

Materials Science and Engineering (BMEE209L)

by

Dr. Mrutyunjay Panigrahi

School of Mechanical Engineering (SMEC)

VIT Chennai Campus

Chennai, Tamil Nadu, India

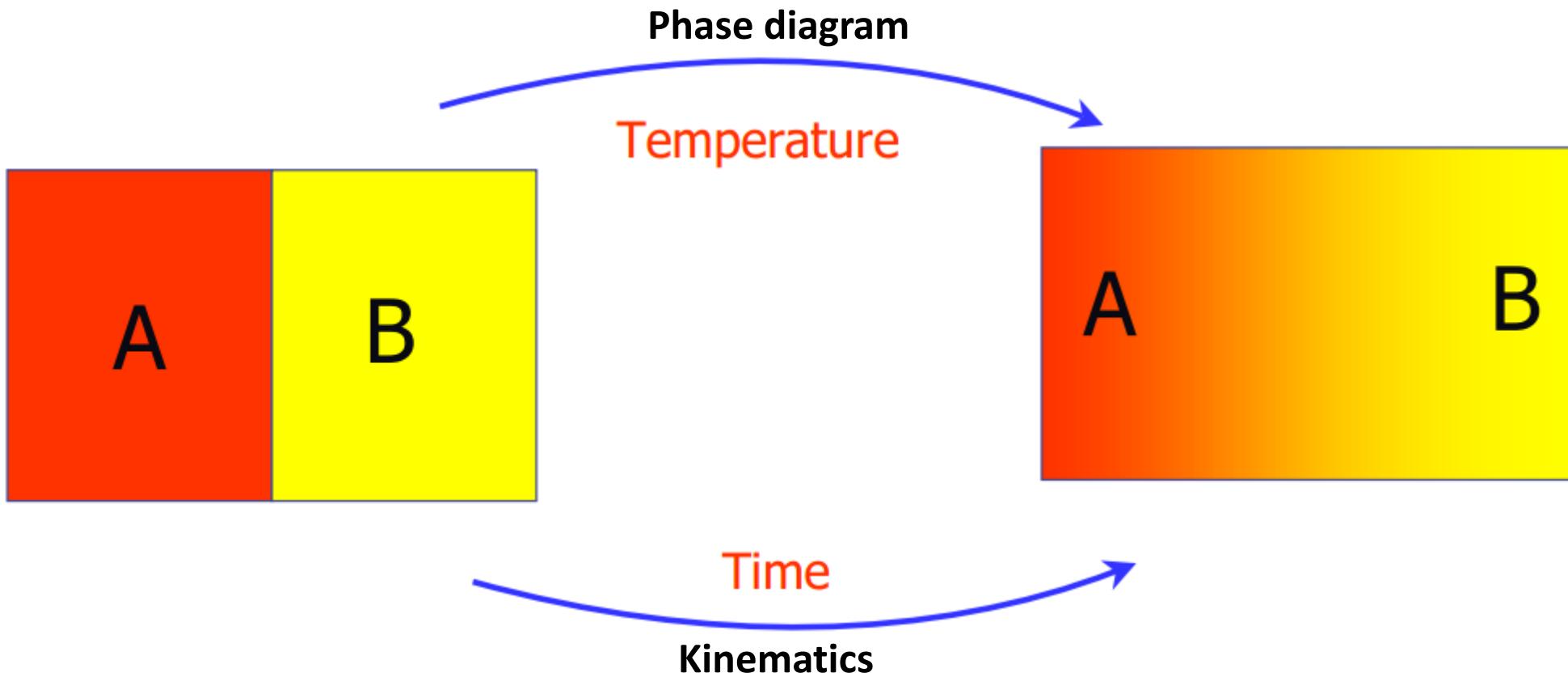


Content

□ **Module: 3 Solidification, Diffusion, and Phase Transformation** covers the following:

- Phase Diagram – Introduction
- Equilibrium Phase Diagram
- Advantages of Equilibrium Phase Diagram
- Types of Phase Diagram
- Unary or One Component Phase Diagram
- Binary Isomorphous Phase Diagram
- Gibbs Phase Rule
- Solid Solutions
- Hume-Rothery Rules
- Equilibrium Phase Diagrams – Binary Systems
- Tie Line and Lever Rule
- Equilibrium Cooling in a Cu-Ni Binary System
- Iron-Carbon Phase Diagram – Introduction
- Iron-Cementite Phase Diagram – Features
- Limitations on Fe-Fe₃C Phase Diagram
- Fe-Fe₃C Phase Diagram (Microstructural Aspects)

Phase Diagram – Motivation



New structure, concentration (mixing level)

(at what temperature? for how long?)



Phase Diagram – Introduction

- Many materials systems can exist in a variety of forms depending on the temperature, pressure and overall composition is known as **allotropy**.
- In other words, **the existence of two or more different physical forms of a chemical element.**
- A “**phase diagram**” is a graphical representation which details the form(s) of the material takes under specific conditions.
- Phase diagrams are one of the most important sources of information concerning the behavior of elements, compounds and solutions.
- They provide us with the knowledge of phase composition and phase stability as a function of temperature (T), pressure (P) and composition (C).
- Furthermore, they permit us to study and control important processes such as phase separation, solidification, sintering, purification, growth and doping of single crystals for technological and other applications.
- Although phase diagrams provide information about systems at equilibrium (**equilibrium diagrams**), they can also assist in predicting phase relations, compositional changes and structures in systems not at equilibrium.



Basic Concepts

System

- Set of possible alloys from same component (e.g., iron-carbon system.)

Component

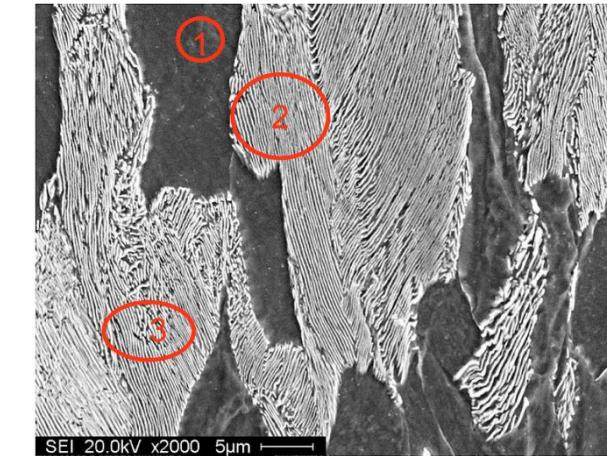
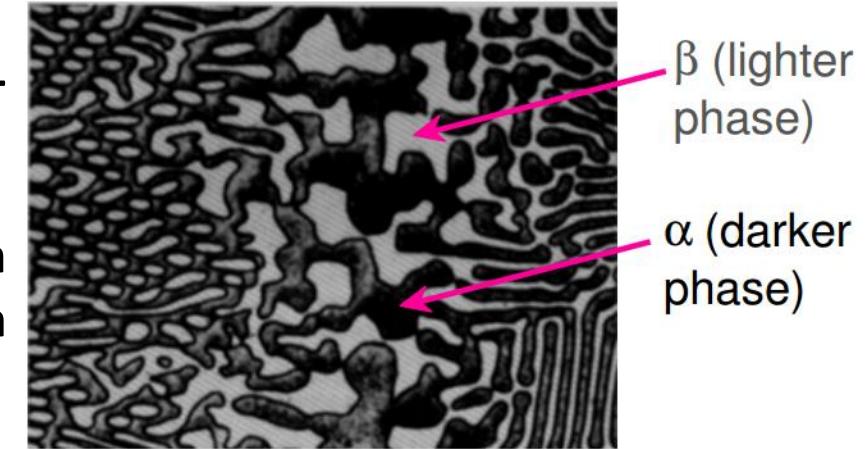
- Chemical substance or compound with fixed composition that can form part of a phase or alloy. Examples: Aluminum (Al) and Copper (Cu).

Phase

- Chemically and structurally homogeneous area that forms part of the microstructure.
- Could be formed by one or various components.
- Examples: Ferrite (solid solution Fe-C with BCC structure), austenite (solid solution Fe-C with FCC structure), α and β .

Micro-constituent

- Each one of different structures that can be observed on a polished surface of the material.
- Can be formed by one or various phases.
- 1: Ferrite
- 2 and 3: pearlite (ferrite + cementite)



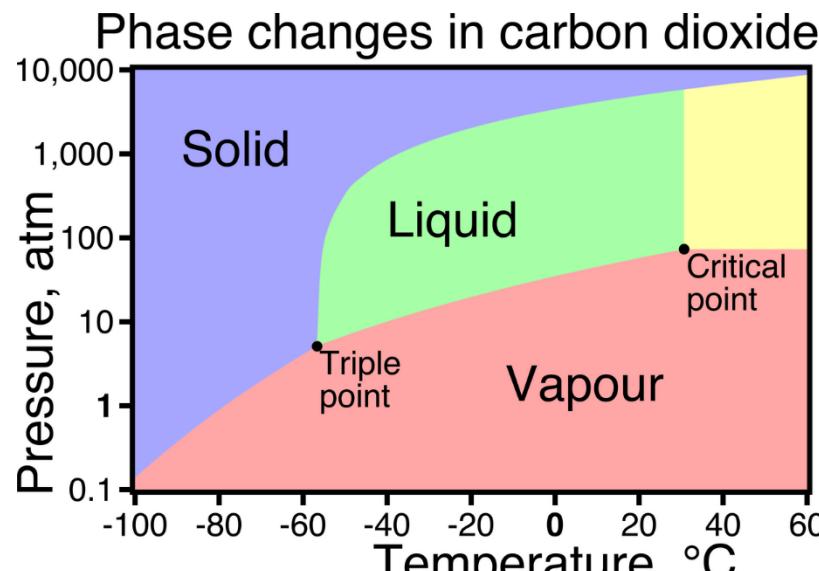
Secondary electron image of a polished and etched section of a steel helical gear.

Microstructure consists of pearlite in a ferrite matrix. Etched in 3% nital. 2000X



Equilibrium Phase Diagram

- Map of the phases in thermodynamic equilibrium that are present in a system of materials at different pressures, temperatures and compositions.
- Any material (elemental or compound) can exist as a gas, a liquid or a solid, depending on the relative magnitude of the attractive inter-atomic or inter-molecular forces vs the disruptive thermal forces.



Phase diagram of CO₂

- There is no liquid CO₂ at T_{room} and ambient pressure.
- Gradient of P/T > 0, as it is in almost all substances.
- **Triple-point:** gas, liquid and solid are at equilibrium.
- At T below the triple point CO₂ can sublime: gas → solid (dry ice).
- Above T_c = 32 °C and P_c = 73 atm → supercritical CO₂ fluid (used to extract caffeine from coffee)
- **Critical point:** a point on a phase diagram at which both the liquid and gas phases of a substance have the same density, and are therefore indistinguishable.

Contd...

Equilibrium

- ❑ Thermodynamic definition: a system is at equilibrium if its free energy is at a minimum.
- ❑ Characteristics of the system do not change with time, i.e., the system is stable.
- ❑ If you change the temperature, pressure, or composition, the free energy will change.

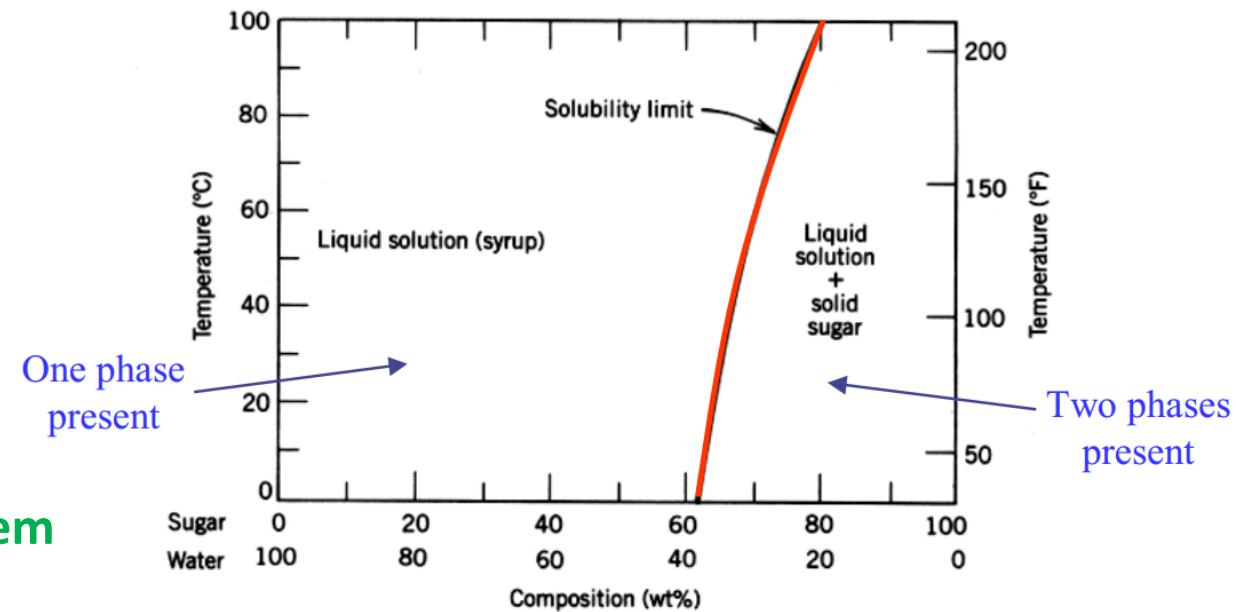
System variables

- ❑ Composition (in terms of components) "C", temperature "T" and pressure "P".

