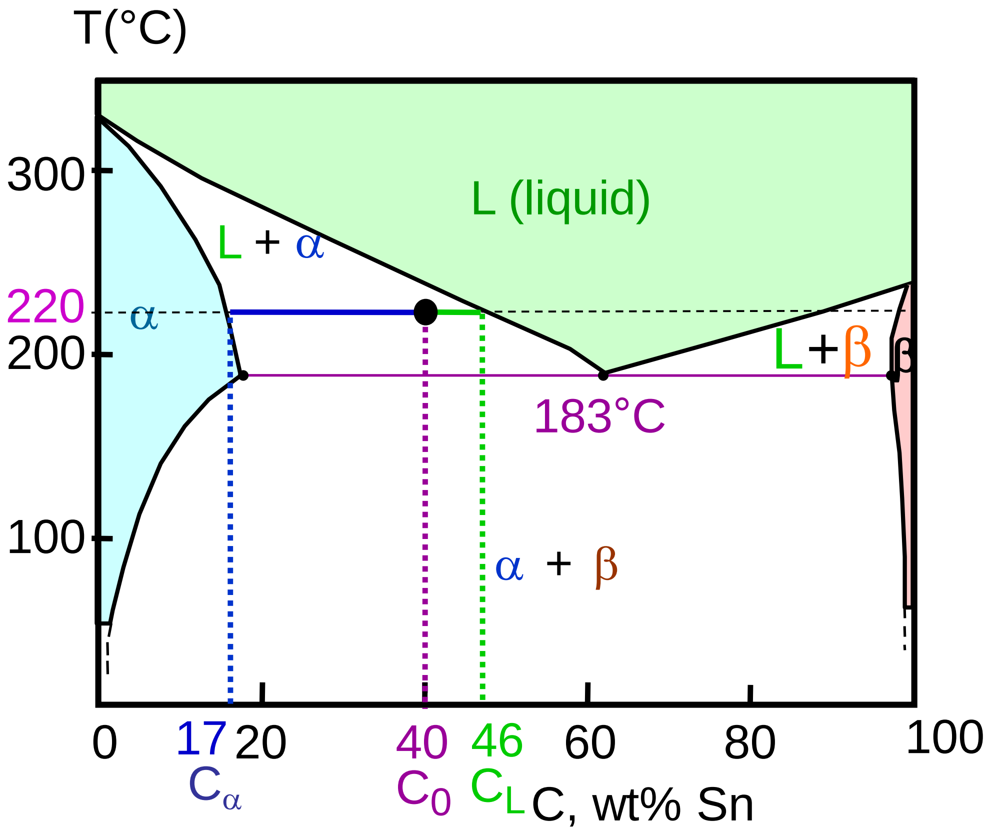
  -- the relative amount of each phase

  Answer:

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

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

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



Microstructures In Eutectic Systems: Equilibrium Cooling - I

•Composition range: a pure component (e.g. Pb)
- its maximum solid solubility at ***room*** (20 ^{0}C) temperature
e.g. alloys where
$C_0 < 2$ wt% Sn

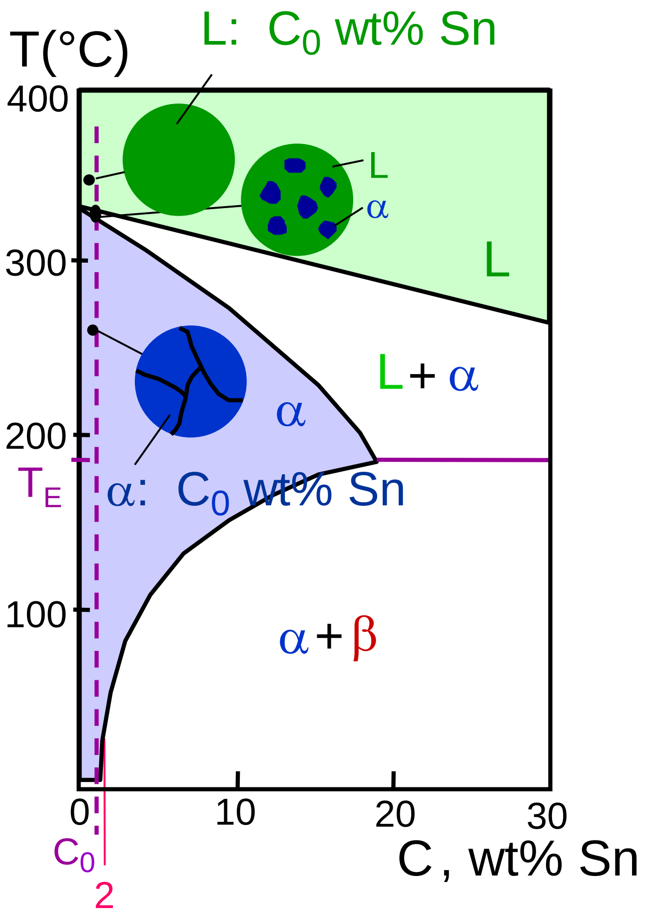
T>T_L=330 °C – ***liquid alloy*** with C_0 comp

T_S< T<T_L – very narrow region: a ***solid*** phase in ***liquid*** (L) and compositions of phases are defined by **tie-line method**

T<T_S - ***polycrystal*** of α ***grains*** with uniform composition of C_0

Result at room temperature is a polycrystalline with grains of α phase having composition C_0

Pb-Sn system



(room T solubility limit)

Microstructures In Eutectic Systems: Equilibrium Cooling - II

•<u>Composition range</u>: maximum solid solubility at ***room*** (20°C) temperature (C = 2wt%) and maximum solid solubility at ***eutectic*** temperature, T_E=183°C (C=18.3%) (e.g. **2 wt% Sn < C_2 < 18.3 wt% Sn**)

- $T>T_L$ – ***liquid alloy*** with C_2 composition

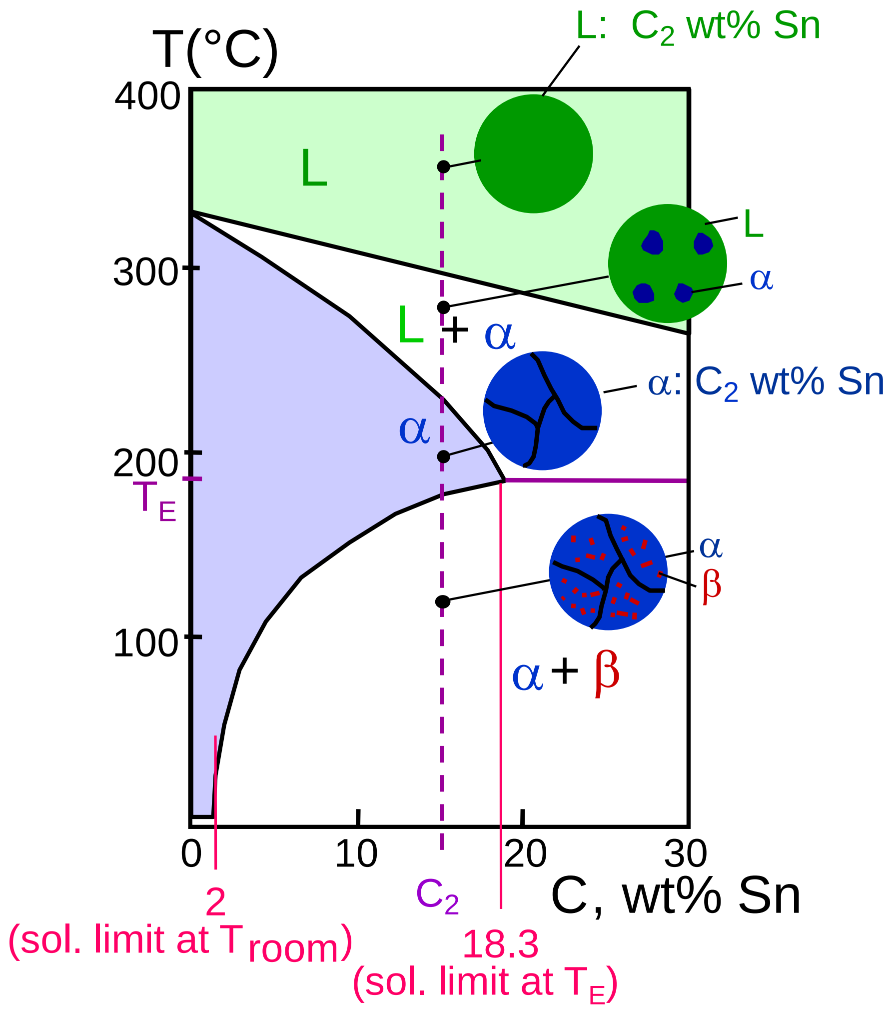
- $T_{solidus}<T<T_L$ – ***solid*** α phase in ***liquid*** (L) and compositions of phases are defined by tie-line method

- $T_{solvus} < T < T_{solidus}$ - ***polycrystal*** of α ***grains*** with uniform composition of C_2

- $T < T_{solvus}$ - α ***polycrystal*** with fine β ***crystals;*** the compositions of phases are defined by tie-line method and the amount of each phase by Level rule.

- Results in polycrystalline microstructure with α grains and small β-phase particles at lower temperatures.

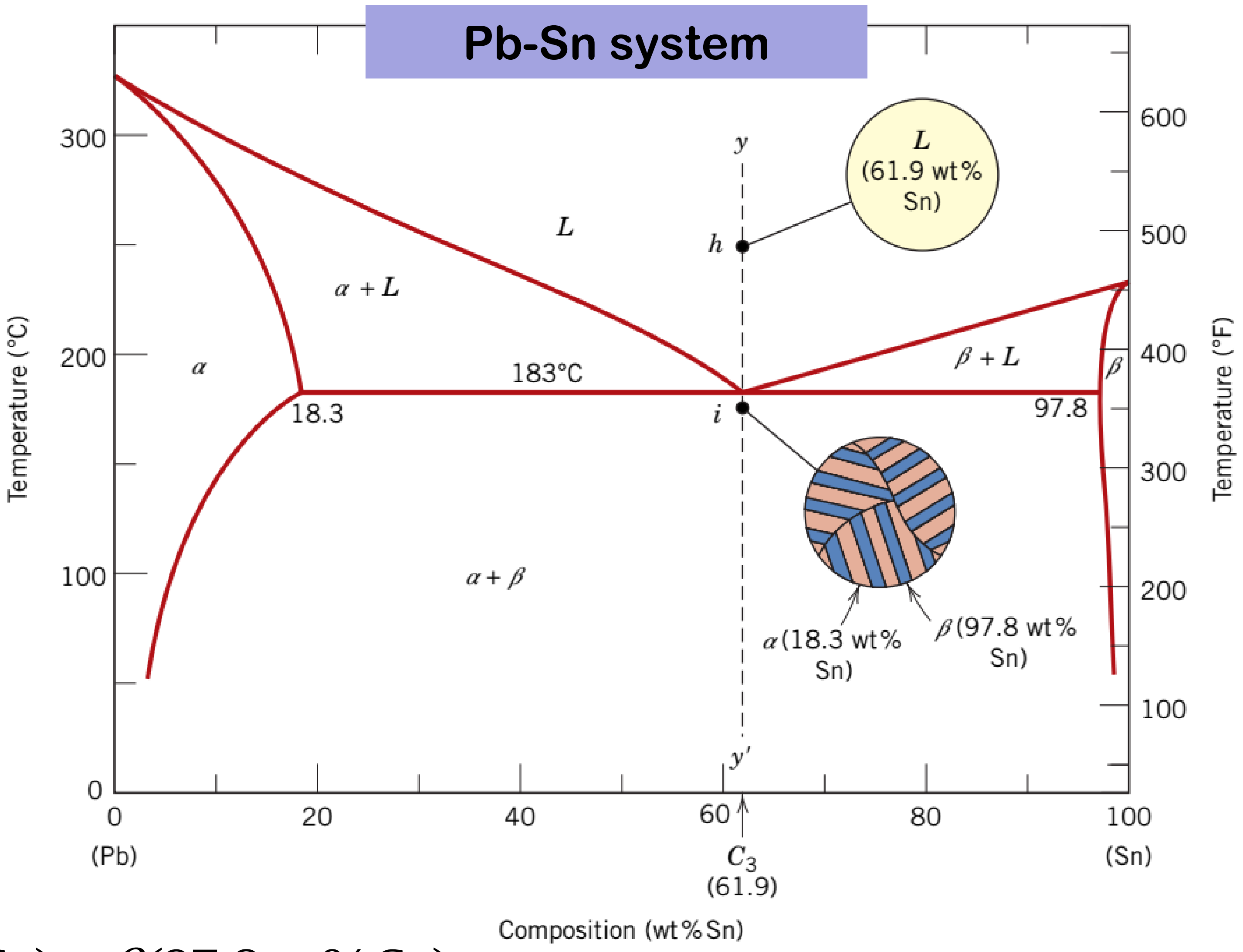
Pb-Sn system



Microstructures in Eutectic Systems - III

- $T > T_E$: ***liquid*** with $C = C_E$ = 61.9 wt% Sn
- $T < T_E$: **alternating layers of α and β crystals**.