Solubility

- ❑ Solubility limit: Sugar in Water

water-sugar system



Phase Diagram



Contd...

Phase composition

- ☐ A particular phase can have variable composition (i.e., can be a solution).

Solute and Solvent

- ☐ Solvent (component present in greatest amount)
- ☐ Solute (present in minor concentration)

Solution and Mixture

- Solution: A solution is a single homogeneous phase of variable composition.
- Mixture:- A mixture is heterogeneous (more than one phase present)

Solubility limit

- ☐ Maximum allowed concentration of solute in solvent.
- ☐ Depends on species, temperature and pressure.

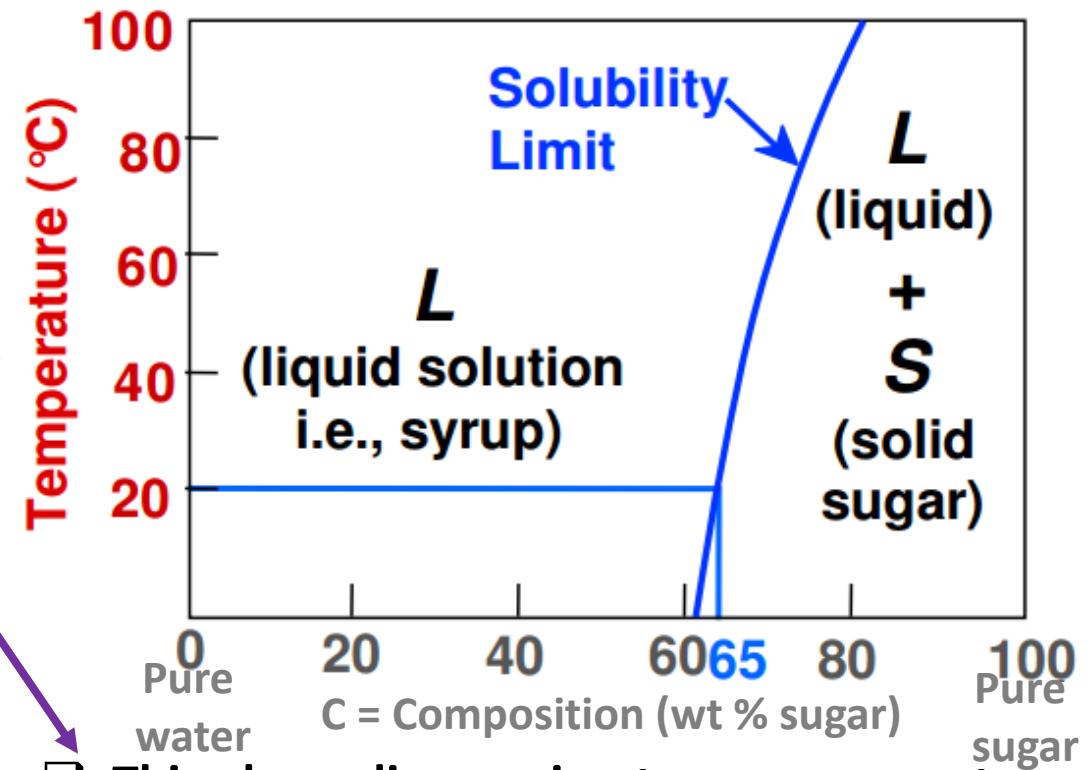
Question: What is the solubility limit at 20 °C?

Answer: 65 wt% sugar

If $C < 65$ wt% sugar: syrup

If $C > 65$ wt% sugar: syrup + sugar

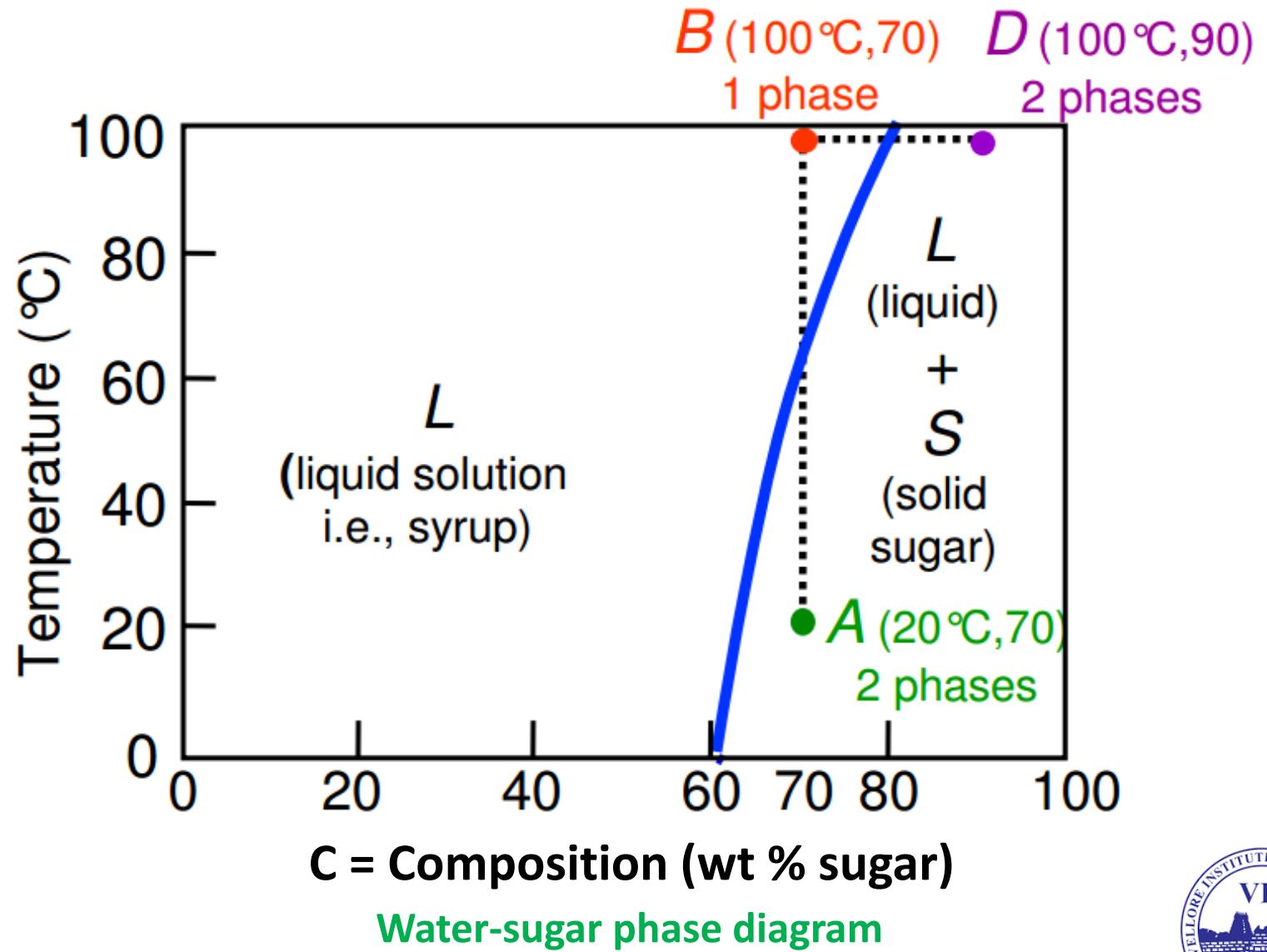
Sucrose/Water Phase Diagram



- ☐ This phase diagram is a two-component system, sugar and water.
- ☐ What are the phases in this system?
- ☐ liquid ("syrup" or sugar -in-water sol'n) and a solid (pure crystalline sugar)

Effect of Temperature and Composition

- ✓ Changing T can change of phases: path A to B.
- ✓ Changing C can change of phases: path B to D



Phase Characteristics

- A phase **does not** have to be **both** physically and chemically distinct.

- Example of a physically, but not chemically distinct phase?

- Water, ice, steam or diamond, graphite

- Example of a chemically, but not physically distinct phase?

- Oil and water (both are liquids)



Phase Equilibrium

Equilibrium

- ❑ Minimum energy state for a given T, P, and C (i.e. equilibrium state will persist indefinitely for a fixed T, P and C).

Phase equilibrium

- ❑ If there is more than 1 phase present, phase characteristics will stay constant over time.

Phase diagrams

- ❑ Tells about equilibrium phases as a function of T, P and C (here, always keep P constant for simplicity).



Advantages of Equilibrium Phase Diagram

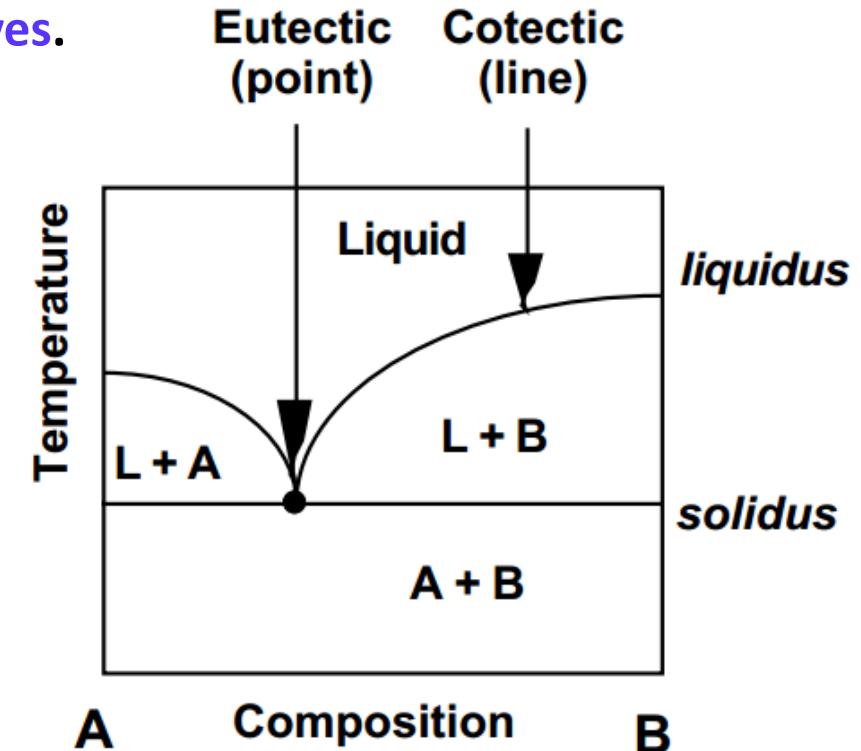
- A diagram that represents existence of different phases of a system under equilibrium is termed as **phase diagram**. It is also known as **equilibrium** or **constitutional diagram**.
- Equilibrium phase diagrams represent the relationships between temperature and the compositions and the quantities of phases at equilibrium.
- In general practice it is sufficient to consider only solid and liquid phases, thus pressure is assumed to be constant (1 atm.) in most applications.
- These diagrams **do not indicate the dynamics** when one phase transforms into another.
- However, it represents information related to microstructure and phase structure of a particular system in a convenient and concise manner.

- A phase diagram can be summarized as follows:
 - To show phases are present at different compositions and temperatures under slow cooling (equilibrium) conditions.
 - To indicate equilibrium solid solubility of one element/compound in another.
 - To indicate temperature at which an alloy starts to solidify and the range of solidification.
 - To indicate the temperature at which different phases start to melt.
 - Amount of each phase in a two-phase mixture can be obtained.



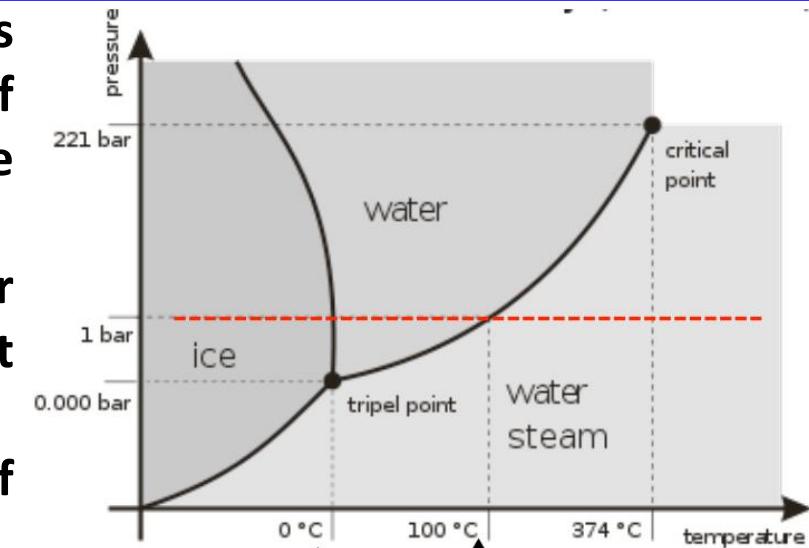
Types of Phase Diagram

- A phase diagram is actually a collection of solubility limit curves.
- Set of solubility curves that represents locus of temperatures above which all compositions are liquid are called liquidus, while solidus represents set of solubility curves that denotes the locus of temperatures below which all compositions are solid.
- Every phase diagram for two or more components must show a liquidus and a solidus, and melting of a phase occurs over a range of temperature.
- Phase diagrams are classified based on the number of components in the system.
 - Single component systems have unary diagrams
 - Two-component systems have binary diagrams
 - Three-component systems are represented by ternary diagrams, and so on.
- When more than two components are present, phase diagrams become extremely complicated and difficult to represent.



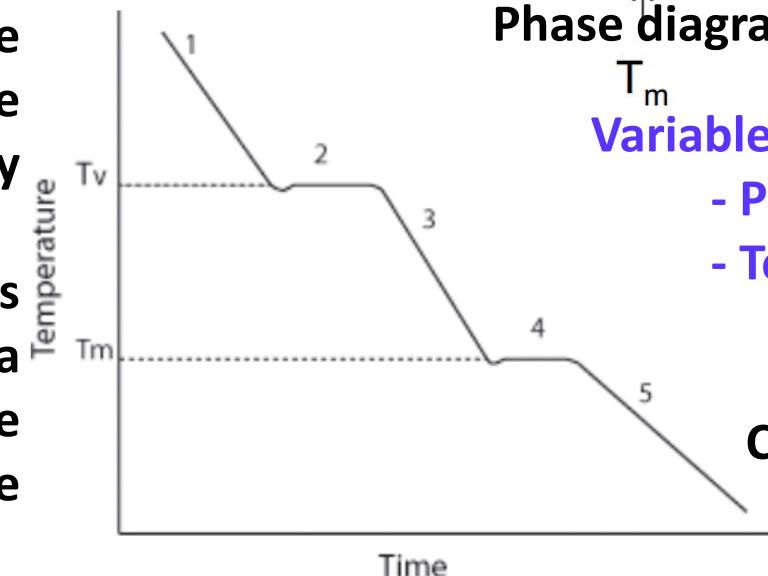
Unary or One Component Phase Diagram

- In these systems there is no composition change ($C=1$), thus only variables are temperature and pressure. Thus in region of single phase two variables (temperature and pressure) can be varied independently.
- If two phases coexist then, according to Phase rule, either temperature or pressure can be varied independently, but not both.
- At **triple points**, three phases can coexist at a particular set of temperature and pressure.
- At these points, neither temperature nor the pressure can be changed without disrupting the equilibrium i.e. one of the phases may disappear.
- A **cooling curve** is a line graph that represents the change of phase of matter, typically from a gas to a solid or a liquid to a solid. The independent variable (X-axis) is time and the dependent variable (Y-axis) is temperature.

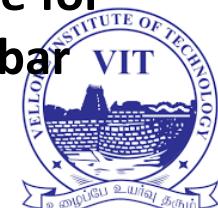


Phase diagram of water

Variables:
- Pressure "P"
- Temperature "T"



Cooling curve for
water at 1 bar



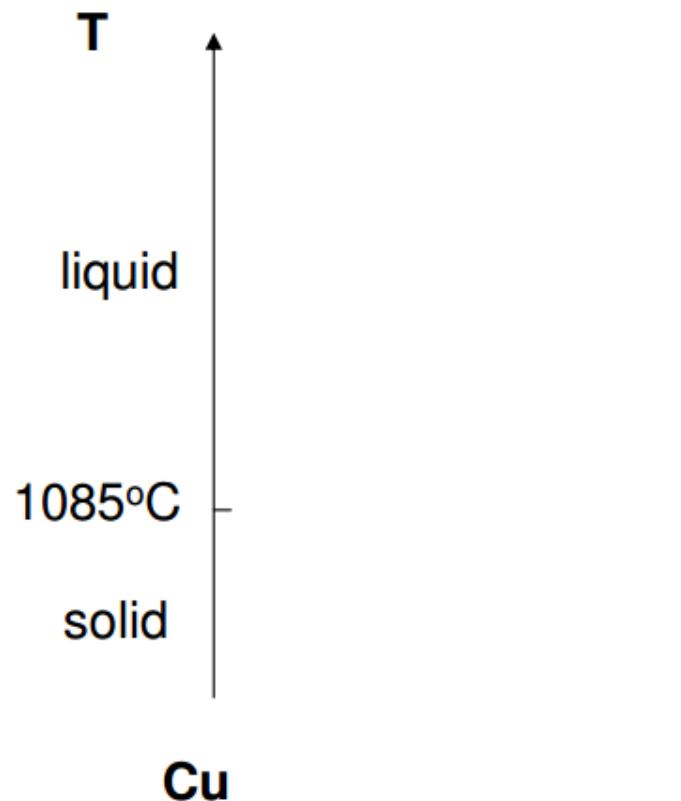
Contd...

Single component system

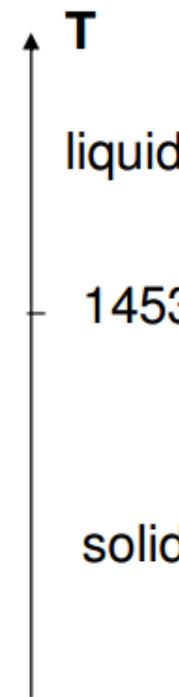
Consider 2 metals:

Cu has melting $T = 1085^\circ\text{C}$

Ni has melting $T = 1453^\circ\text{C}$



(at standard $P = 1 \text{ atm}$)



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

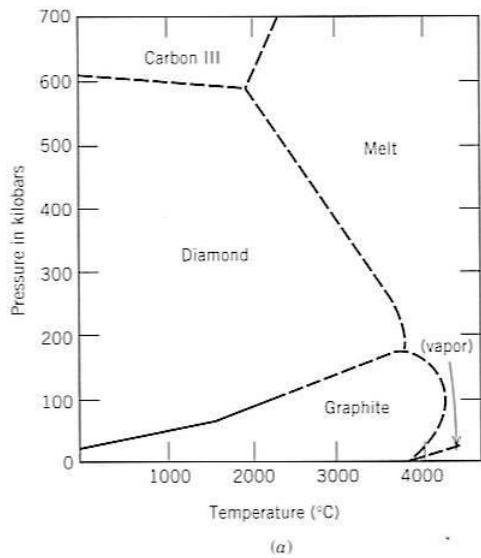
- ✓ Both have the same crystal structure (FCC) and have similar electro negativities and atomic radii ([W. Hume – Rothery rules](#)) suggesting high mutual solubility.
- ✓ Ni and Cu are totally miscible in all proportions.

What happens when Cu and Ni are mixed?

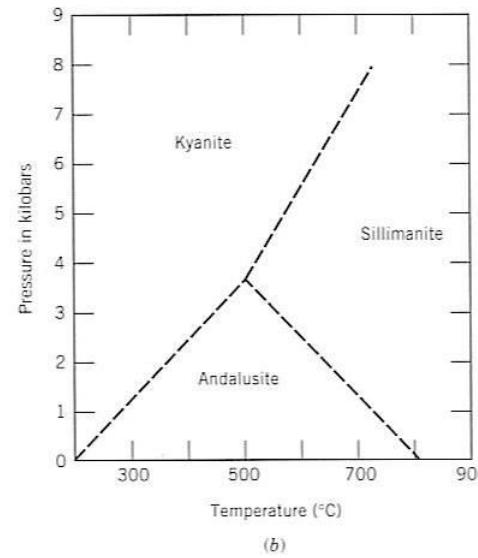


Contd...

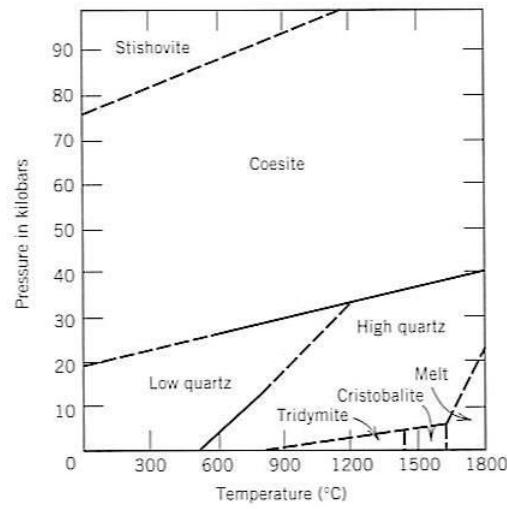
A high-pressure crystal form of silica.



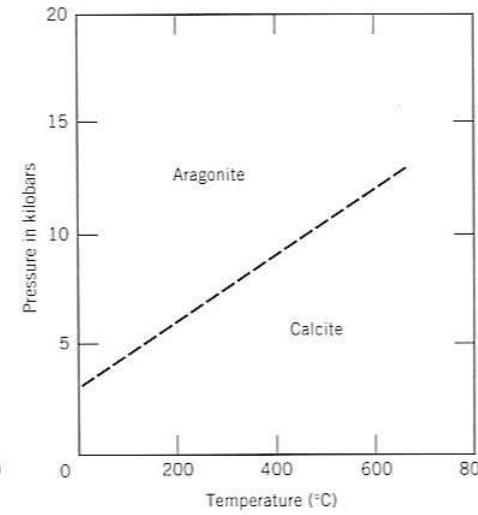
(a)



(b)



(c)



(d)

A blue aluminosilicate mineral.

A CaCO₃ mineral normally found in pearls.

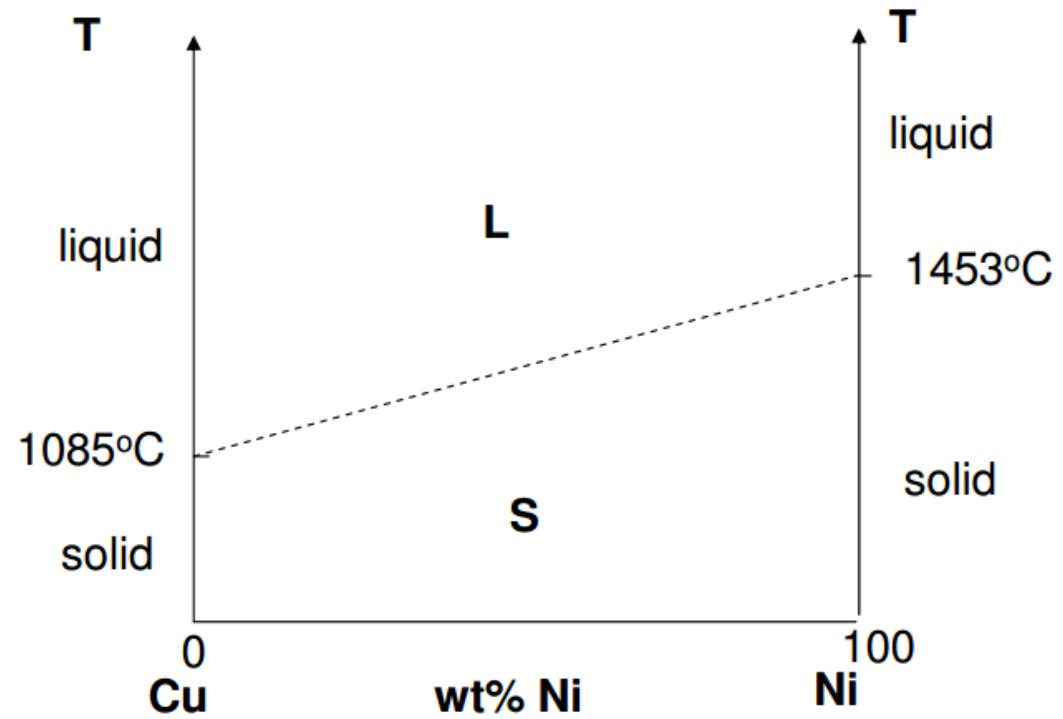


Binary Isomorphous Phase Diagram

Binary isomorphous system In the isomorphous systems, only one solid phase forms; the two components in the system display complete solid solubility.