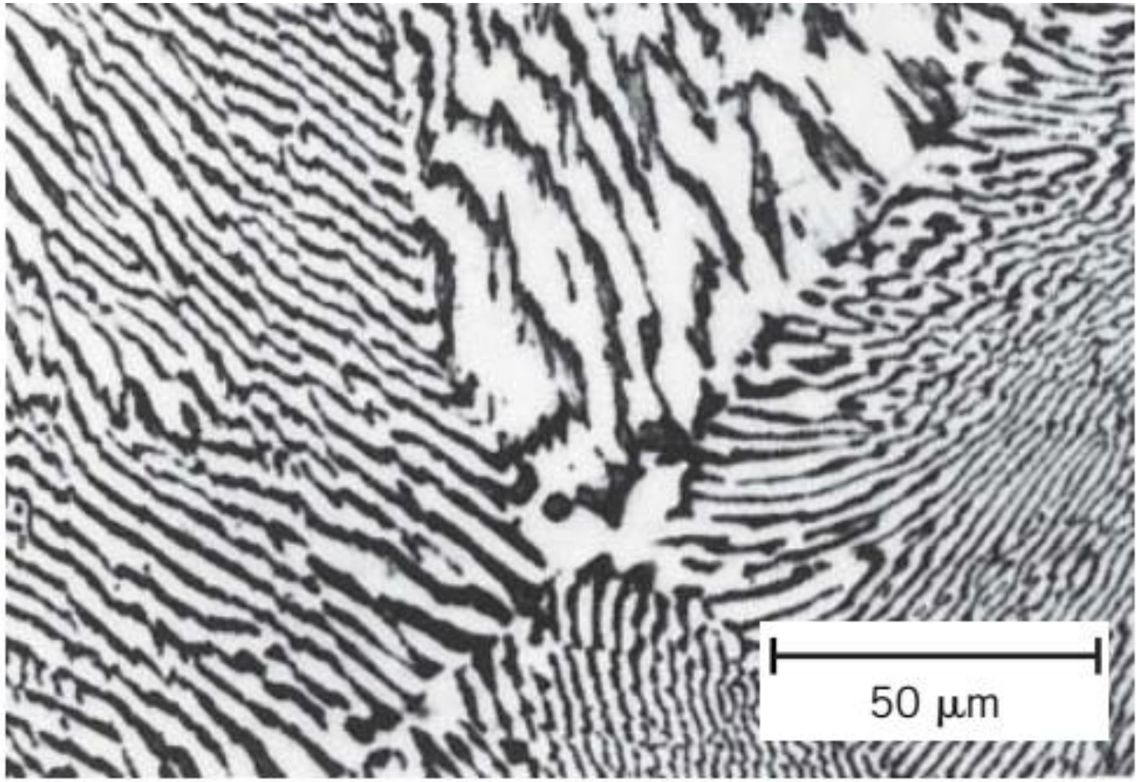
- $C_3 = C_E$
- Results in a eutectic microstructure with alternating layers of α and β crystals.

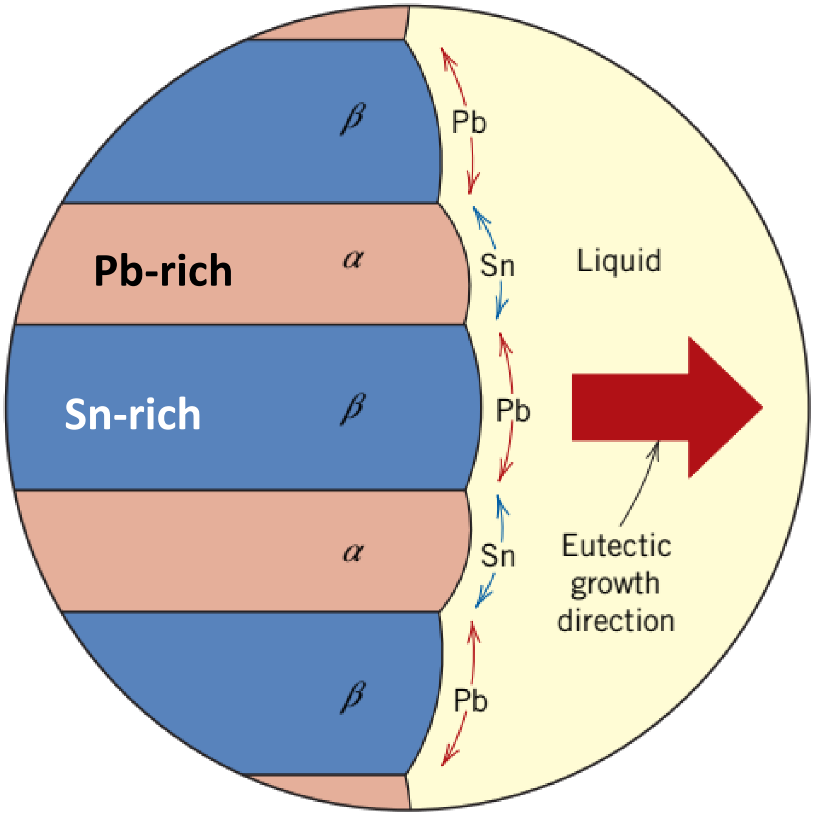


$$L(61.9\,\text{wt\% Sn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(18.3\,\text{wt\% Sn}) + \beta(97.8\,\text{wt\% Sn})$$

Lamellar Eutectic Structure

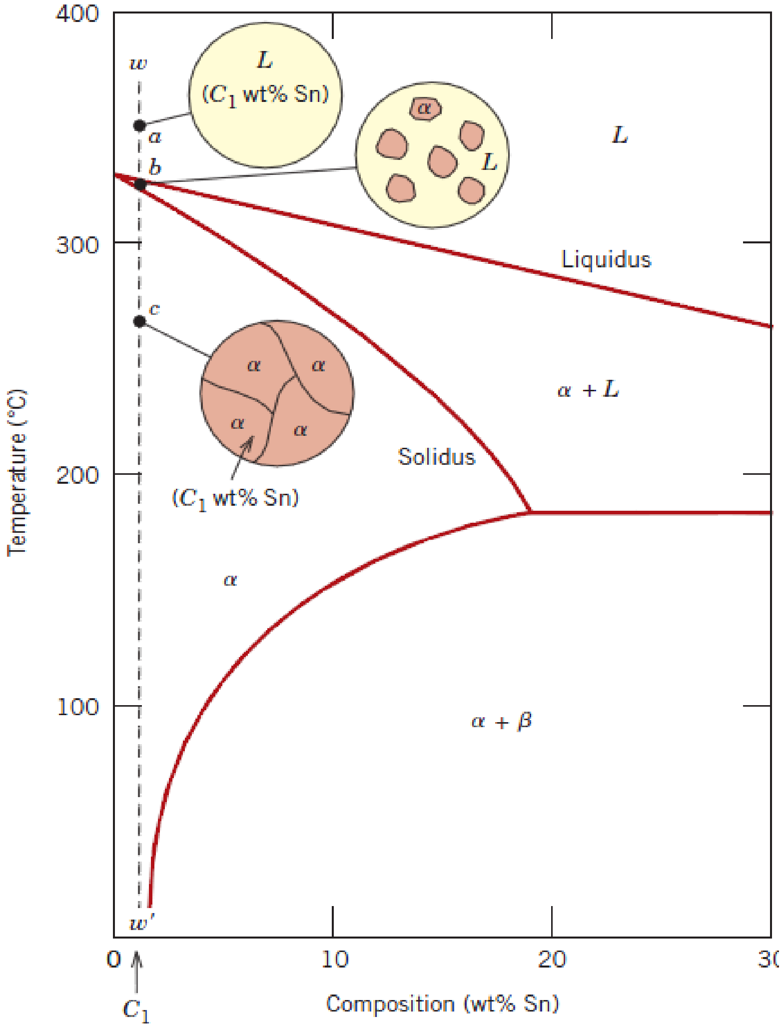
- A 2-phase microstructure resulting from the solidification of a liquid having the eutectic composition where the phases exist as a lamellae that alternate with one another.

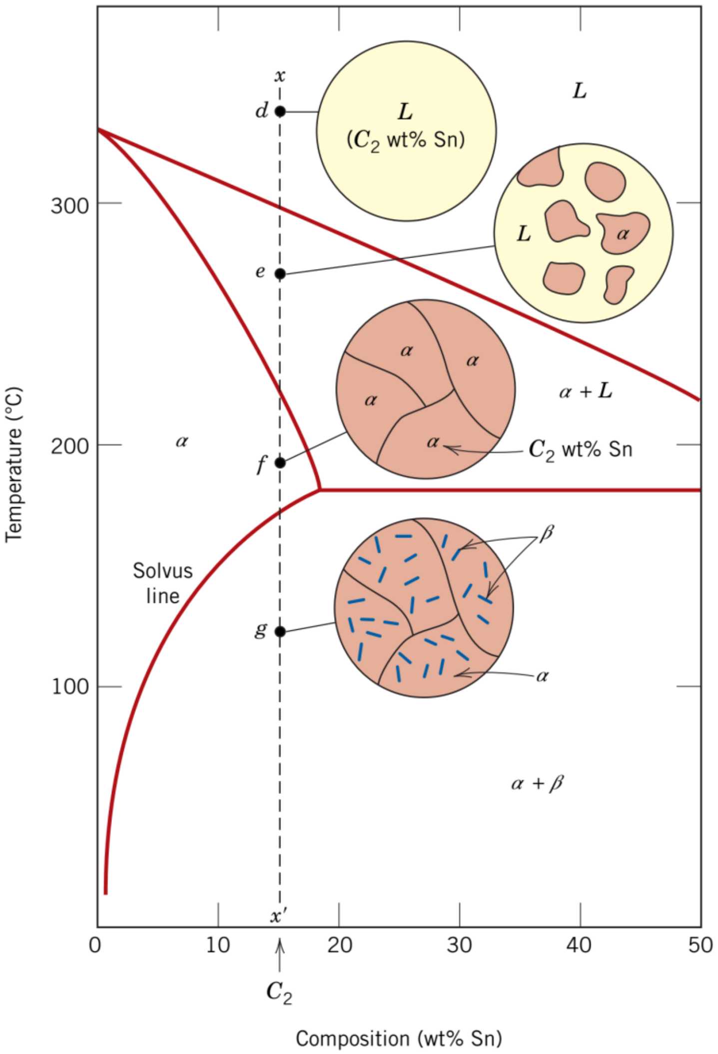


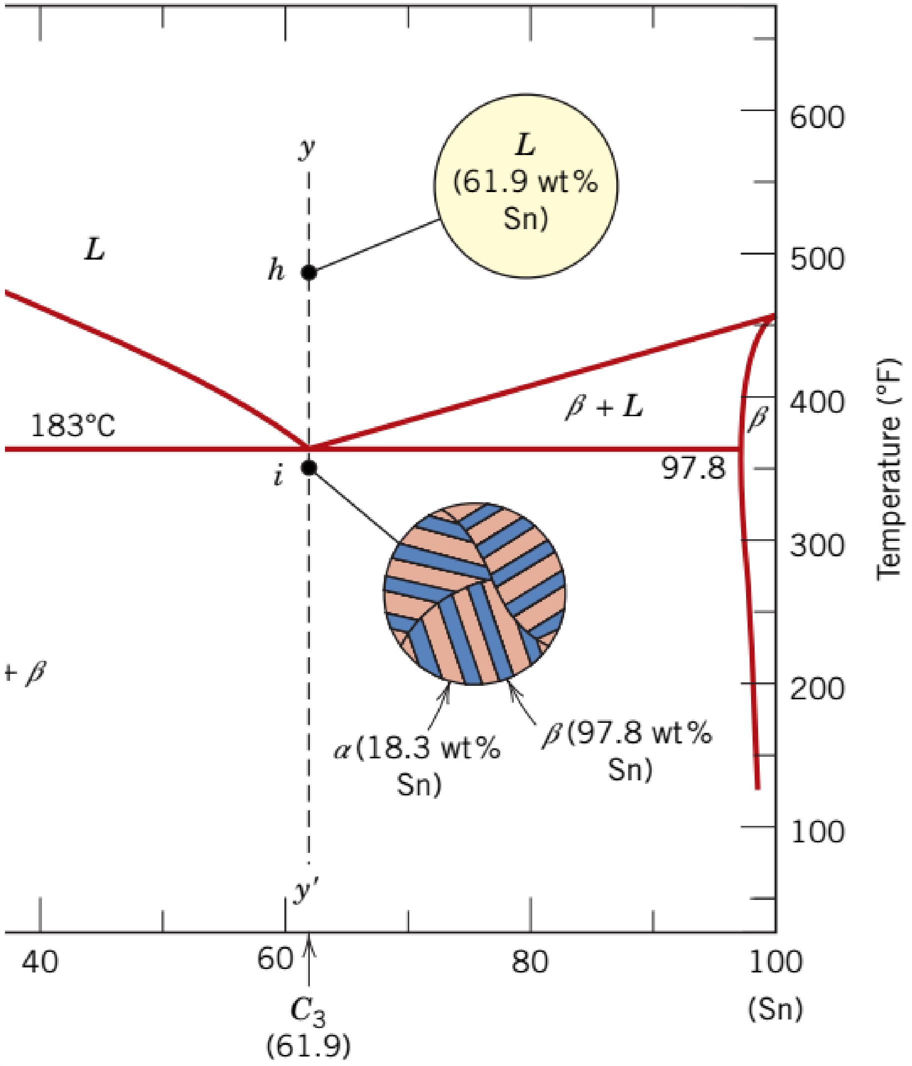


- Formation of eutectic layered microstructure in the Pb-Sn system during solidification at the eutectic composition.
- Compositions of α and β phases are very different. Solidification involves redistribution of Pb and Sn atoms by **atomic diffusion**.