2 components Complete liquid and solid solubility

Expect T_m of solution to lie in between T_m of two pure components

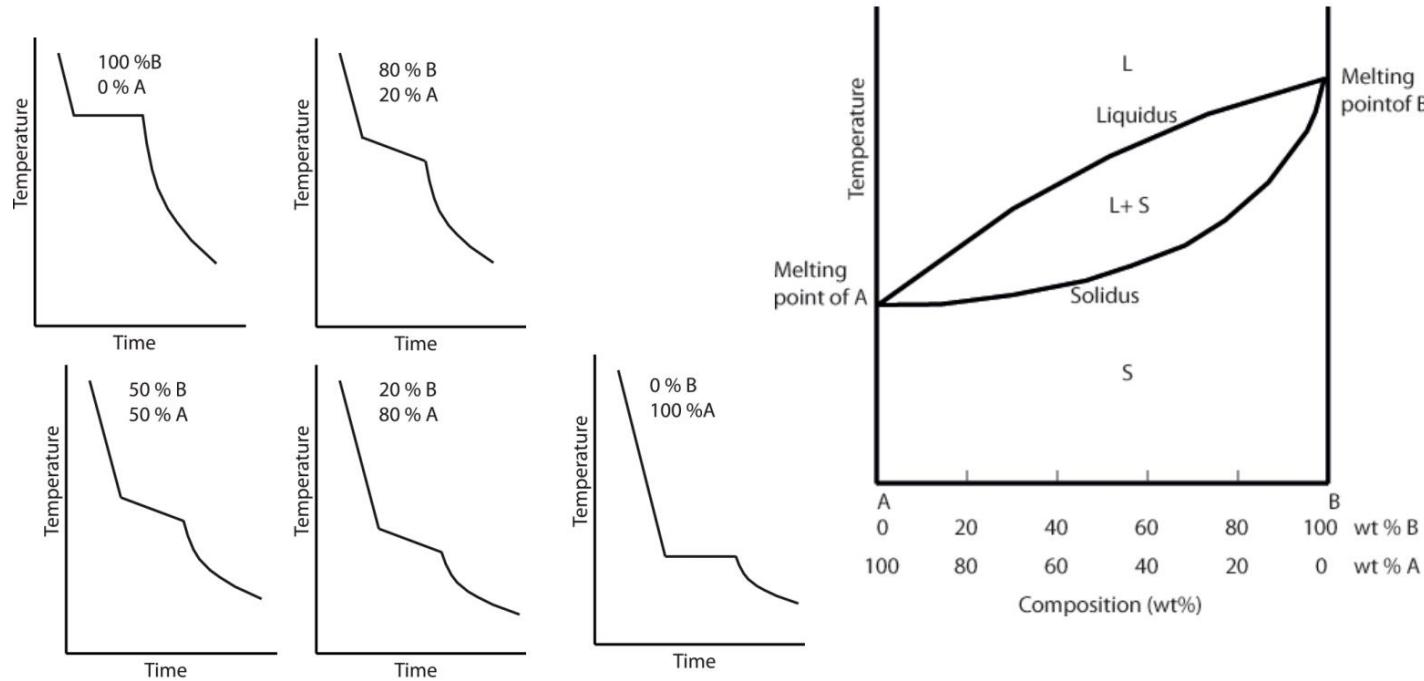


- For a pure component, complete melting occurs before T increases (sharp phase transition).
- But for multicomponent systems, there is usually a coexistence of L and S.

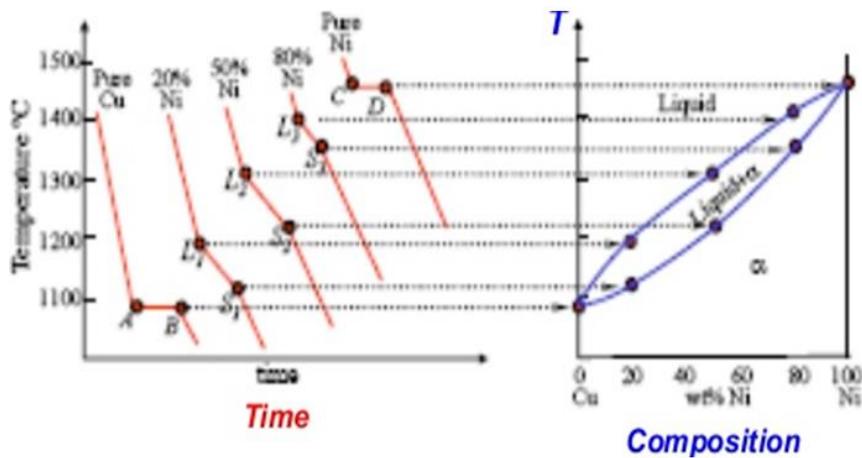


Contd...

SYSTEMS OF 2 COMPONENTS WITH COMPLETE SOLID SOLUBILITY



**Design of a phase diagram
from the cooling curves**



- The **liquidus** divides regions which are entirely liquid (at higher temperatures) from those with a mixture of liquid and solid phases.
- The **solidus** divides regions which are entirely solid (at lower temperatures) from those with a mixture of liquid and solid phases.



Contd...

Complete Solid Solubility

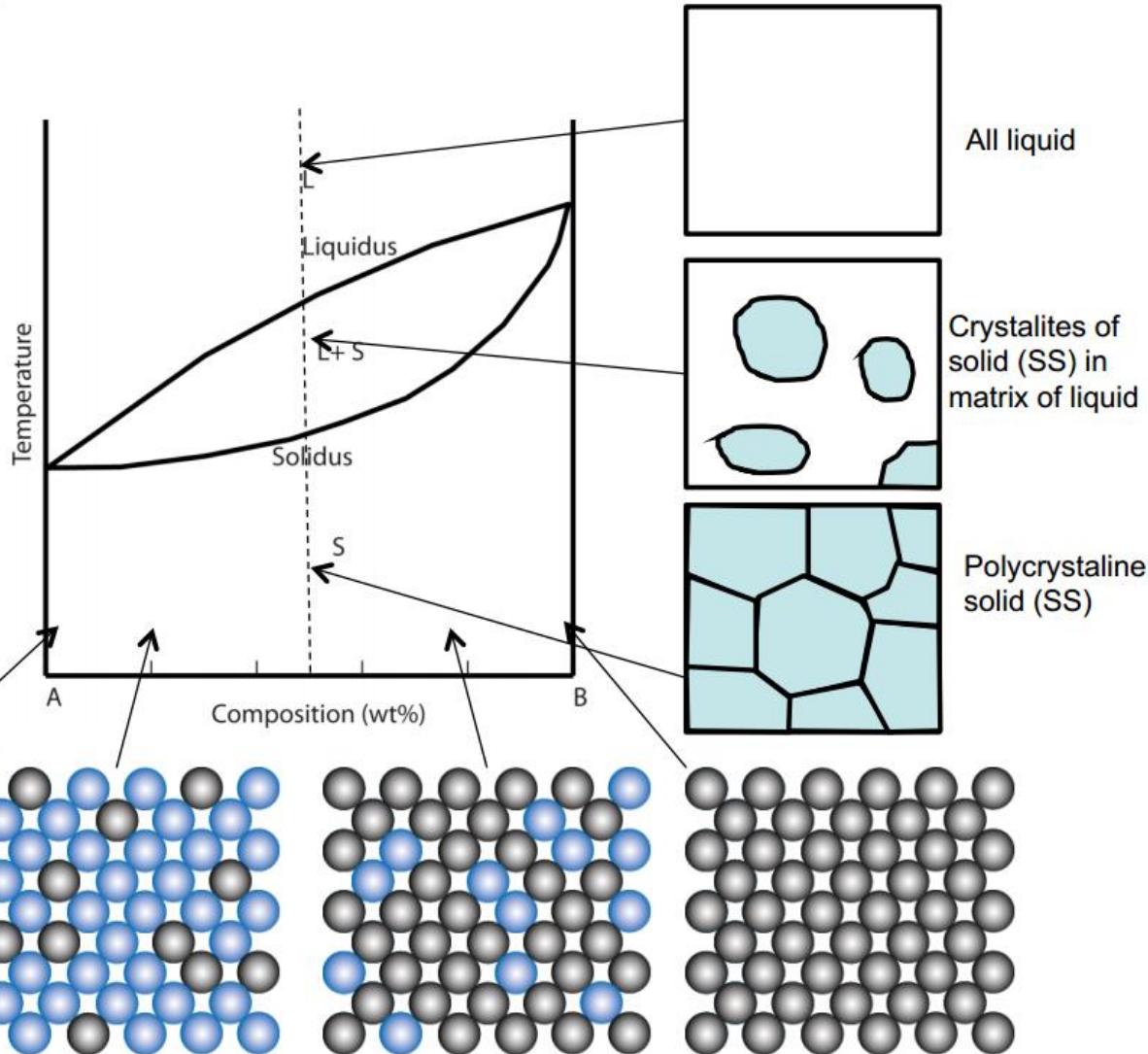
Polycrystalline single phase material.

Its microstructure is not different from that of the pure metal.

When solute is added, T_m is modified

Complete solubility in solid state.

The alloy **does not solidify at a constant temperature** but at a range of temperatures



Gibbs Phase Rule

$$F = C - P + N$$

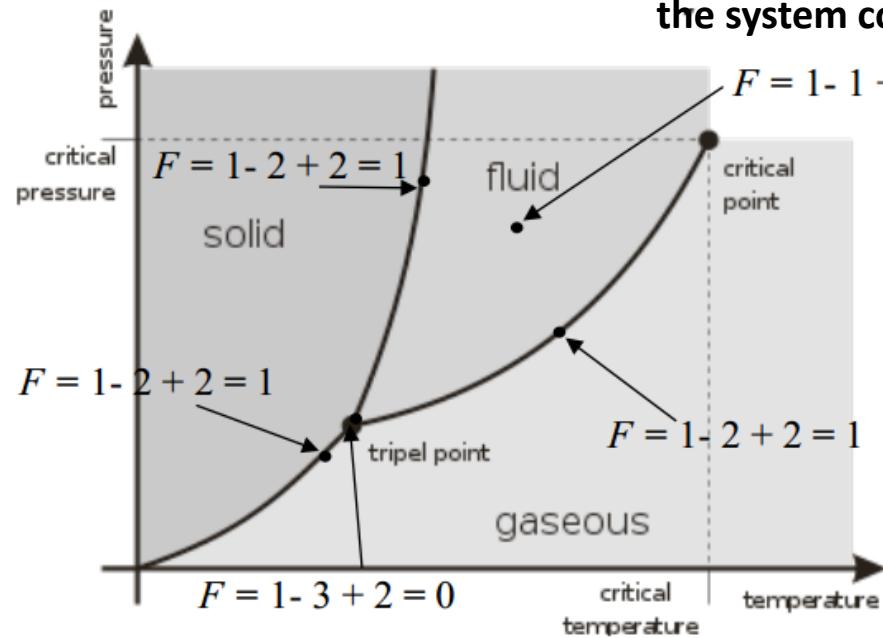
F = Degrees of freedom (No. of independent variables available to the system)

C = No. of components

P = No. of phases

N = No. of noncompositional variables (e.g. pressure and temperature)

$$F = C - P + 2$$



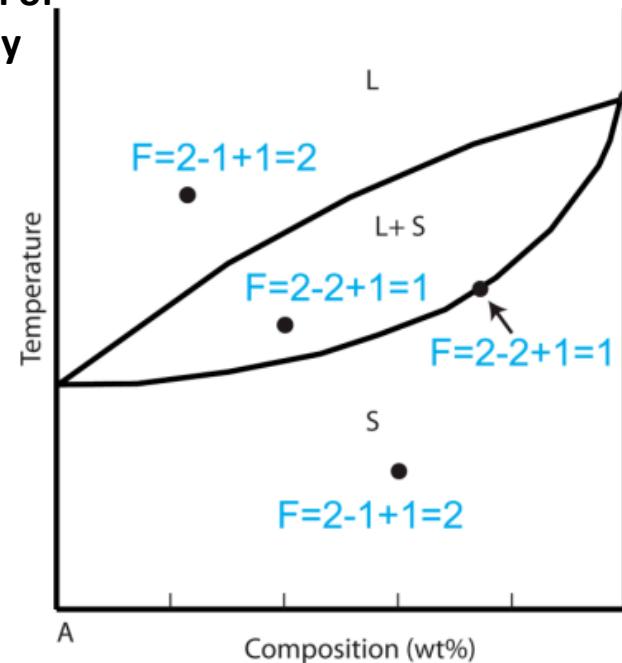
$N = 1$ or 2 for T (temperature) and P (pressure)

$N = 1$ if P = constant or T = constant

(HINT: P is usually constant so N is usually 1)

For routine processing of materials, we can consider the pressure to be fixed at 1 atm:

$$\Rightarrow F = C - P + 1$$



- Josiah Willard Gibbs – 18th century physicist
- Based on thermodynamics
- Predicts the number of phases that will coexist within a system at EQUILIBRIUM
- Does not apply in non-equilibrium situations

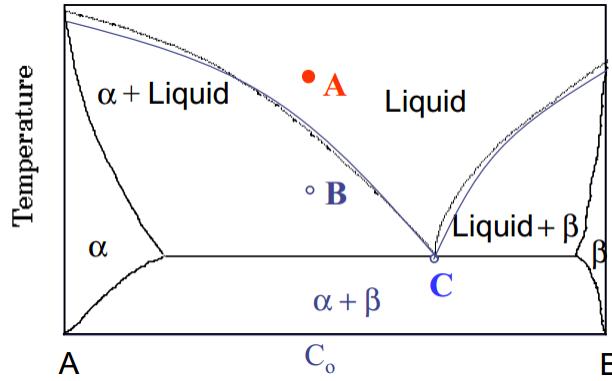


Gibbs Phase Rule – Some More Examples

- These diagrams constitutes two components, e.g.: two metals (Cu and Ni), or a metal and a compound (Fe and Fe₃C), or two compounds (Al₂O₃ and Si₂O₃), etc.
- Binary diagrams are usually drawn showing variations in temperature and composition only. It is also to be noted that all binary systems consist only one liquid phase i.e. a component is completely soluble in the other component when both are in liquid state.
- Hence, binary systems are classified according to their solid solubility. If both the components are completely soluble in each other, the system is called **isomorphous system**, eg. Cu-Ni, Ag-Au, Ge-Si, Al₂O₃-Cr₂O₃.
- Extent solid solubility for a system of two metallic components can be predicted based on Hume-Ruthery conditions.



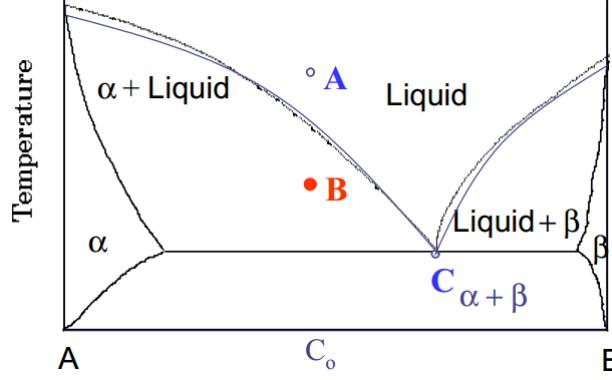
Contd...



Point: A

$$P + F = C + 1 \quad (N = 1, p = \text{const.})$$

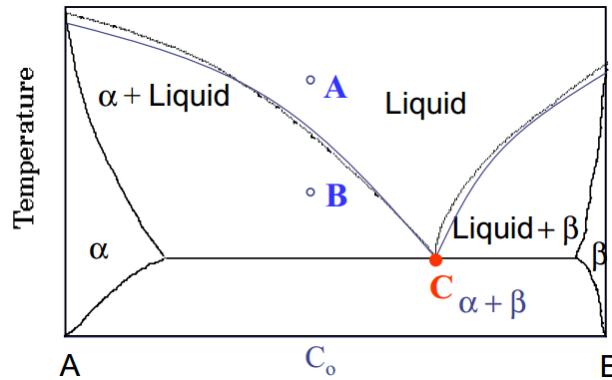
$$C = 2 \text{ (A and B)} \quad P = 1 \text{ (liquid)} \rightarrow F = C+1-P = 2+1-1=2$$



Point: B

$$P + F = C + 1 \quad (N = 1, p = \text{const.})$$

$$C = 2 \text{ (A and B)} \quad P = 2 \text{ (liquid and } \alpha\text{)} \rightarrow F = C+1-P = 2+1-2 = 1$$



Point: C

$$P + F = C + 1 \quad (N = 1, p = \text{const.})$$

$$C = 2 \text{ (A and B)} \quad P = 3 \text{ (liquid and } \alpha\text{ and } \beta\text{)} \rightarrow F = C+1-P = 2+1-3 = 0$$

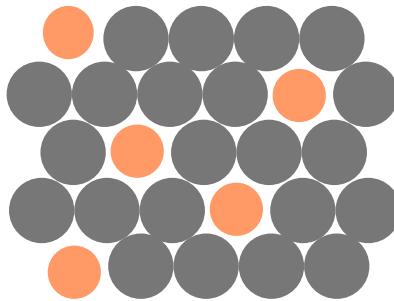


Solid Solutions

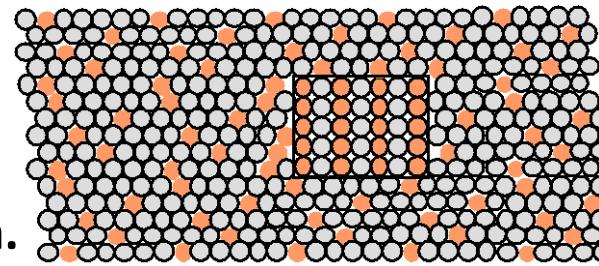
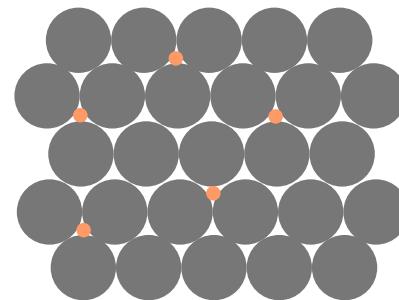
Alloys

- In real world we don't work with pure metals but rather we work with alloys.
- Alloys are “metal soup” in which impurities have been added intentionally (or unintentionally through processing) to produce specific properties.
- An alloy is a phase comprising of one or more components.
- Generally there are **three distinguished alloys**:
 - Substitutional – Solute substitutes the solvent in the crystal lattice without structural changes.
 - Interstitial – Solute does not occupy the sites in the lattice of the solvent but resides in crystallographic pores.
 - Transformational – A complete new lattice is formed. Usually occurs as a result of intermetallic compound formation.

Solid solutions



Substitutional solid soln. (e.g., Cu-Ni, Cd-Mg, Mo-W)
Interstitial solid soln. (e.g., C in Fe)



Transformational
– different **composition**
– often different structure



Hume-Rothery Rules

- Several factors determine the **limits of solubility**. These are expressed as a series of rules often called **William Hume-Rothery Rules**.
- Hume-Rothery (1899-1968) was a metallurgist who studied the alloying of metals. His research was conducted at Oxford University where in 1958, he was appointed to the first chair in metallurgy.
- His research led to some simple and useful rules on the extent to which an element might dissolve in a metal. The rules are still used widely. For example, the miscibility gap in Au-Ni is correlated with the fact that the lattice parameter of Au is 1.15 times that of Ni, thus acting maximally according to Hume-Rothery.
- If a solute differs in its atomic size by more than about 15% from the host, then it is likely to have a low solubility in that metal. The size factor is said to be unfavourable.
- If a solute has a large difference in electronegativity (or electropositivity: loss of electron) when compared with the host, then it is more likely to form a compound. Therefore the solubility in the host would be limited.
- A metal with a lower valency is more likely to dissolve in one which has a higher valency, than vice versa.
- The Hume-Rothery rules are a set of basic rules describing the conditions under which an element could dissolve in a metal, forming a solid solution. There are two sets of rules, one which refers to substitutional solid solutions, and another which refers to interstitial solid solutions.



Contd...

Conditions for substitutional solid solutions

Hume-Rothery rule-1: Atomic size factor (the 15%) rule

Extensive substitutional solid solution occurs only if the relative difference between the atomic diameters (radii) of the two species is less than 15%. If the difference > 15%, the solubility is limited. Comparing the atomic radii of solids that form solid solutions, the empirical rule is given by Hume-Rothery is given as:

$$\text{Mismatch} = \left(\frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \right) \times 100 \leq 15\%$$

Hume-Rothery rule-2: Crystal structure rule

For appreciable solid solubility, the crystal structures of the two elements must be identical.

Hume-Rothery rule-3: Valency rule

A metal will dissolve a metal of higher valency to a greater extent than one of lower valency. The solute and solvent atoms should typically have the same valence in order to achieve maximum solubility.

Hume-Rothery rule-4: The electronegativity rule

Electronegativity difference close to 0 gives maximum solubility. The more electropositivity one element and the more electronegativity the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution. The solute and the solvent should lie relatively close in the electrochemical series.



Contd...

Conditions for interstitial solid solutions

- Similarly Hume-Rothery rules can be applied for interstitial solid solutions
- Interstitial solid solutions are formed if,
 - A solute is smaller than pores in the lattice of a solvent
 - A solute has approximately the same electronegativity as a solvent
- There are very few elements that create ions, small enough to fit in interstitial positions, therefore appreciable solubility is rare for interstitial solid solutions.
 - Ions that often may be a solute in solid solutions are: H, Li, Na, and B
 - Examples of partially interstitial solid solutions PdH_n , AlLi_n , BeLi etc.

Application of Hume-Rothery rules

1. Predict more Al or Ag to dissolve in Zn?

- More Al because size is closer
- Val. is higher (but not too much)
- FCC in HCP

2. More Zn or Al in Cu?

- Surely Zn since size is closer thus causing lower distortion

3. Will C form substitutional or interstitial solid solution with iron?

- Interstitial solid solution

Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valence
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2



Equilibrium Phase Diagrams – Binary Systems

- I. Binary isomorphous (complete solid solution)
- II. Binary eutectic with no solid solution
- III. Binary eutectic with limited solid solution
- IV. Eutectoid
- V. Peritectic
- VI. Intermediate Phase
- VII. General

I. Binary Isomorphous (Complete Solid Solution)

- Complete liquid and solid solubility of both components
- Common in some alloy systems (e.g. Cu-Ni)
- Seen in some salt systems KCl-KBr
- Solid phase is a “solid solution”
- It’s like a liquid solution e.g. water and alcohol (not like a liquid mixture e.g. oil and water)
- How do they form? (Usually by introducing solute atoms into the solvent lattice)
- Why are solid solutions important? (Improve mechanical, electrical, magnetic properties for industrial applications)
- Note that the solid solution phase is called α