Microstructure obtained with different compositions

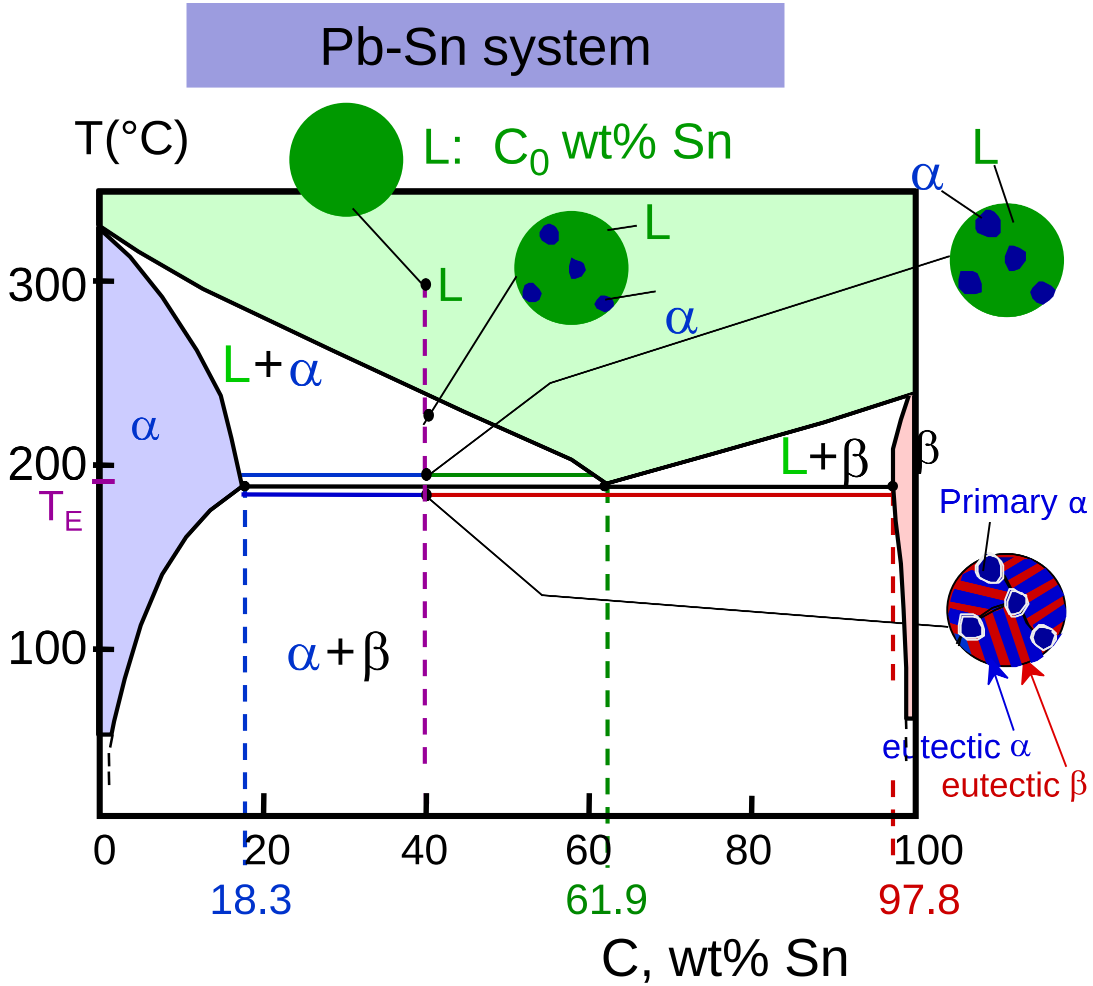






Microstructures in Eutectic Systems - IV

- For alloys with18.3 wt% Sn < C_0 < 61.9 wt% Sn
- Result: α phase particles and a eutectic microconstituent



- Just above T_E :

C_α = 18.3 wt% Sn

C_L = 61.9 wt% Sn

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = 0.50$$

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

- Just below T_E :

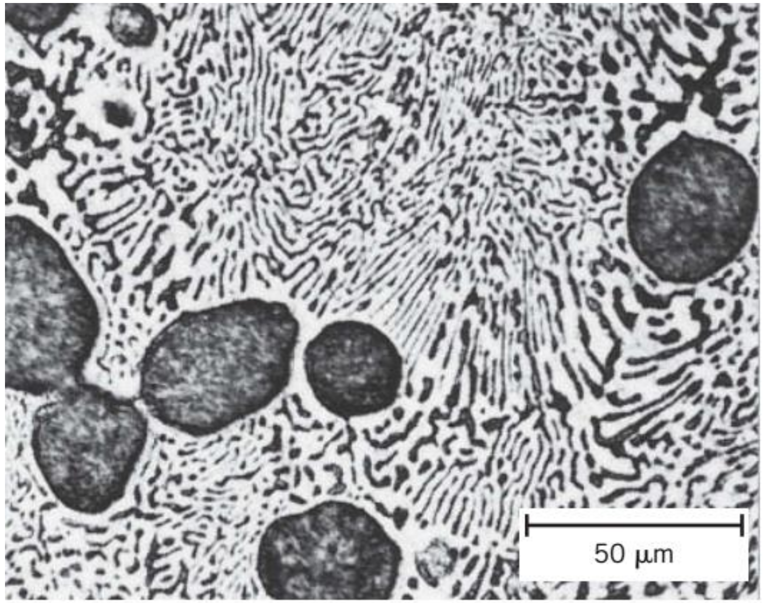
C_α = 18.3 wt% Sn

C_β = 97.8 wt% Sn

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = 0.727$$

W_β = 0.273 wt% Sn

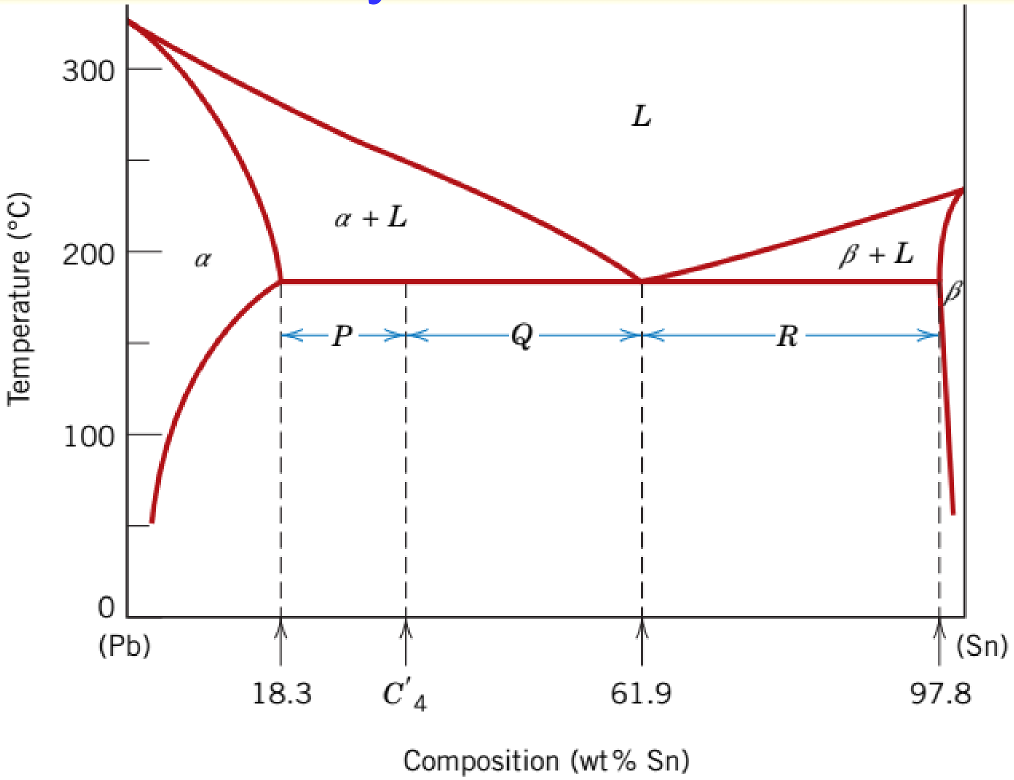
Microstructures in Eutectic Systems - IV



Microstructure of a lead–tin alloy of composition
50 wt% Sn–50 wt% Pb

To distinguish one *α* from the other, that which resides in the eutectic structure is called **eutectic** *α*, whereas the other that formed prior to crossing the eutectic isotherm is termed **primary** *α.*

Microconstituent—an element of the microstructure having an identifiable and characteristic structure (Example primary *α* and the eutectic structure)



The fraction of the eutectic microconstituent W_e is just the same as the fraction of liquid W_L from which it transforms,