Cu-Ni Phase Diagram

- Rule 1: If we know T and C_o, then we know the types of phases present

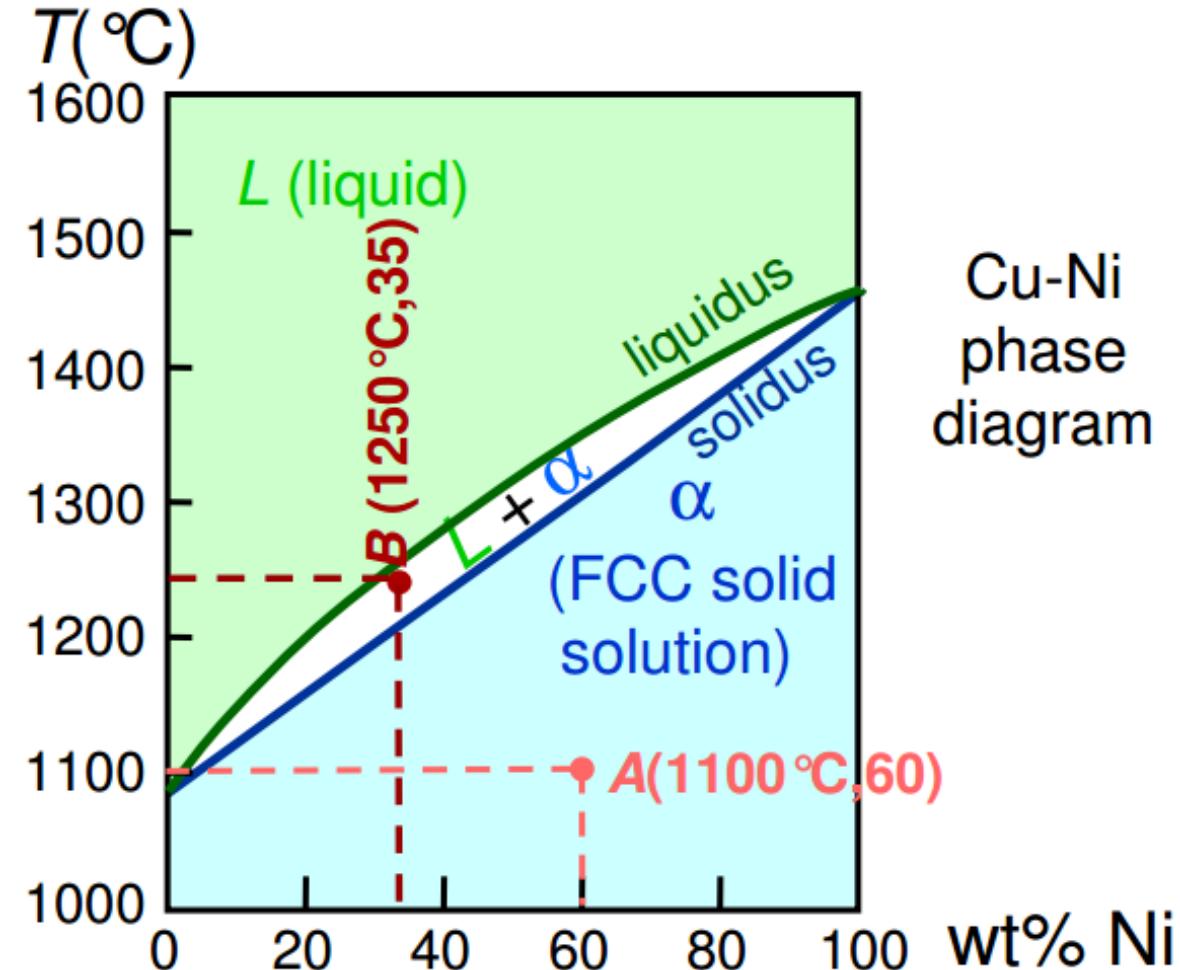
- Examples:

A(1100 °C, 60):

1 phase: α

B(1250 °C, 35):

2 phases: L + α



Cu-Ni
phase
diagram



Contd...

- Rule 2: If we know T and C_o , then we know the composition of each phase

- Examples:

$$C_o = 35 \text{ wt\% Ni}$$

At $T_A = 1320^\circ\text{C}$:

Only Liquid (L)

$$C_L = C_o \quad (= 35 \text{ wt\% Ni})$$

At $T_D = 1190^\circ\text{C}$:

Only Solid (α)

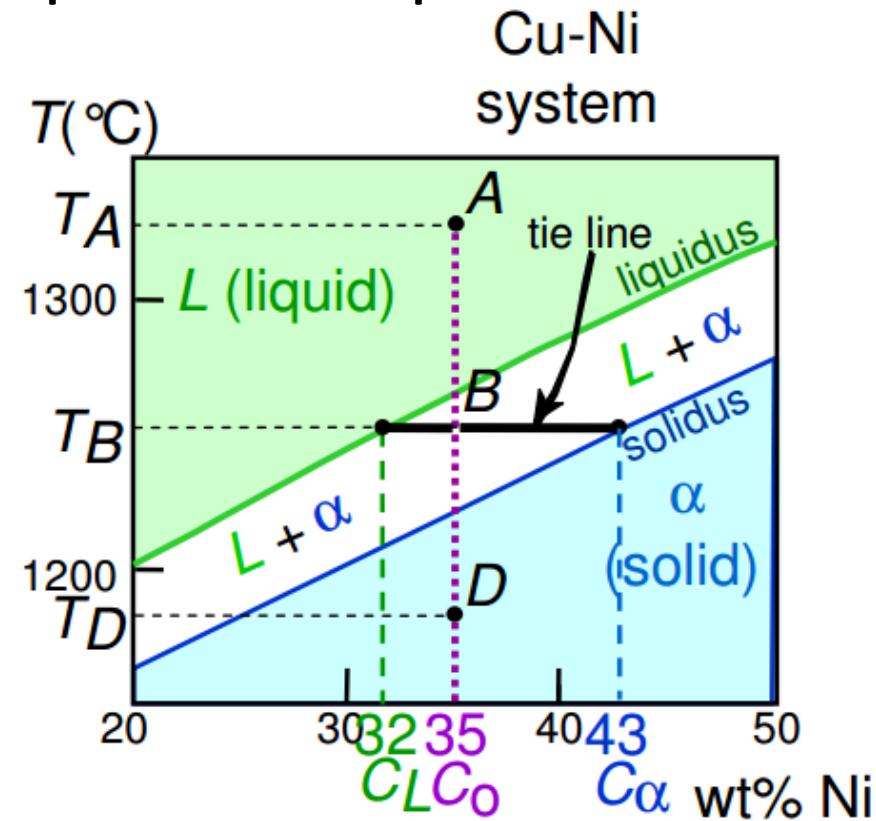
$$C_\alpha = C_o \quad (= 35 \text{ wt\% Ni})$$

At $T_B = 1250^\circ\text{C}$:

Both α and L

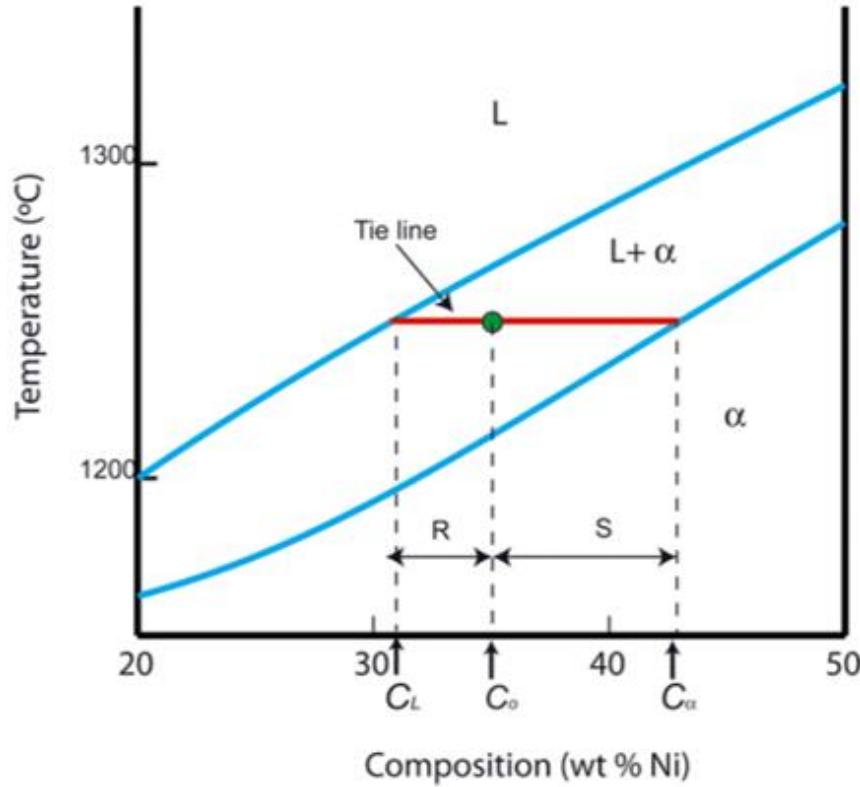
$$C_L = C_{\text{liquidus}} \quad (= 32 \text{ wt\% Ni here})$$

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



Tie Line and Lever Rule

- Determination of Phase composition: Tie line
- Determination of Phase Amounts: Lever rule



$$W_L = \text{fraction of liquid phase}$$
$$W_\alpha = \text{fraction of } \alpha \text{ phase}$$

Phase composition (Tie Line):

- Intersections of the tie line with phase boundaries
- Composition of the respective phases is given by the composition axis

LEVER RULE

Determination of Phase Amounts

- The fraction of each phase is computed by taking the length of the tie line from the overall alloy composition to the phase boundary of the other phase, and dividing by the total line length

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

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

Determining phase composition in 2-phase region:

1. Draw the tie line.
2. Note where the tie line intersects the liquidus and solidus lines (i.e. where the tie line crosses the phase boundaries).
3. Read off the composition at the boundaries:

Liquid is composed of C_L amount of Ni (31.5 wt% Ni).

Solid is composed of C_α amount of Ni (42.5 wt% Ni).



Lever Rule: Derivation

Since we have only 2 phases:

$$W_L + W_\alpha = 1 \quad (1)$$

Conservation of mass requires that:

Amount of Ni in α -phase + amount of Ni in liquid phase = total amount of Ni
or

$$W_\alpha C_\alpha + W_L C_L = C_o \quad (2)$$

From 1st condition, we have: $W_\alpha = 1 - W_L$

Sub-in to (2): $(1 - W_L)C_\alpha + W_L C_L = C_o$

Solving for W_L and W_α gives :

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

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



Contd...

- Rule 3: If we know T and C_o , then we know the amount of each phase (in wt%)

- Examples:

$$C_o = 35 \text{ wt\% Ni}$$

At T_A : Only Liquid (L)

$$W_L = 100 \text{ wt\%}, W_\alpha = 0$$

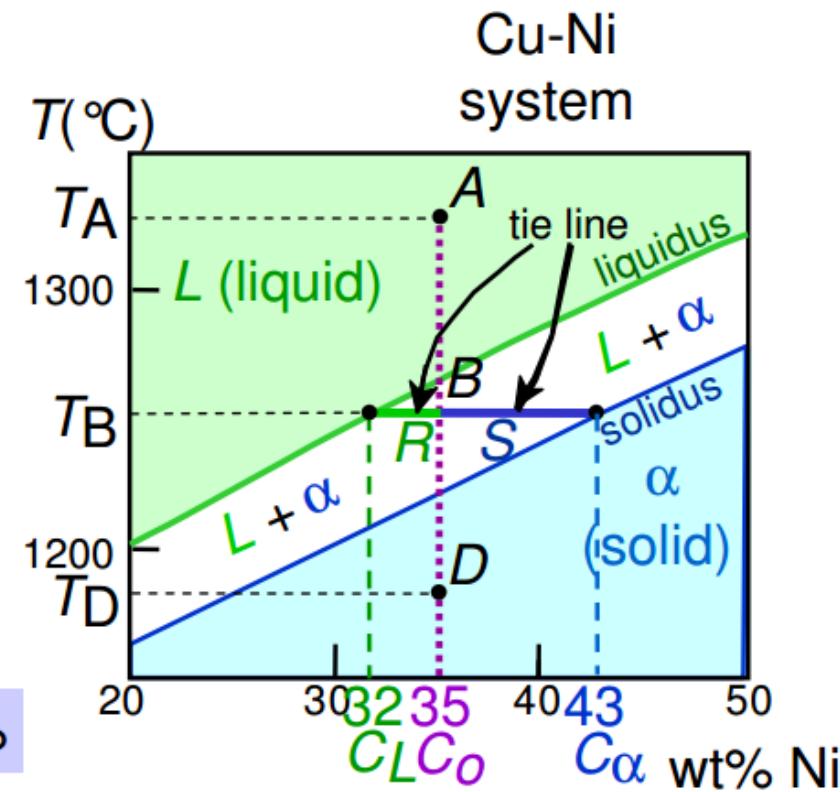
At T_D : Only Solid (α)