$$W_e = W_L = \frac{P}{P+Q}$$

fraction of primary *α*

$$W_{\alpha'} = \frac{Q}{P+Q}$$

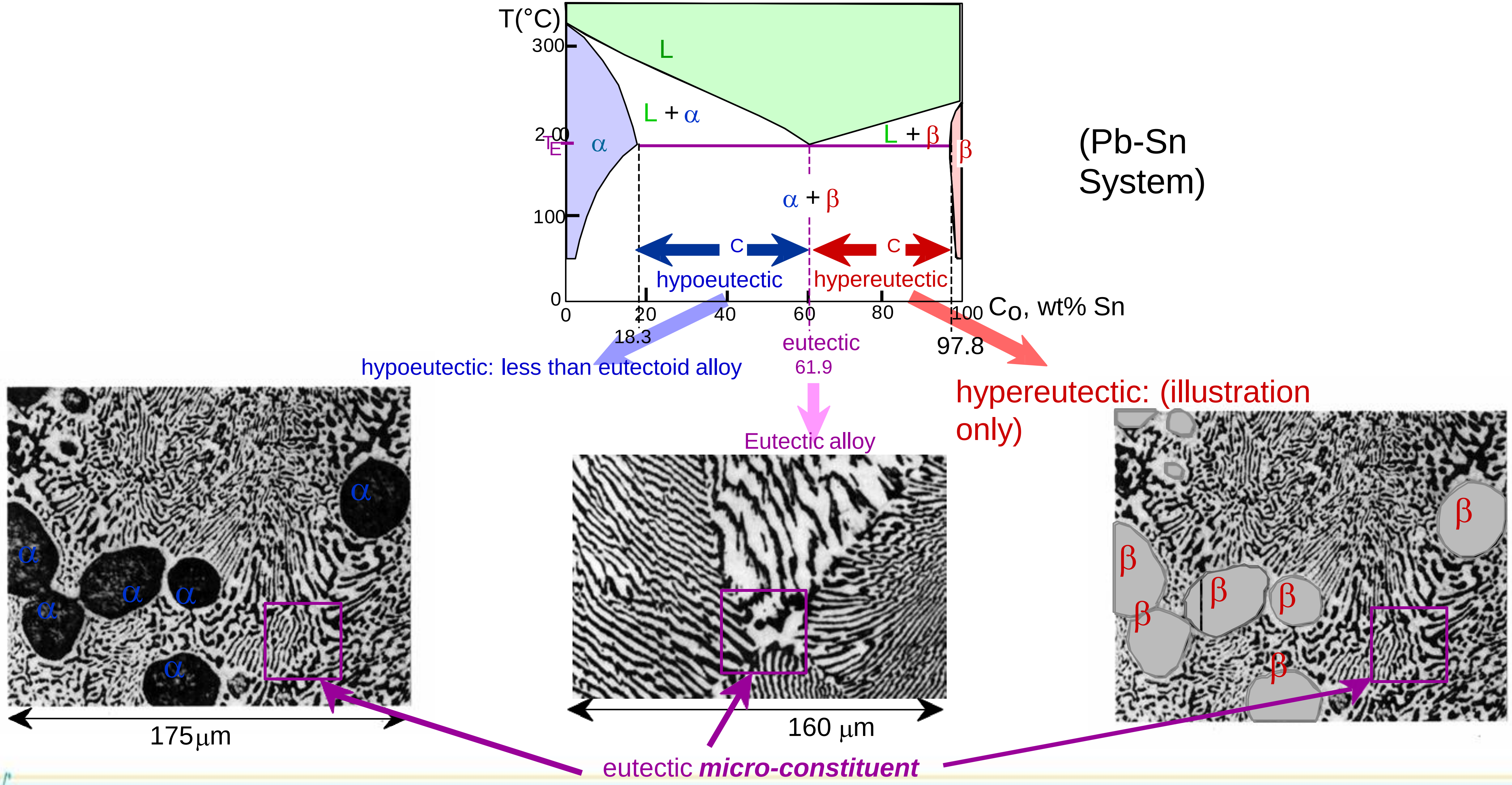
Fractions of *total α*,

$$W_\alpha = \frac{Q+R}{P+Q+R}$$

Fraction of β

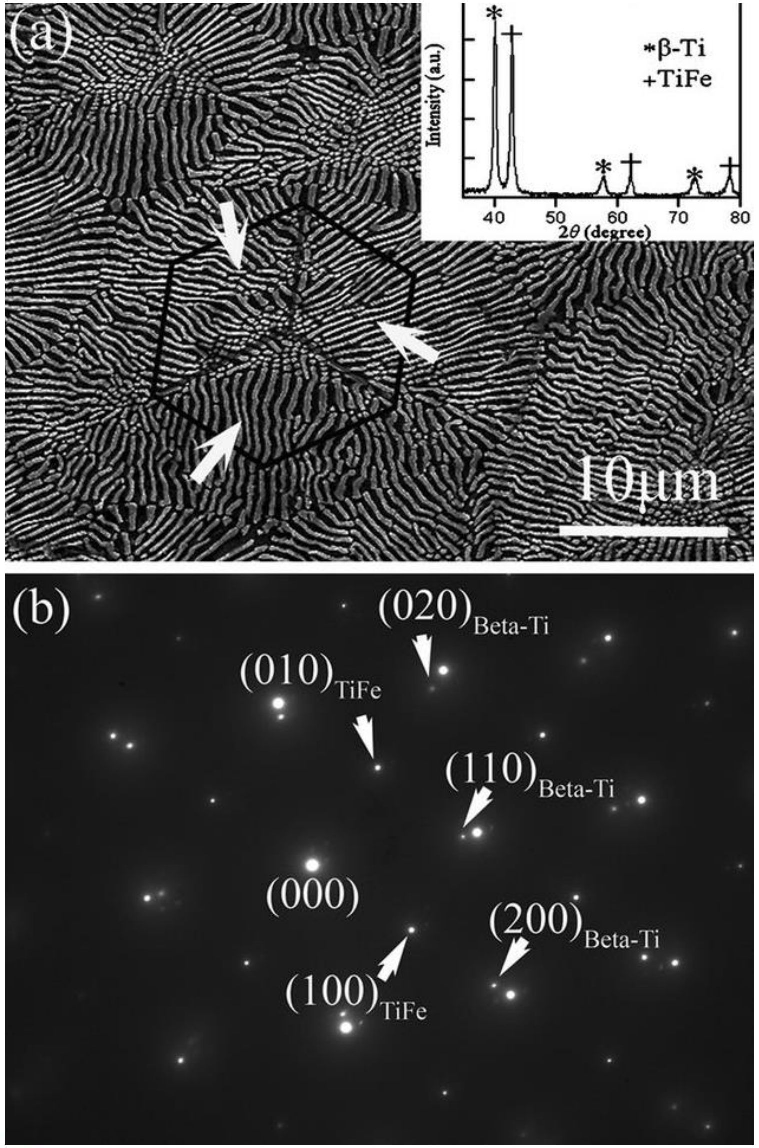
$$W_\beta = \frac{P}{P+Q+R}$$

Hypoeutectic & Hypereutectic



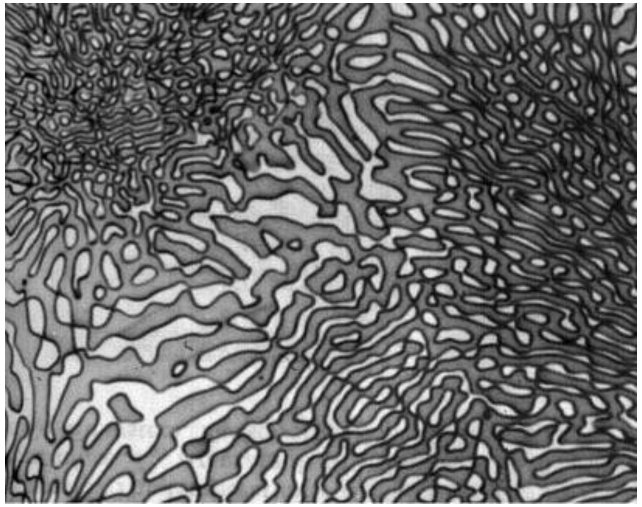
Lamellar Eutectic Structure

lamellar Ti-Fe eutectics

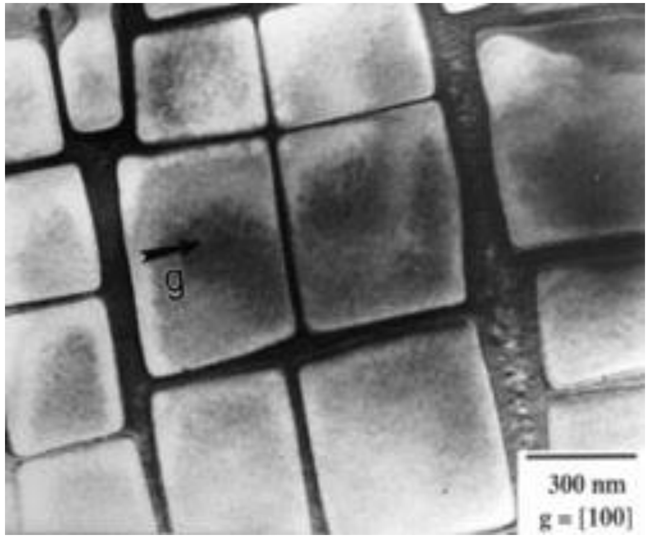


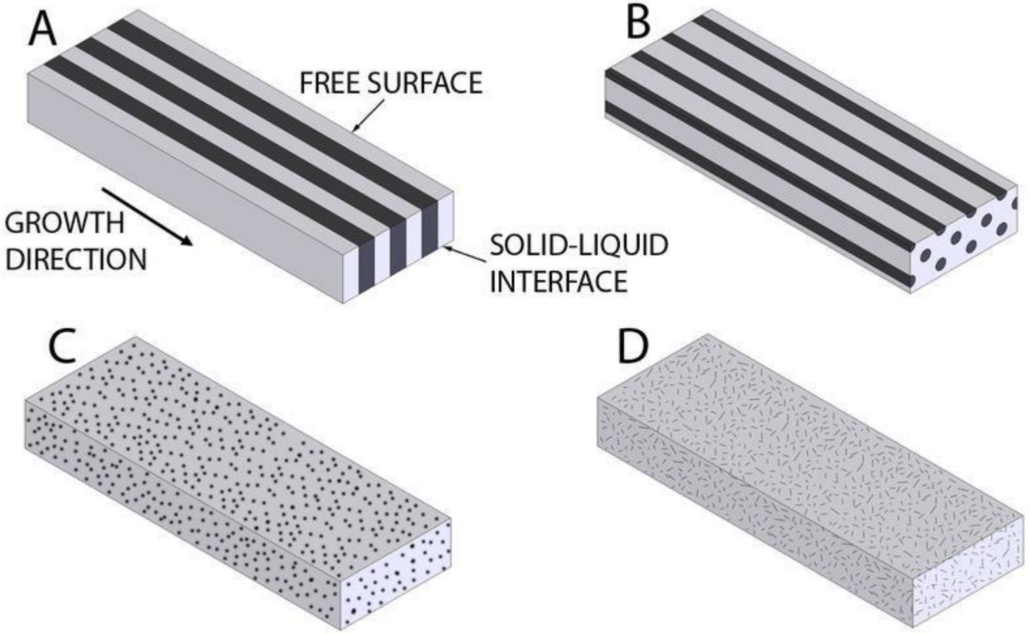
F. Zhu et al. App. Phys Lett 2011

Copper phosphorus eutectic



Ni-Al





Each eutectic alloy has its own characteristic microstructure : spheroidal, nodular, or globular; acicular (needles) or rod; and lamellar (platelets, Chinese script or

Well-Aligned Nanocylinder Formation in Phase-Separated Metal-Silicide–Silicon and Metal-Germanide–Germanium Systems

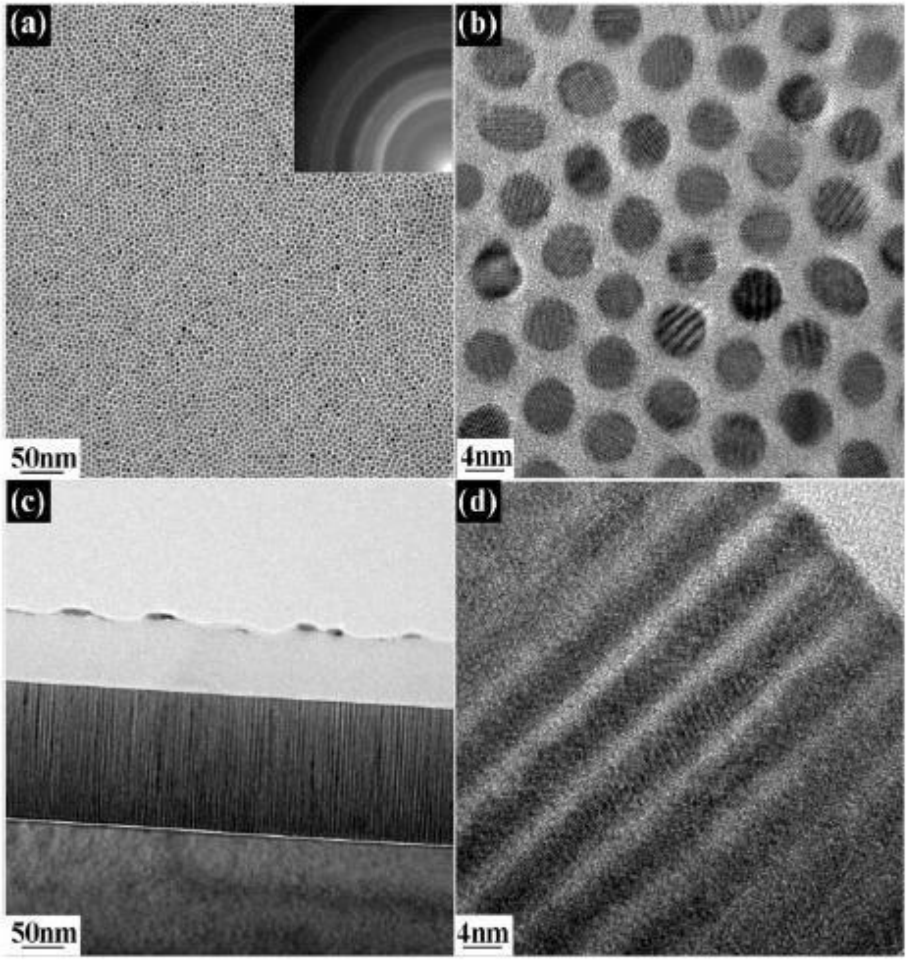


Figure 4. HRTEM images of the Pd_2Si-Si system sputtered by using deposition condition 1. a) A low-magnification image and b) high-magnification lattice image in plane view. c) A low-magnification image and d) high-magnification image in cross-sectional view.

Table 1. List of the examined materials and their eutectic temperatures

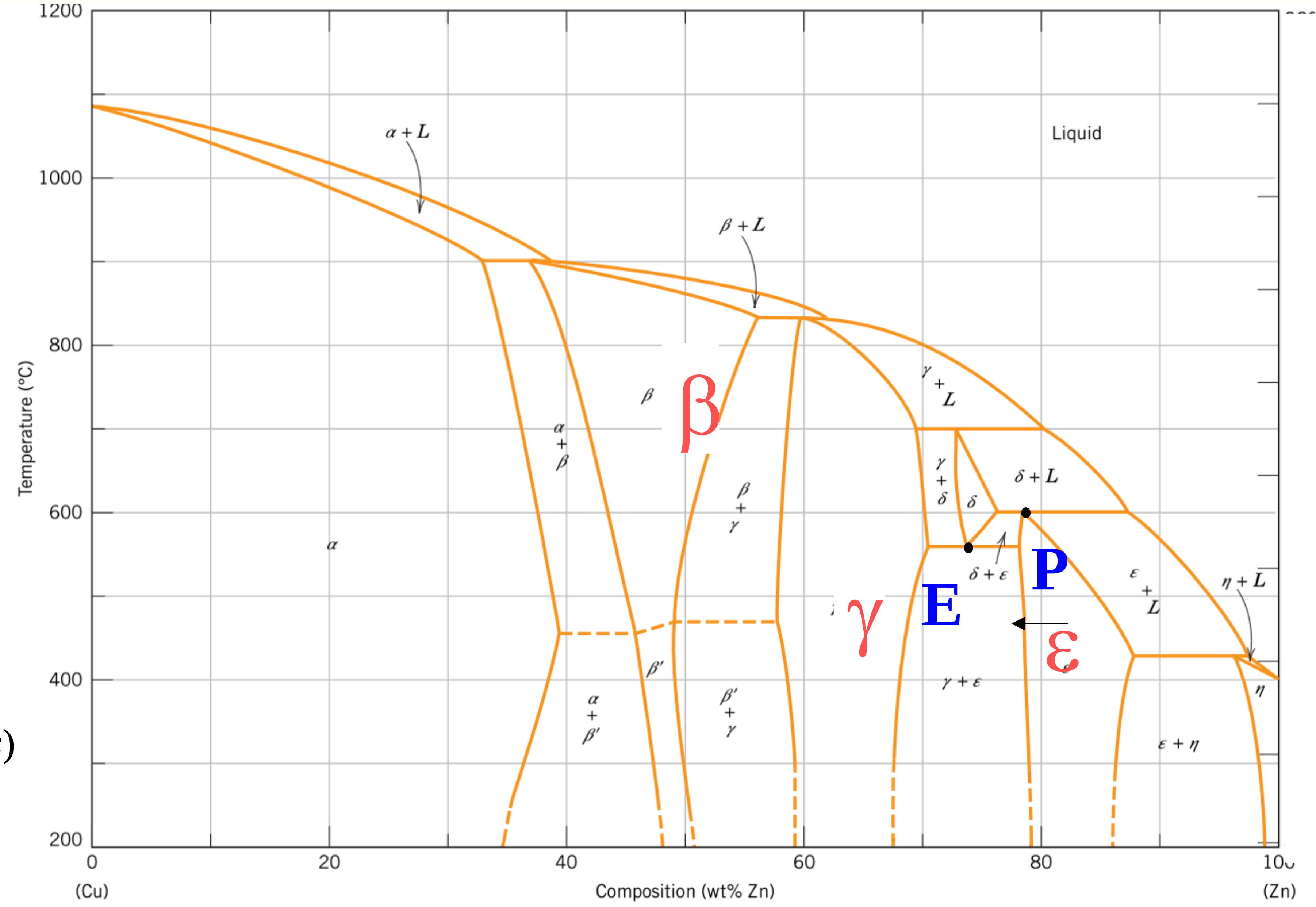
Materials [silicide]	Eutectic Temperature [°C]	Materials [germanide]	Eutectic Temperature [°C]
Al-Si [11,18]	577	Al-Ge [12, 18]	420
Cu_3Si-Si [18]	802	Cu_3Ge-Ge [18]	644
Pd_2Si-Si [19]	825	Ag-Ge [18]	651
$NiSi_2$-Si [20]	960	$Mn_{11}Ge_8$-Ge [28]	720
PtSi-Si [18]	979	PdGe-Ge [18]	725
RhSi-Si [21]	1060	NiGe-Ge [18]	762
$Mn_{11}Si_{19}$-Si [18]	1142	$PtGe_2$-Ge [18]	802
$FeSi_2$-Si [18]	1207	$Co_{0.875}Ge_2$-Ge [18]	810
$IrSi_3$-Si [22]	1221	Rh_3Ge_4-Ge [18]	850
$CoSi_2$-Si [18]	1259	$Cr_{11}Ge_{19}$-Ge [18]	895
$NbSi_2$-Si [18]	1302		
$CrSi_2$-Si [18]	1305		
$TiSi_2$-Si [18]	1330		
$ZrSi_2$-Si [23]	1353		
$HfSi_2$-Si [18]	1360		
Ru_2Si_3-Si [24]	1370		
VSi_2-Si [25]	1382		
$TaSi_2$-Si [18]	1385		
$ReSi_{1.75}$-Si [26]	1380		
$MoSi_2$-Si [18]	1400		
WSi_2-Si [27]	1400		

Equilibrium Diagrams with Intermediate Phases or Compounds

Terminal solid solutions:
only two solid phases/composition extremes

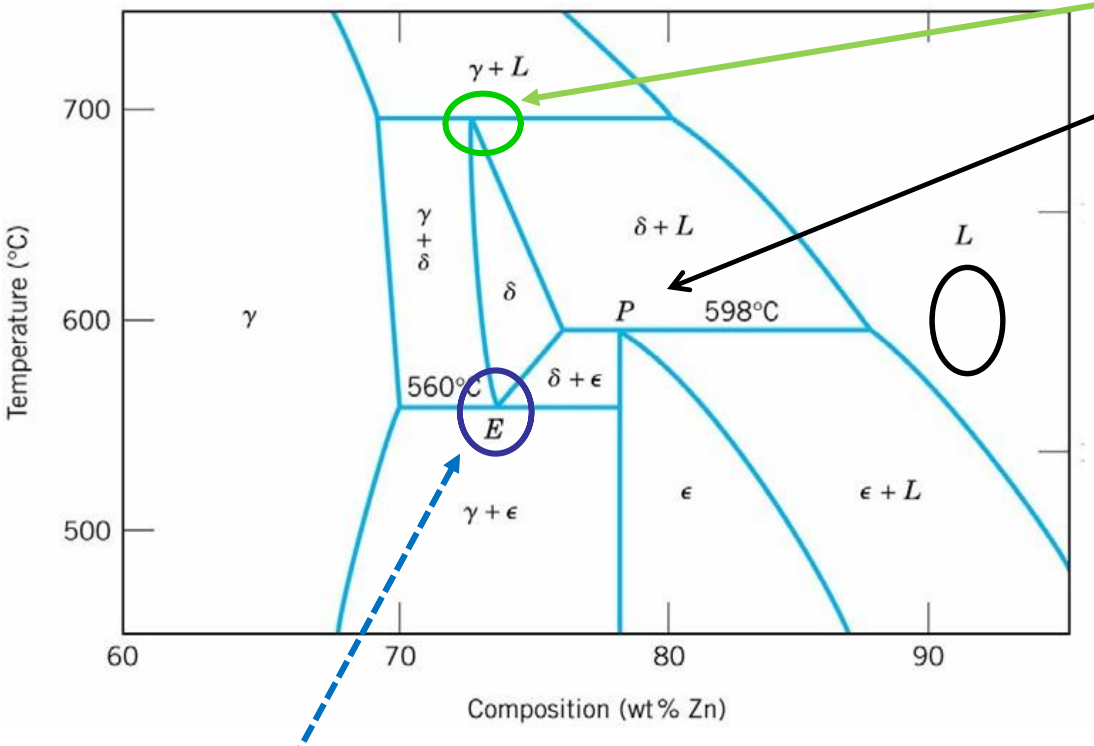
Intermediate solid solutions :
other than the two composition extremes
For example Cu-Zn phase diagram: there are six different solid solutions—**two terminal (*α* & *η*)** and **four intermediate**

- α and η are **terminal solid solutions**: exist near the concentration *extremities* of the phase diagram
- β,γ,ε,δ are **intermediate solid solutions** (or *intermediate phases*)
- new types (not eutectic) of ***invariant points*** (e.g. **E, P**)



Eutectoid and Peritectic Reactions

Cu-Zn Phase diagram



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

Point P (78.6 wt%Zn at 598°C):

three phases are in ***equilibrium*** (δ,L,ε) in this case upon **heating** a ***solid*** phase transforms to liquid and another ***solid*** phases: a ***peritectic reaction***:

$$\delta + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \varepsilon$$

$$\delta\,(76\text{wt\%Zn}) + L(88\text{wt\%Zn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \varepsilon\,(78.6\text{wt\%Zn})$$

•**Point E** (74 wt%Zn at 560°C): again (as in eutectic) ***three phases*** are in ***equilibrium*** (δ,γ,ε)

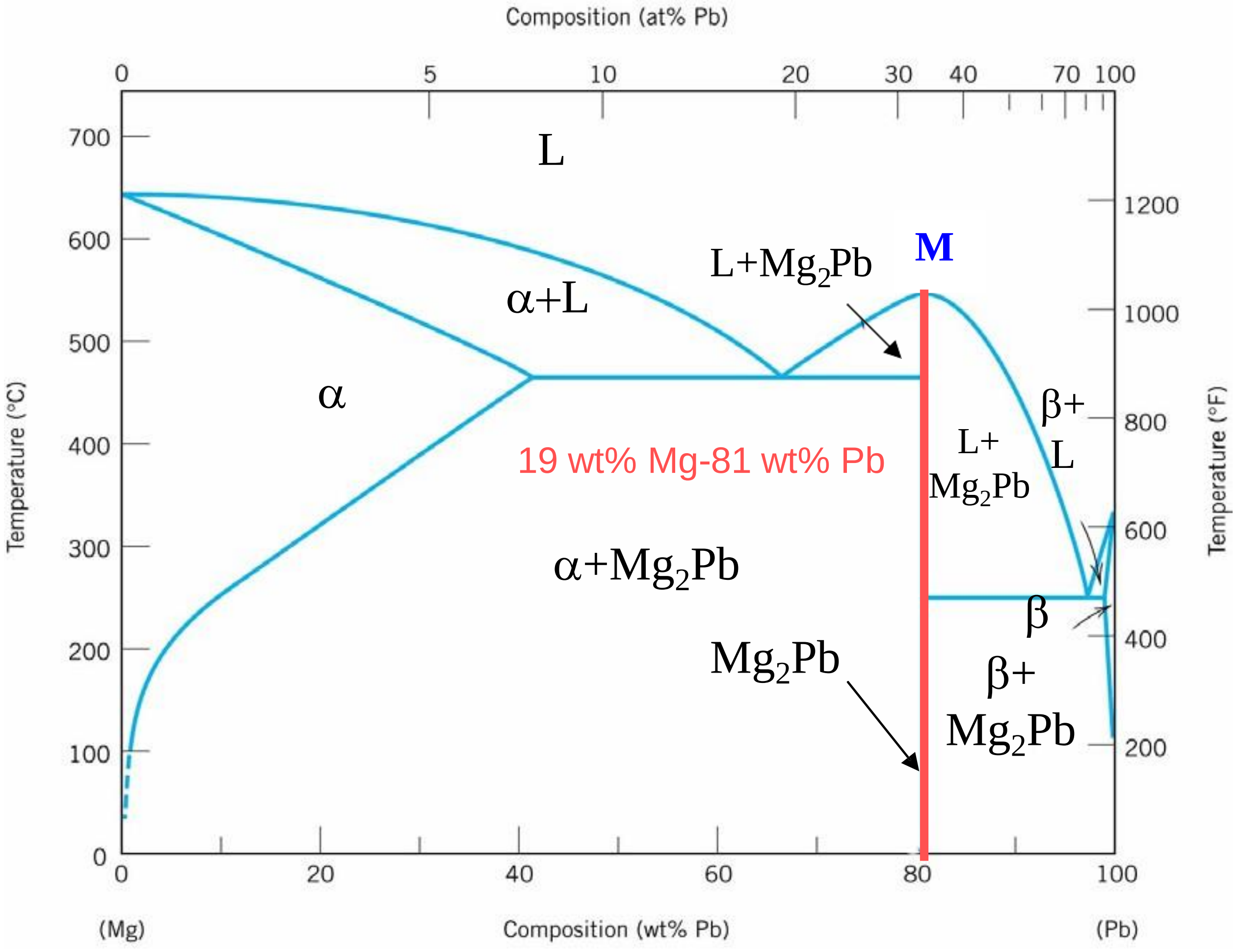
Eutectoid reaction

•but in this case upon cooling a ***solid*** phase transforms to ***two solid*** phases, so-called a ***eutectoid reaction***:

$$\delta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma + \varepsilon$$

$$\delta\,(74\text{wt\%Zn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma\,(69.5\text{wt.\%Zn}) + \varepsilon(78.6\text{wt\%Zn})$$

Equilibrium Diagrams with Intermediate Compounds



- Mg_2Pb melts at approximately 550°C
- The solubility of Pb in Mg is rather extensive
- Solubility of Mg in Pb is extremely limited

<u>Example:</u> Magnesium-Lead System

- Mg_2Pb is a ***intermetallic compound*** with a distinct chemical formula (not a solution)
- for this specific example, the intermediate compound exists by itself only at this precise composition (region of its existence has small ***width-just a line***!!)
- the phase diagram in Mg- Pb system can be thought of a ***two simple eutectic diagrams*** joined back to back, one for Mg-Mg_2Pb system and other Mg_2Pb-Pb system

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

$$\text{Solid}_1 \leftrightarrow \text{Solid}_2 + \text{Solid}_3$$

$$\gamma \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + Fe_3C$$ (For Fe-C, 727°C, 0.76 wt% C)

- Peritectic - liquid and one solid phase transform to a 2nd solid phase

$$\text{Solid}_1 + \text{Liquid} \leftrightarrow \text{Solid}_2$$

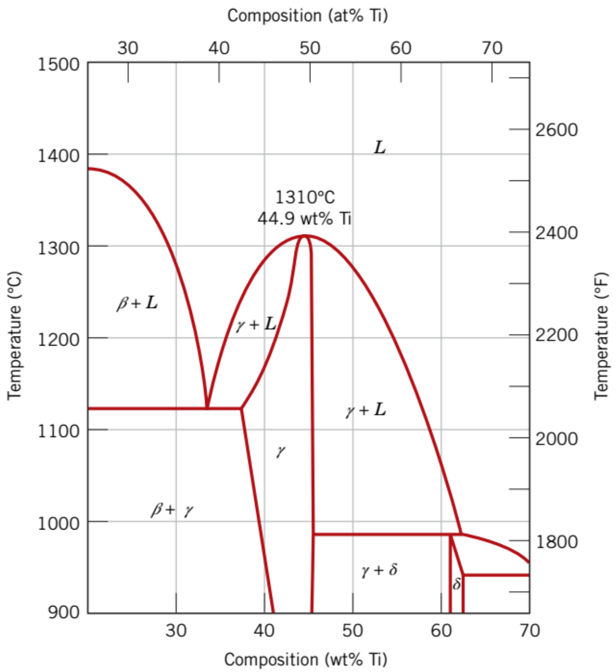
$$\delta + L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \varepsilon$$ (For Cu-Zn, 598°C, 78.6 wt% Zn)

Congruent Phase Transformations

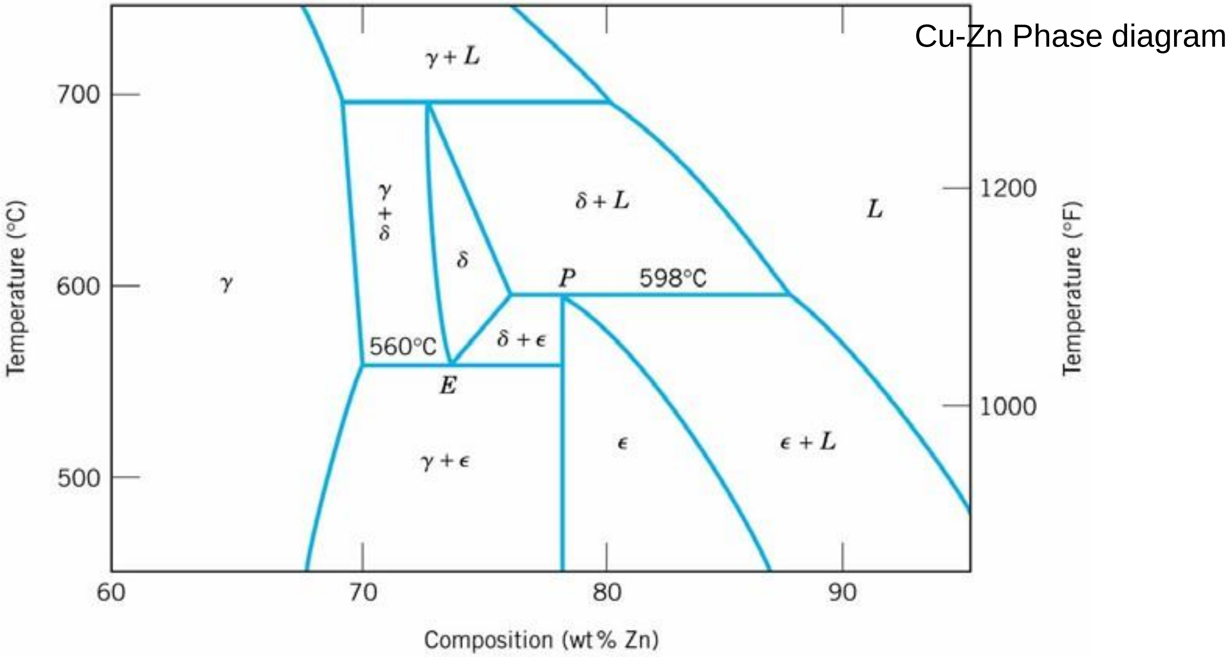
Phase transformations may be classified according to whether there is any change in composition for the phases involved.

There are no compositional alterations are said to be **congruent transformations**

Incongruent transformations, at least one of the phases experiences a change in composition.



Ni–Ti phase diagram, showing a congruent melting point for the γ-phase solid solution at 1310°C and 44.9 wt% Ti



•γ ***solid solution*** at 1310°C and C = 44.9 wt% Ti melts without changing of the composition

•***Congruent transformation:*** melting of pure metals, allotropic transformations are ***congruent***

The intermetallic compound Mg_2Pb melts congruently at the point designated *M* on the Mg-Pb phase diagram

•P melting at 598°C: $\varepsilon \Rightarrow \delta + L$ (peritectic reaction) occurs with ***changing of phase*** composition

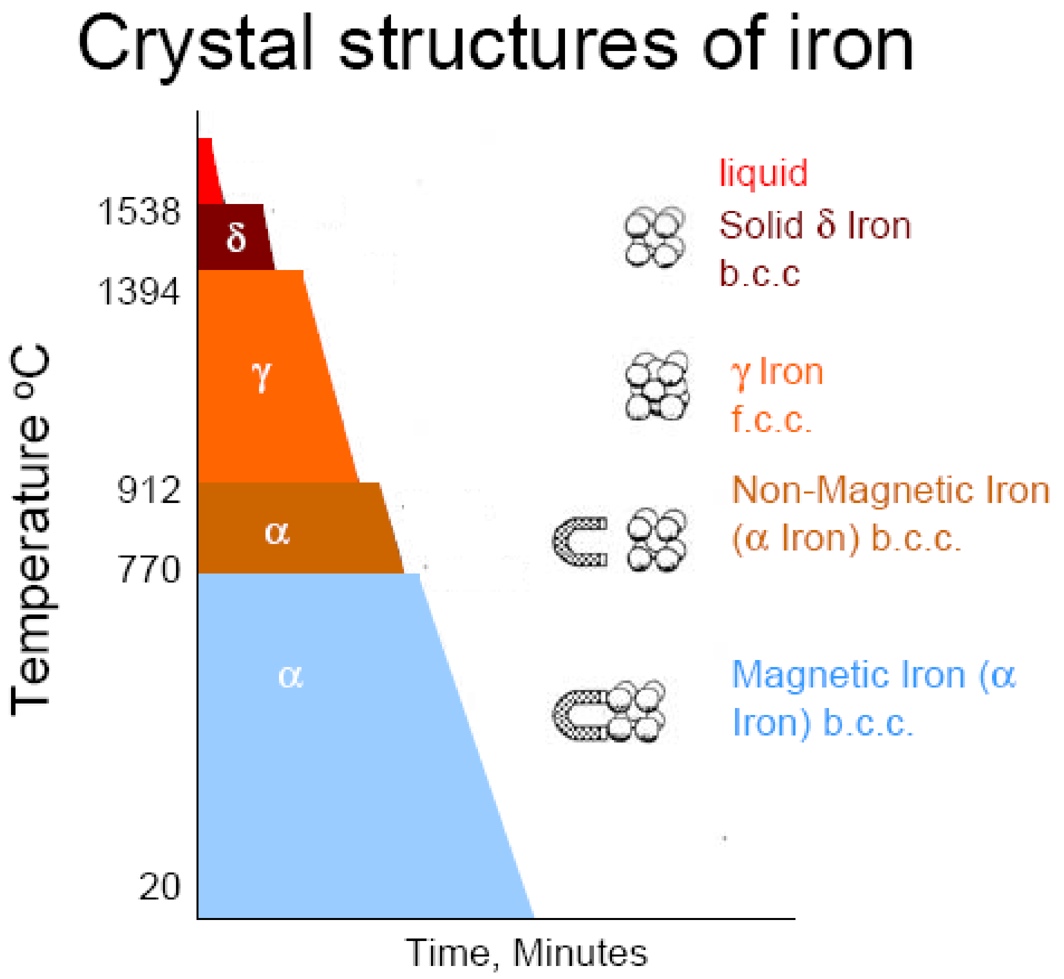
• ***Incongruent phase transformation***

•Eutectic, eutectoid and peritectic reactions are examples of incongruent transformations

Iron-Carbon System

- Pure iron when heated experiences 2 changes in crystal structure before it melts.
- At room temperature, ferrite (α iron) has a BCC crystal structure.