$$W_L = 0, W_\alpha = 100 \text{ wt\%}$$

At T_B : Both α and L

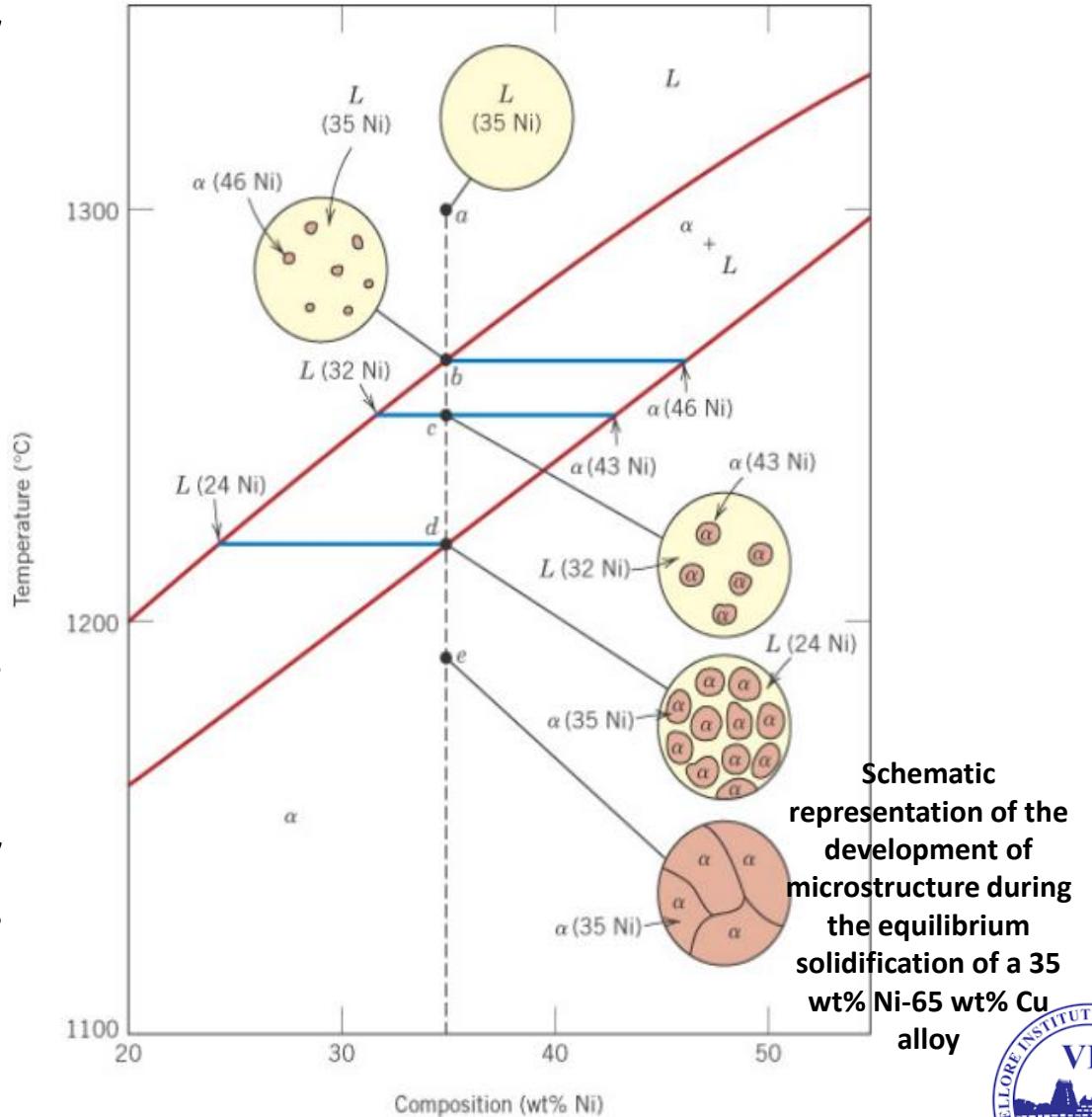
$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 73 \text{ wt\%}$$

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



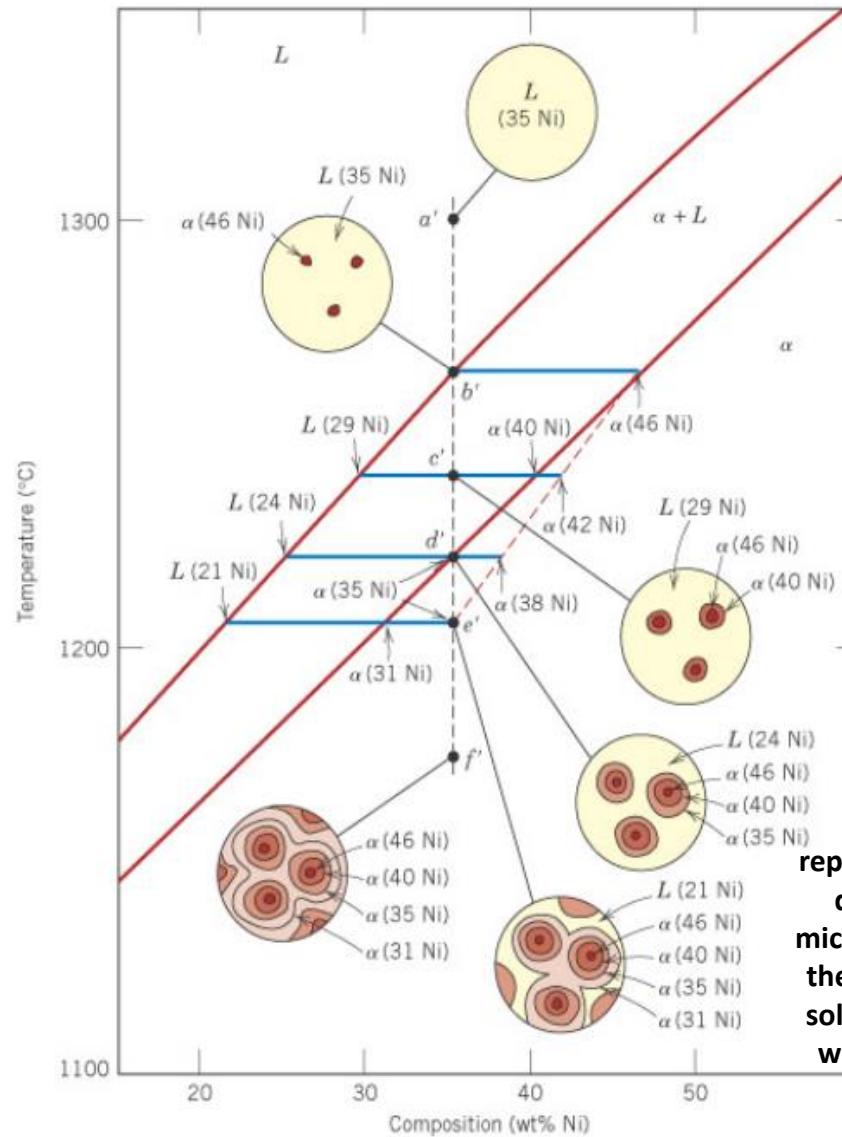
Equilibrium Cooling in a Cu-Ni Binary System

- Equilibrium Cooling: Very slow cooling to allow phase equilibrium to be maintained during the cooling process
- Microstructures will vary on the cooling rate (i.e. processing conditions)
- Consider $C_o = 35$ wt%Ni
- **a** ($T > 1260$ °C): start as homogeneous liquid solution
- **b** ($T \sim 1260$ °C): liquidus line reached. α phase begins to nucleate. $C_\alpha = 46$ wt% Ni; $C_L = 35$ wt% Ni
- **c** ($T = 1250$ °C): calculate composition and mass fraction of each phase. $C_\alpha = 43$ wt% Ni; $C_L = 32$ wt% Ni
- **d** ($T \sim 1220$ °C): solidus line reached. Nearly complete solidification. $C_\alpha = 35$ wt% Ni; $C_L = 24$ wt% Ni
- **e** ($T < 1220$ °C): homogeneous solid solution with 35 wt% Ni



Non Equilibrium Cooling

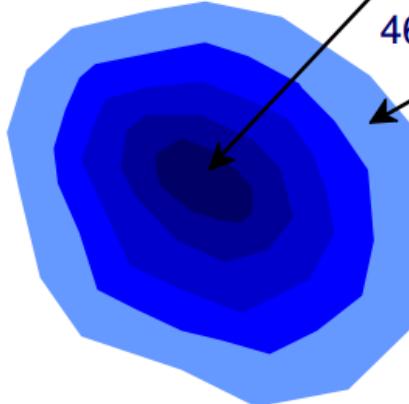
- Non Equilibrium Cooling: Very high cooling rate
- **a'** ($T > 1260$ °C): start as homogeneous liquid solution
- **b'** ($T \sim 1260$ °C): liquidus line reached. α phase begins to nucleate. $C_\alpha = 46$ wt% Ni; $C_L = 35$ wt% Ni
- **c'** ($T = 1250$ °C): solids that formed at point b' remain with same composition (46 wt%) and new solids with 42 wt% Ni form around the existing solids
- **d'** ($T \sim 1220$ °C): solidus line reached. Nearly complete solidification.
- Previously solidified regions maintain original composition and further solidification occurs at 35 wt% Ni
- **e'** ($T < 1220$ °C): Non-equilibrium solidification complete (with phase segregation)



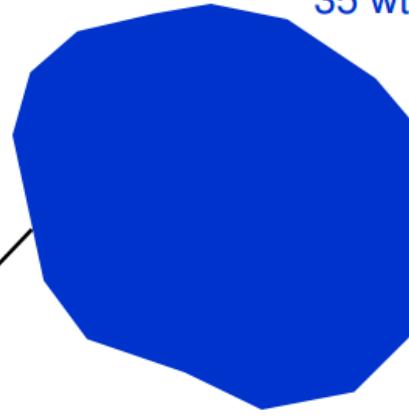
Schematic representation of the development of microstructure during the non-equilibrium solidification of a 35 wt% Ni-65 wt% Cu alloy



Cored vs. Equilibrium Phases

- Nucleation is the first step in the formation of either a new thermodynamic phase or a new structure
 - Grain growth is the increase in size of grains in a material at high temperature
 - Diffusion is the net movement of molecules or atoms from a region of high concentration (or high chemical potential) to a region of low concentration (or low chemical potential)
 - Equilibrium is diffusion dependent
 - Diffusion is time dependent
 - With change in temperature composition of solid-liquid changes
 - System requires time to achieve equilibrium
 - Most cooling processes are fast (non-equilibrium solidification)
- Fast rate of cooling:
Cored structure

First α to solidify:
46 wt% Ni
Last α to solidify:
 < 35 wt% Ni

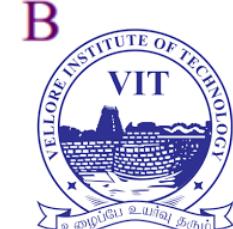
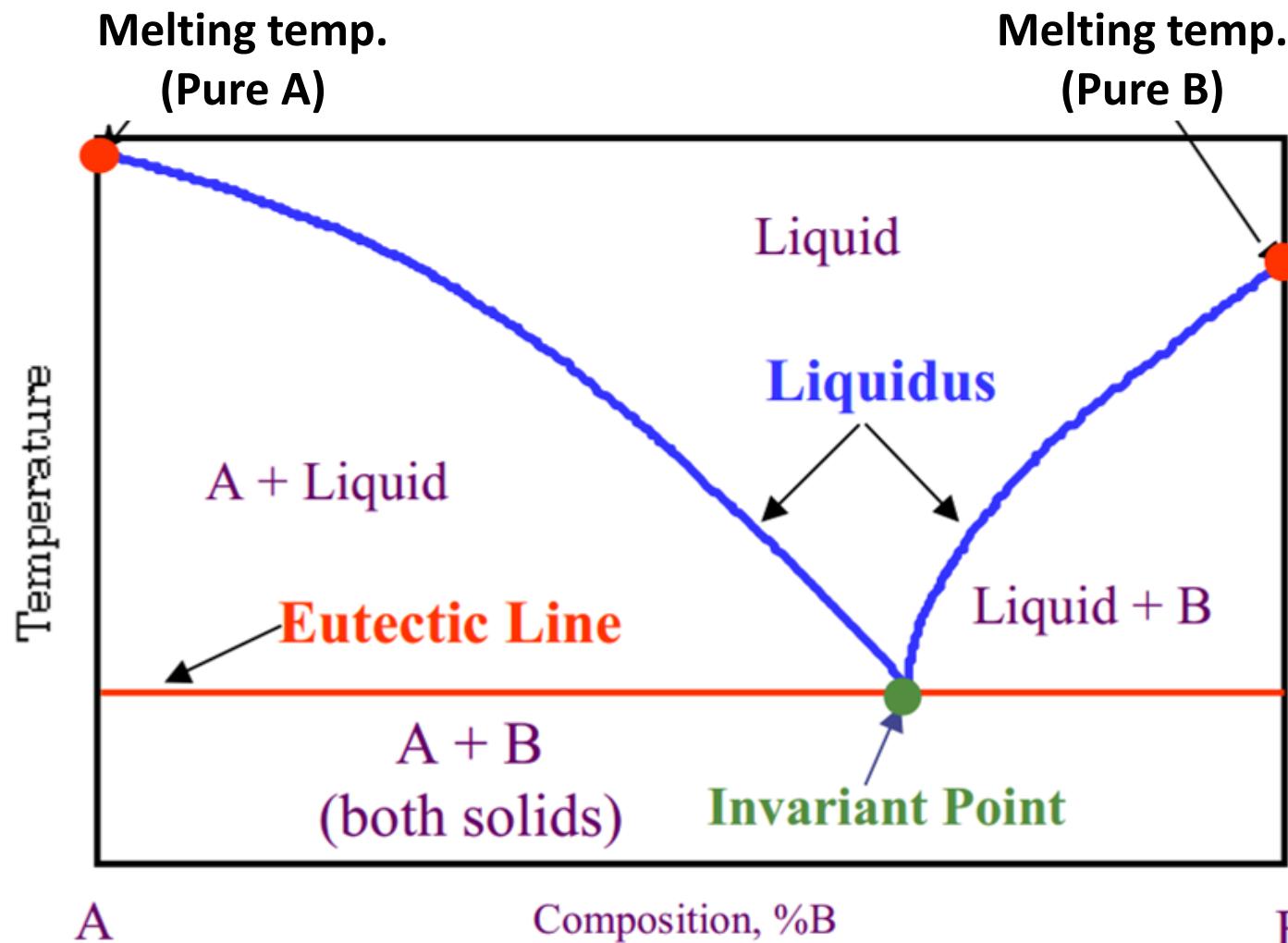
- Slow rate of cooling:
Equilibrium structure
Uniform C_α :
35 wt% Ni
- Cored structure can be eliminated by a homogenization heat treatment at a temperature below the solidus point for the particular alloy composition.