- Ferrite experiences a polymorphic transformation to FCC austenite (γ iron) at 912 ˚C.
- At 1394˚C austenite reverts back to BCC phase δ **ferrite** and melts at 1538 ˚C.
- Carbon is an interstitial impurity in iron and forms a solid solution with the α, γ, δ phases.
- Iron carbide (cementite or Fe_3C) an intermediate compound is formed at 6.7 wt% C.
- Typically, all steels and cast irons have carbon contents less than 6.7 wt% C.



Iron-Carbon (Fe-C) Phase Diagram

- 2 important points
  - Eutectic (A):

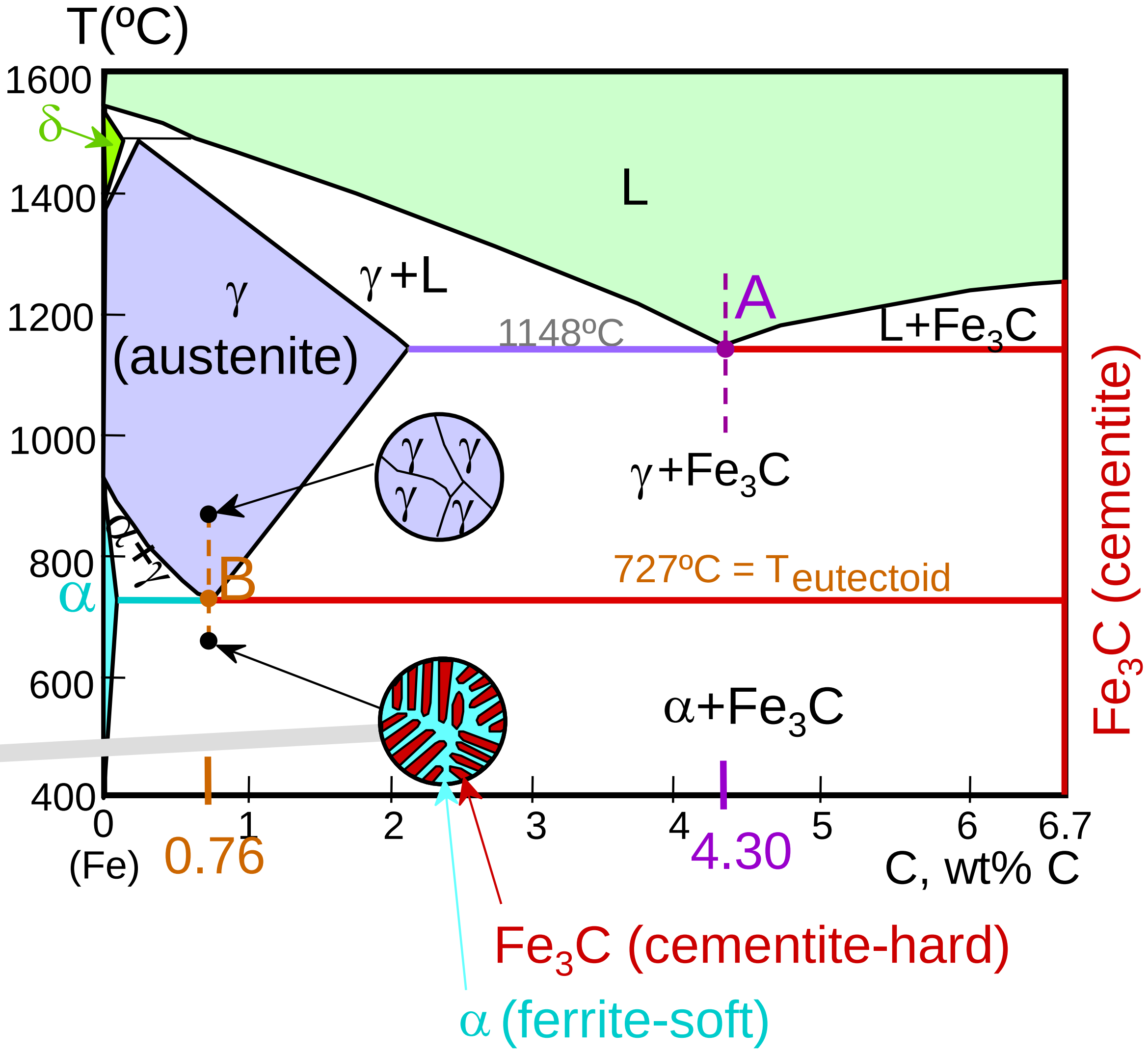
$$L \Rightarrow \gamma + Fe_3C$$

  - Eutectoid (B):

$$\gamma \Rightarrow \alpha + Fe_3C$$

120 μm

Result: Pearlite = alternating layers of α and Fe_3C phases

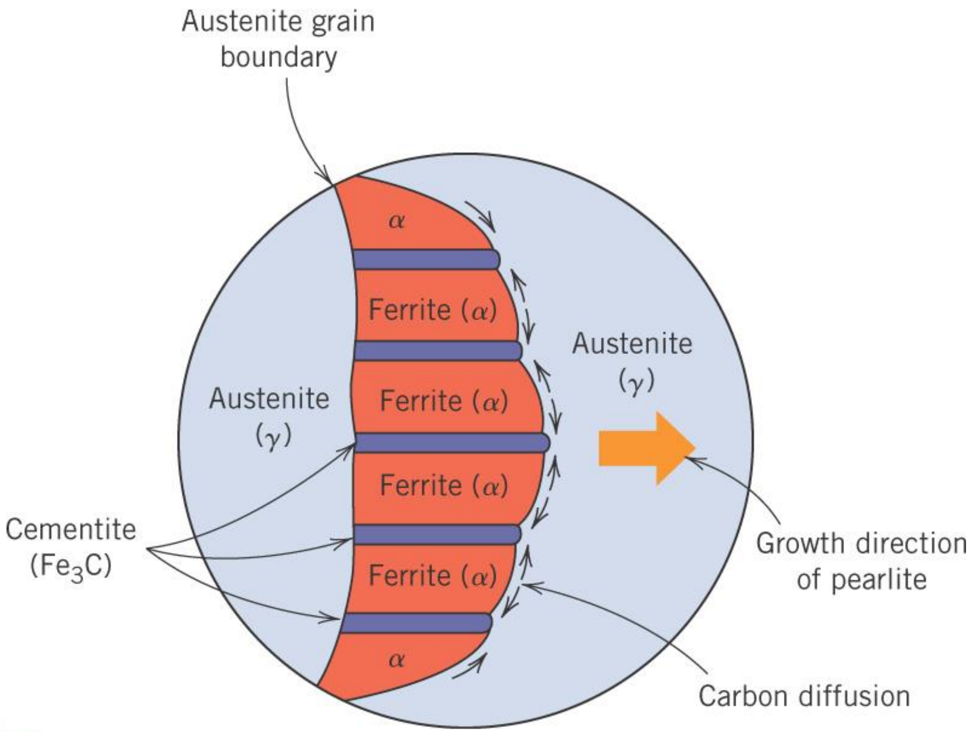


Pearlite

Eutectoid reaction:

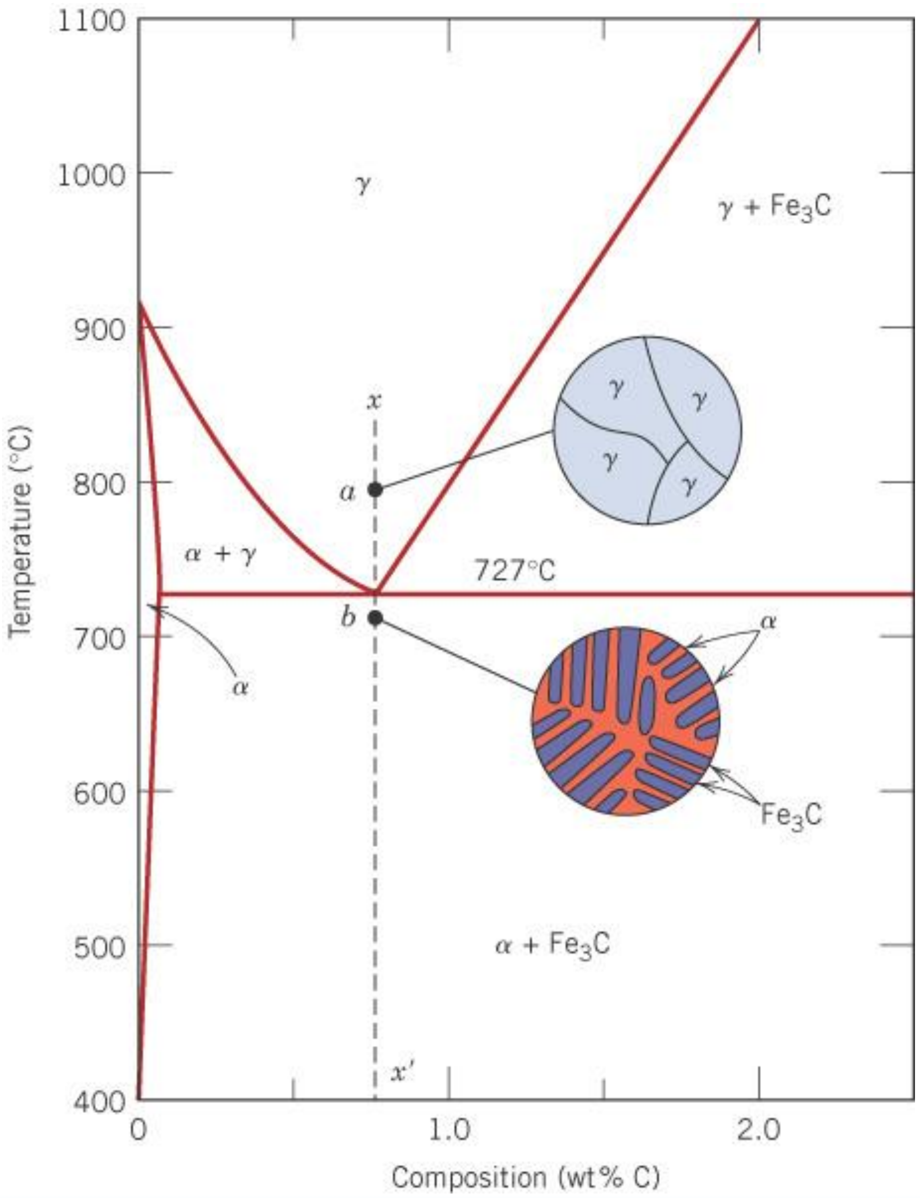
$$\gamma \leftrightarrow \alpha + Fe_3C$$

- formation of the pearlite structure
  - nucleating at γ grain boundaries
  - growth by diffusion of C to achieve the compositions of α and Fe_3C (with structural changes)
  - α lamellae much thicker

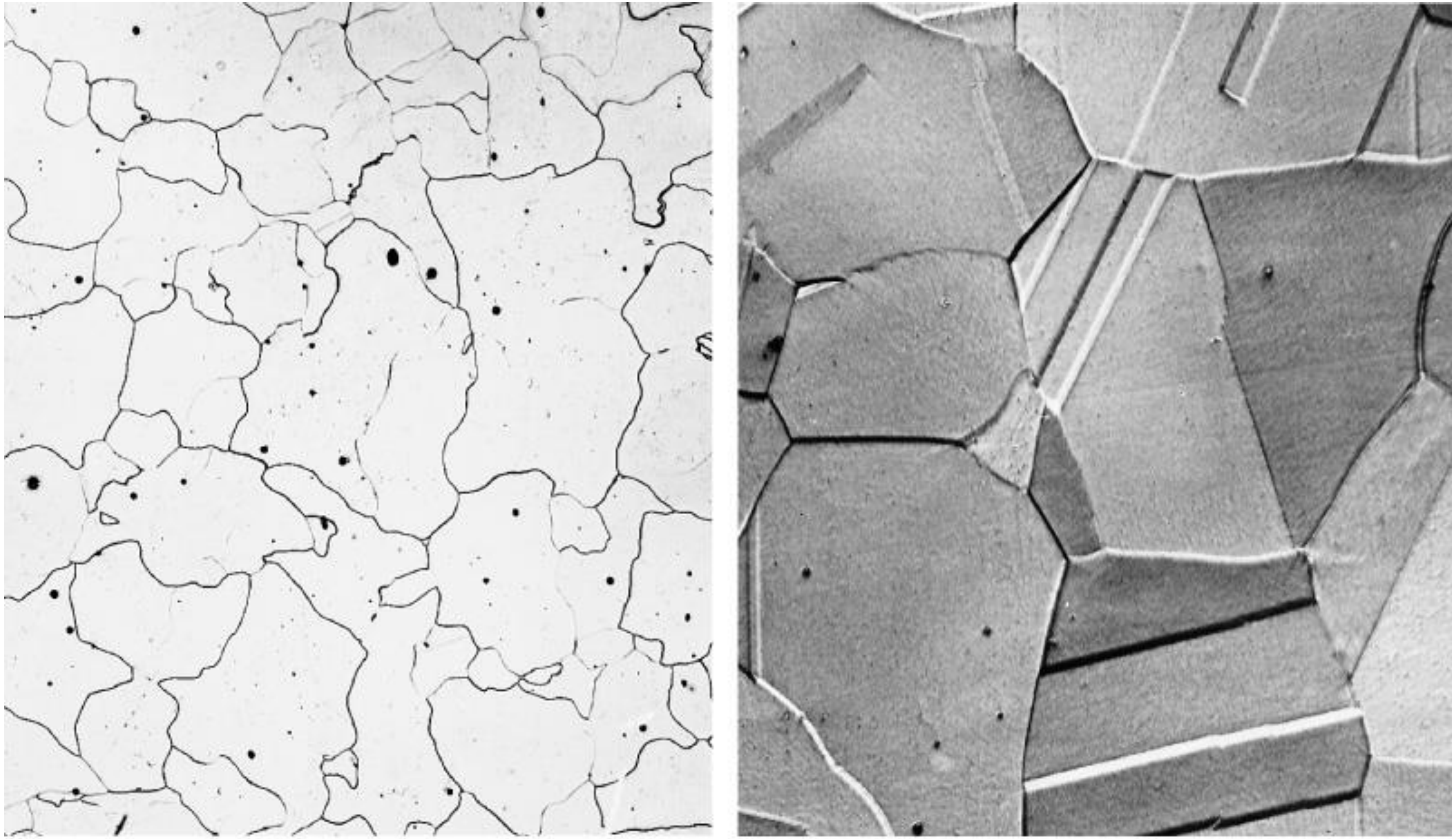


Redistribution of carbon by diffusion

Austenite – 0.76 wt% C
Ferrite - 0.022 wt% C
Cementite - 6.70 wt% C



Iron-Carbon (Fe-C) Phase Diagram



(a) (b)

Though carbon is present in relatively low concentrations, it significantly influences the mechanical properties of ferrite: (a) α ferrite, (b) austenite.

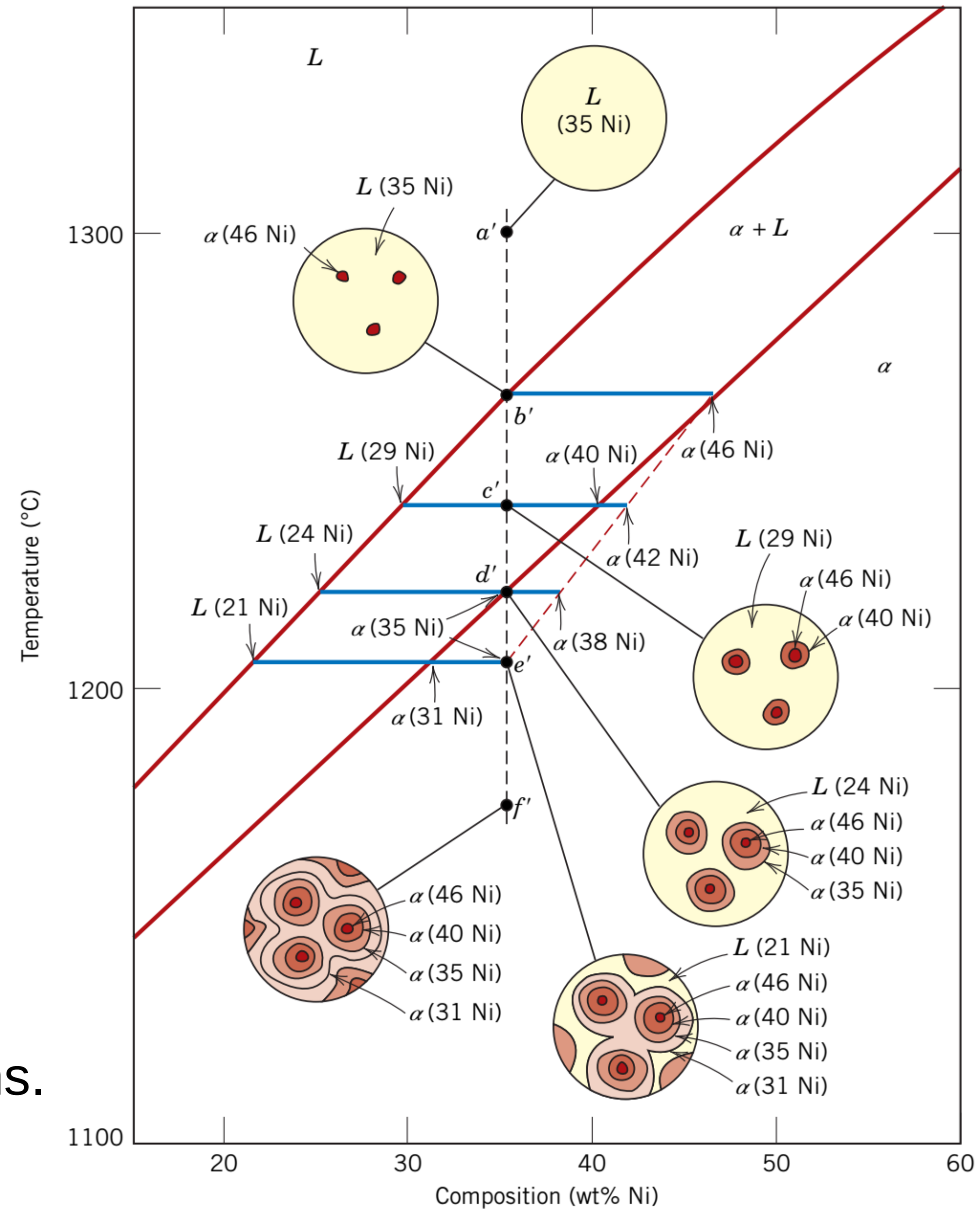
Nonequilibrium Solidification Phenomenon : Cooling

Readjustments of phases are accomplished by diffusional processes—that is, diffusion in both solid and liquid phases and also across the solid–liquid interface.

Diffusion rates (i.e., the magnitudes of the diffusion coefficients) are especially low for the solid phase and, for both phases, decrease with diminishing temperature.

In most solidification situations, cooling rates are **much too rapid** to allow these compositional readjustments and maintenance of equilibrium; consequently, microstructures other than those previously described develops.

- Development of microstructure during the non-equilibrium solidification of a 35 wt% Ni-65 wt% Cu alloy outcome:
- Segregation-nonuniform distribution of elements within grains.
- Weaker grain boundaries if alloy is reheated.



Nonequilibrium Solidification Phenomenon : Cooling

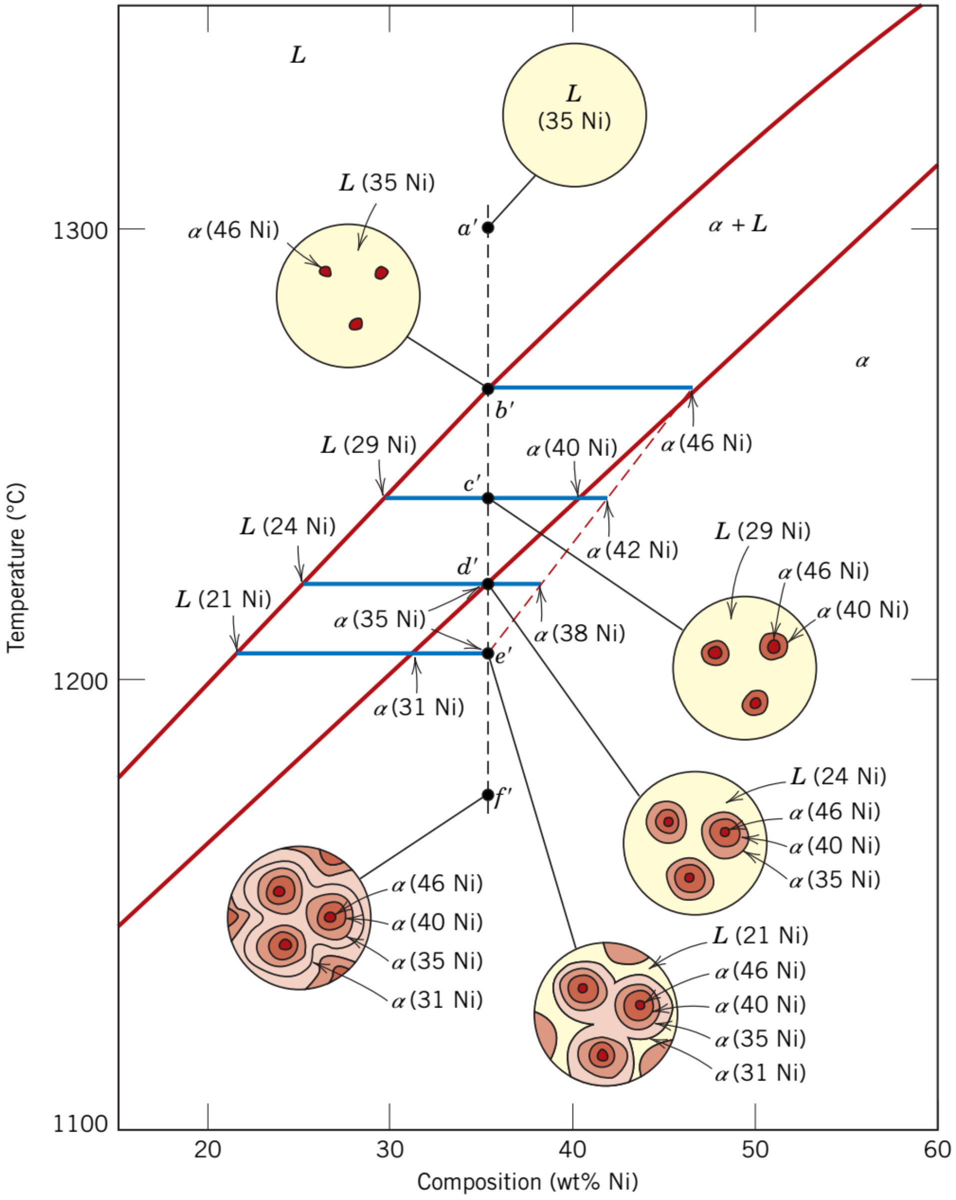
At point *b′* (~1260°C), *α*-phase particles begin to form, Composition 46 wt% Ni–54 wt% Cu [*α*(46 Ni)].

Point *c′* (~1240°C), composition shifted to 29 wt% Ni–71 wt% Cu;

- *α* phase that solidified is 40 wt% Ni–60 wt% Cu [*α*(40 Ni)]
- *α* phase at *b′* has not changed composition appreciably, because diffusion in the solid *α* phase is relatively slow
- composition of the ***α* grains**
- **continuously changes**

  (46 wt% Ni at centers to 40 wt% Ni outer)
- Volume-weighted average composition

  42 wt% Ni–58 wt% Cu [*α*(42 Ni)]
- Solidus line on the phase diagram has been shifted to higher Ni contents



The degree of displacement of the nonequilibrium solidus curve from the equilibrium one depends on the rate of cooling; the slower the cooling rate, the smaller this displacement; if the diffusion rate in the solid phase increases, this displacement decreases

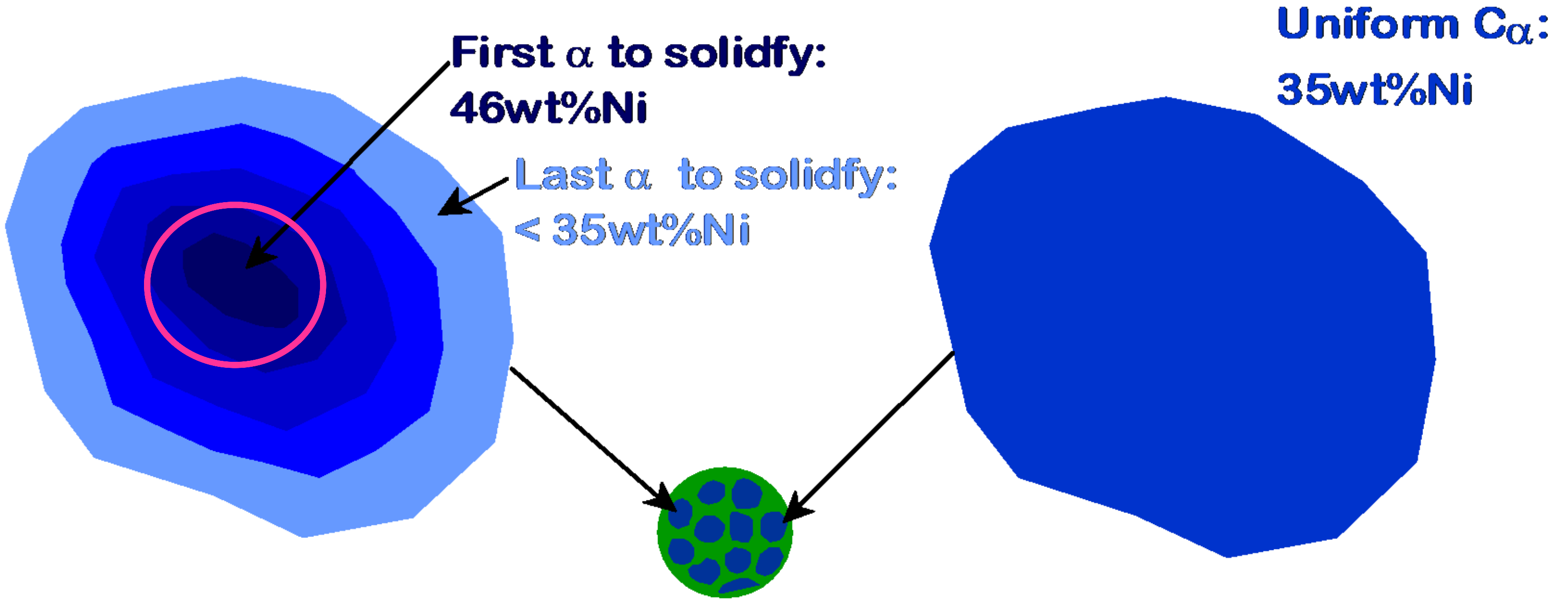
Cored vs Equilibrium Phases

- $\mathbf{C}_\alpha$ changes as it solidifies.
- Cu-Ni case:

First α to solidify has $\mathbf{C}_\alpha$ = 46wt%Ni.
Last α to solidify has $\mathbf{C}_\alpha$ = 35wt%Ni.

- Fast rate of cooling:
  Cored structure

- Slow rate of cooling:
  Equilibrium structure

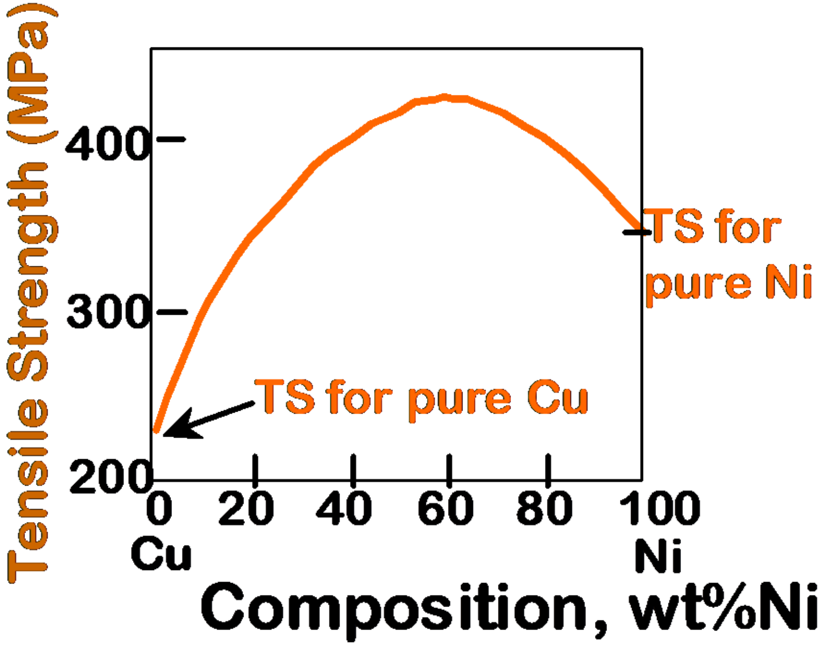


- Coring can be eliminated by means of a homogenization heat treatment carried out at temperatures below the alloy's solidus. During the process, atomic diffusion produces grains that are compositionally homogeneous.

Mechanical Properties: Cu-Ni System

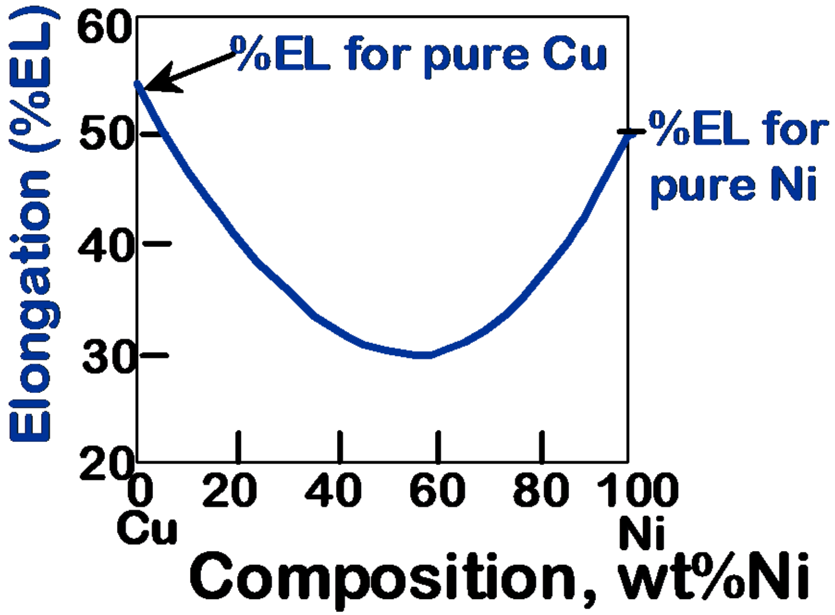
- Effect of solid solution strengthening on:

--Tensile strength (TS)



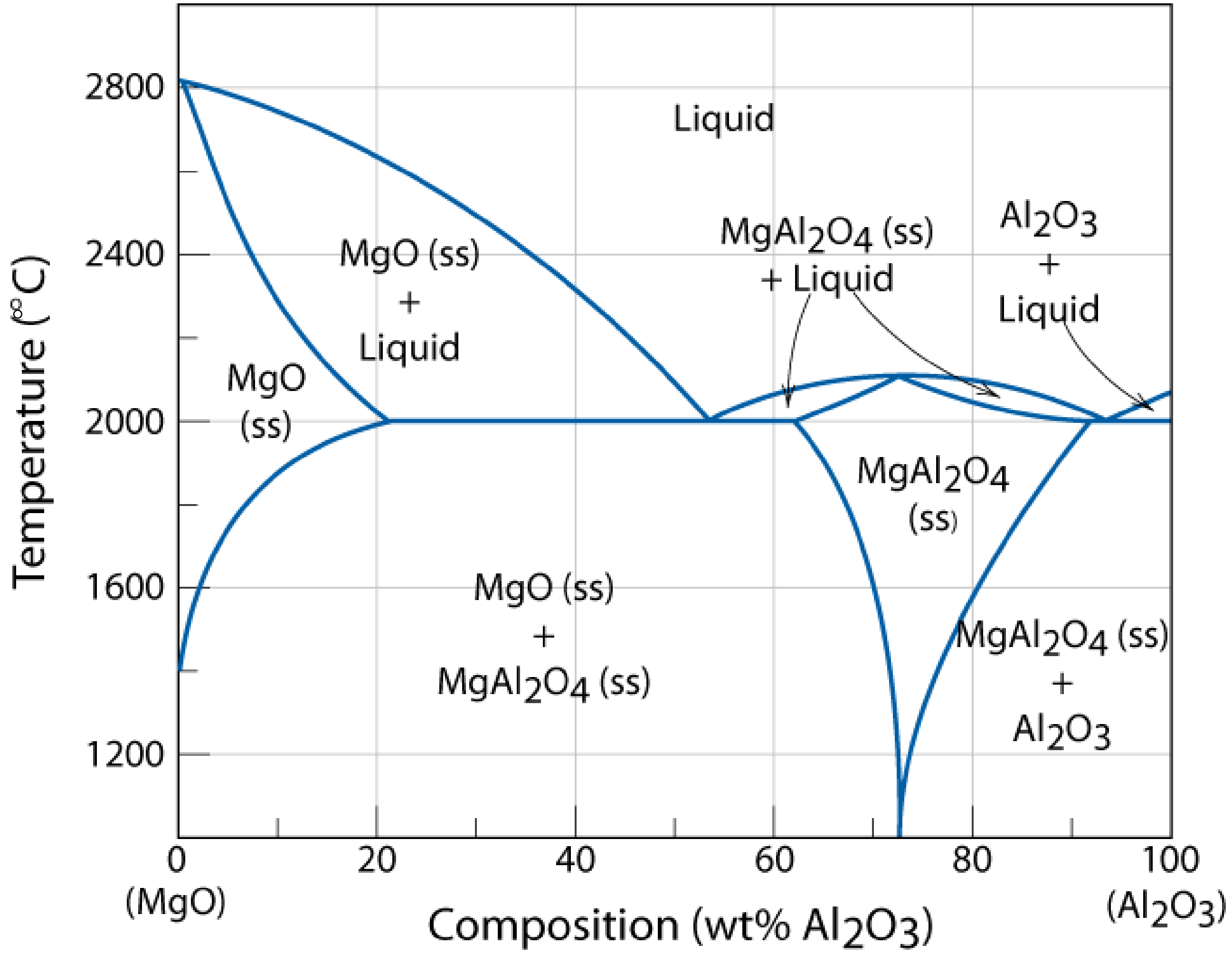
--Peak as a function of C_o

--Ductility (%EL,%AR)



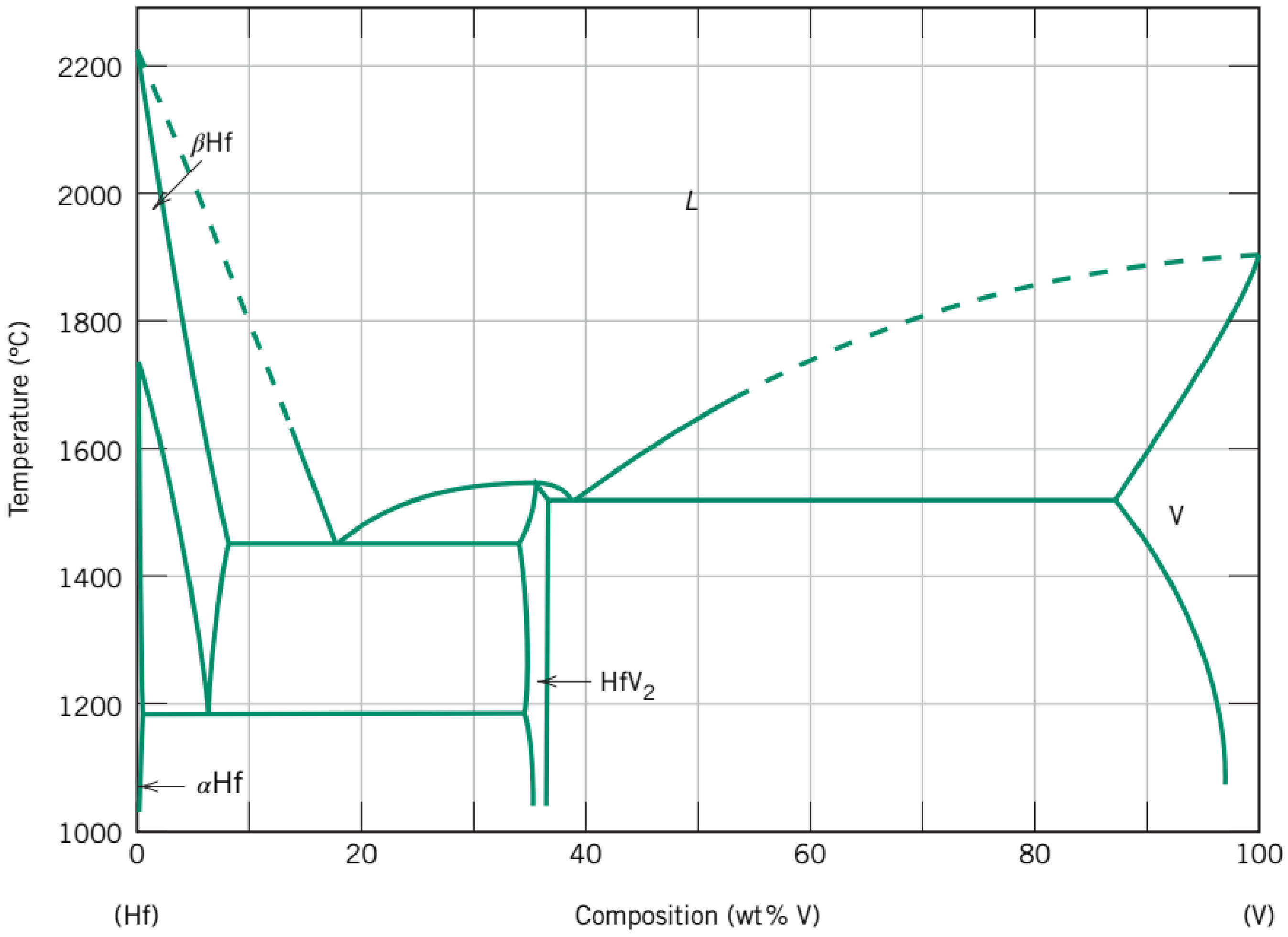
--Min. as a function of C_o

MgO-Al_2O_3 diagram:



Home Assignment

Q. No 9.3 : The following figure is the hafnium–vanadium phase diagram, for which only single-phase regions are labeled. Specify temperature–composition points at which all eutectics, eutectoids, peritectics, and congruent phase transformations occur. Also, for each, write the reaction upon cooling.

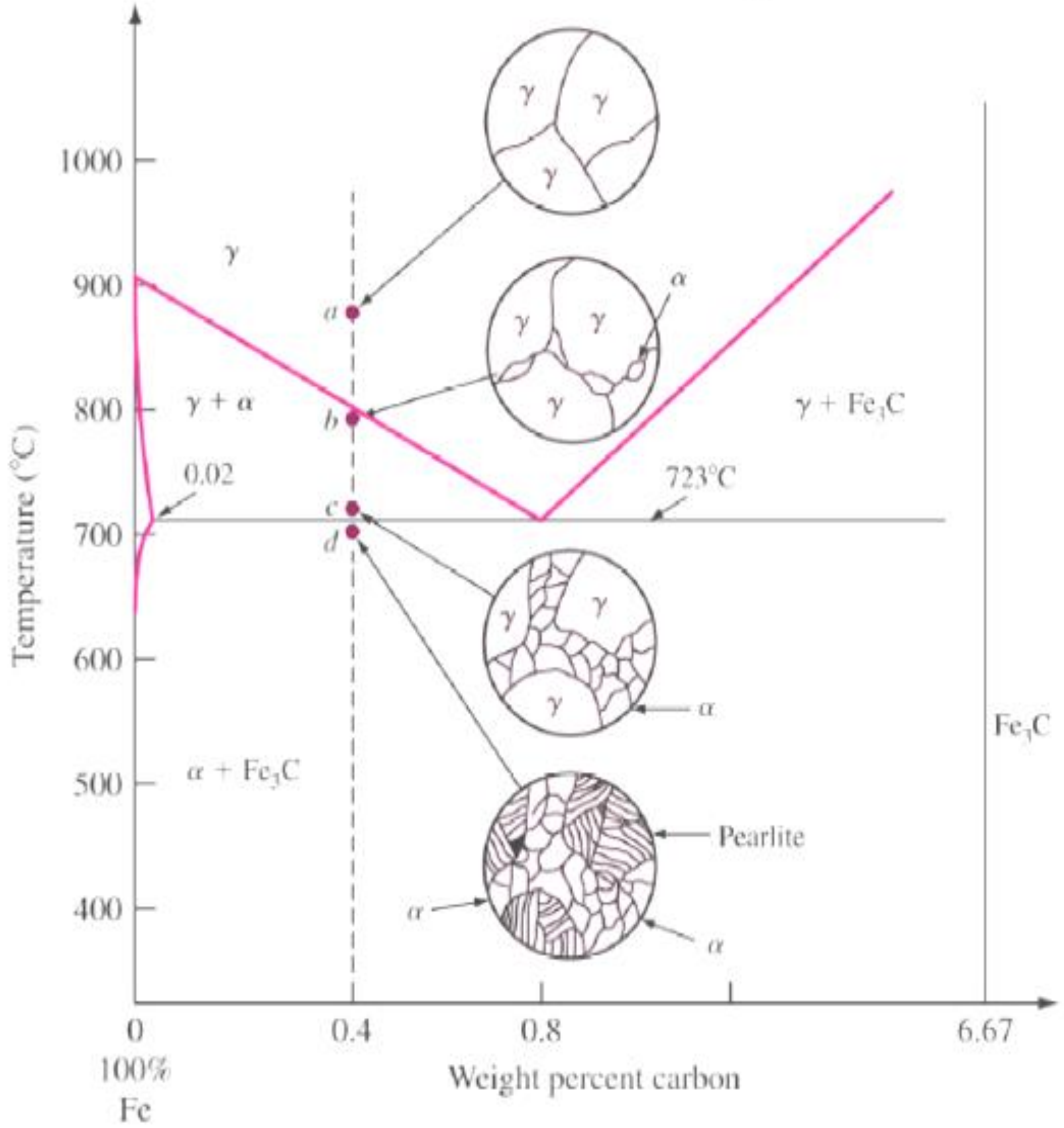


Example Problem

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 (α).

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



Criteria for Solid Solubility: Example

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

	Crystal Structure	Electro-neg	*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.