II. Binary Eutectic With No Solid Solution

- Liquidus** – first solid appears on cooling
- Cotectic** – are lines along which liquids cool and crystallize
- Eutectic Line** – line of 3 phase equilibrium
- Eutectic/Invariant Point** where 2 liquidus lines and eutectic line meet

$$T_{m(eutectic)} < T_{m(A)} \text{ or } T_{m(B)}$$



III. Binary Eutectic With Limited Solid Solution

Limited Solid Solubility

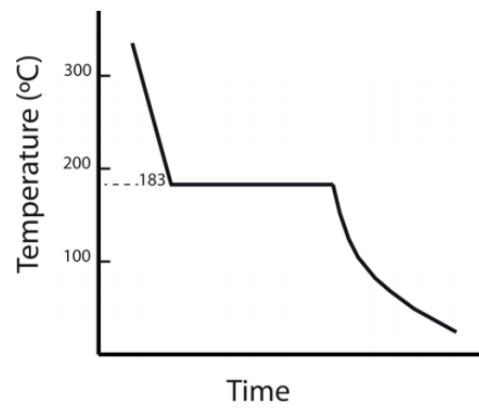
- α is solid A with small amount of solid B dissolved in it
- β is solid B with small amount of solid A dissolved in it

Components have different solid solubilities

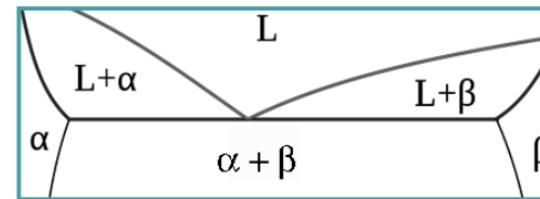
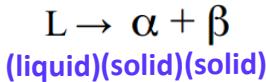
Eutectic (occurs at eutectic temperature)

- Line of three-phase equilibrium

Cooling curve at eutectic Temperature

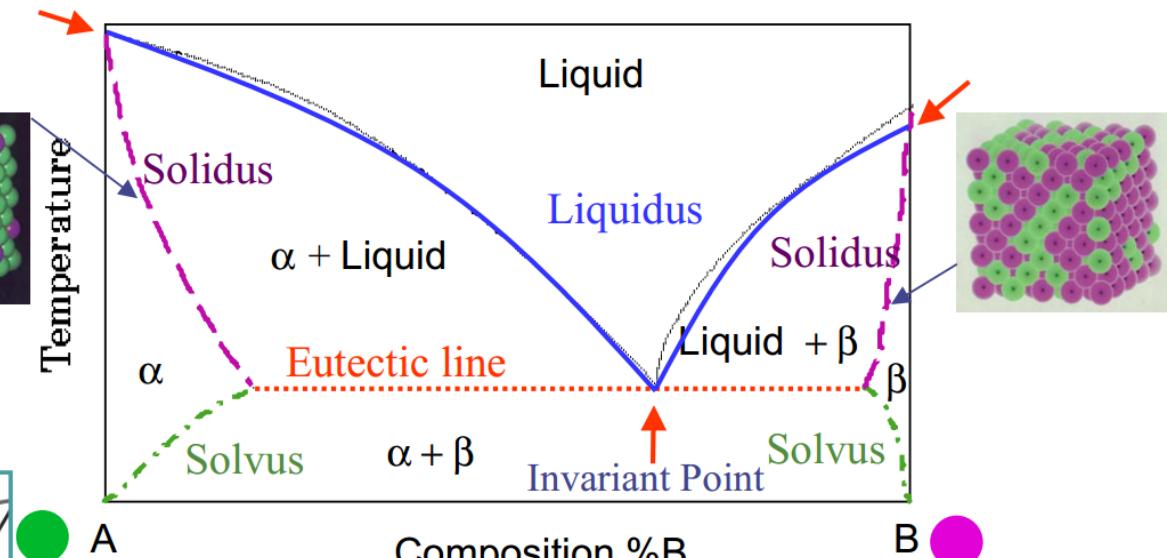


Eutectic reaction



A

B



Limit of solid solubility

- solidus (between solid and liquid and solid solution)
- solvus (between single solid solution and mixture of solid solutions)



Pb-Sn Eutectic System (Example – 1)

For a 40 wt% Sn-60 wt% Pb alloy at 150 °C, find...

--the phases present: α + β

--compositions of phases:

$$C_O = 40 \text{ wt\% Sn}$$

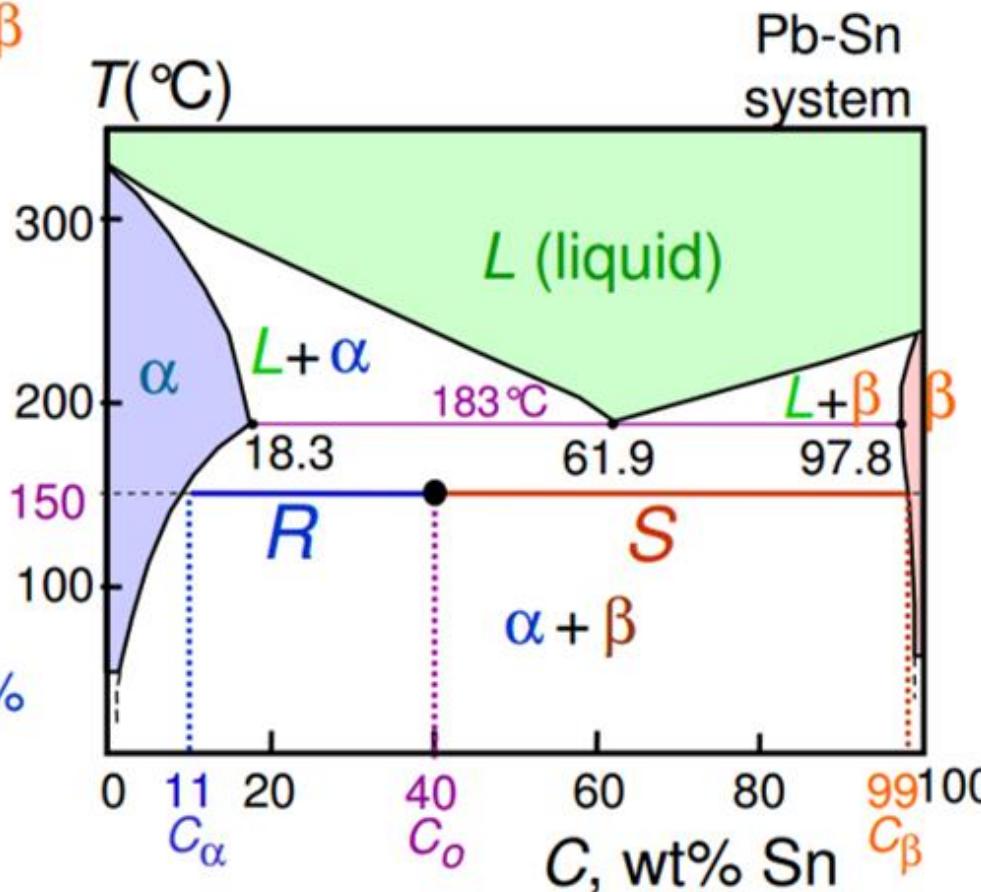
$$C_\alpha = 11 \text{ wt\% Sn}$$

$$C_\beta = 99 \text{ wt\% Sn}$$

--the relative amount of each phase:

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_O}{C_\beta - C_\alpha}$$
$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%}$$

$$W_\beta = \frac{R}{R+S} = \frac{C_O - C_\alpha}{C_\beta - C_\alpha}$$
$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%}$$



Pb-Sn Eutectic System (Example – 2)

For a 40 wt% Sn-60 wt% Pb alloy at 200 °C, find...

--the phases present: α + L

--compositions of phases:

$$C_O = 40 \text{ wt\% Sn}$$

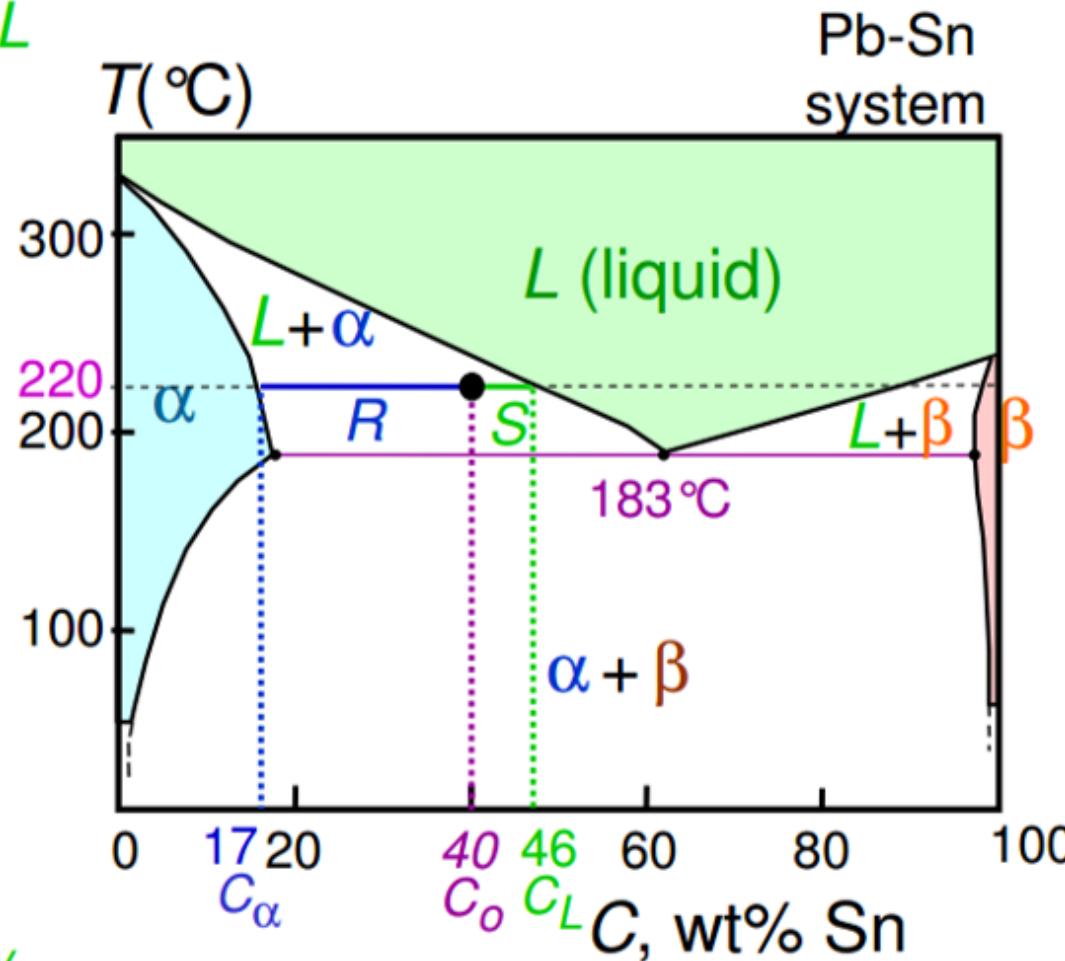
$$C_\alpha = 17 \text{ wt\% Sn}$$

$$C_L = 46 \text{ wt\% Sn}$$

--the relative amount of each phase:

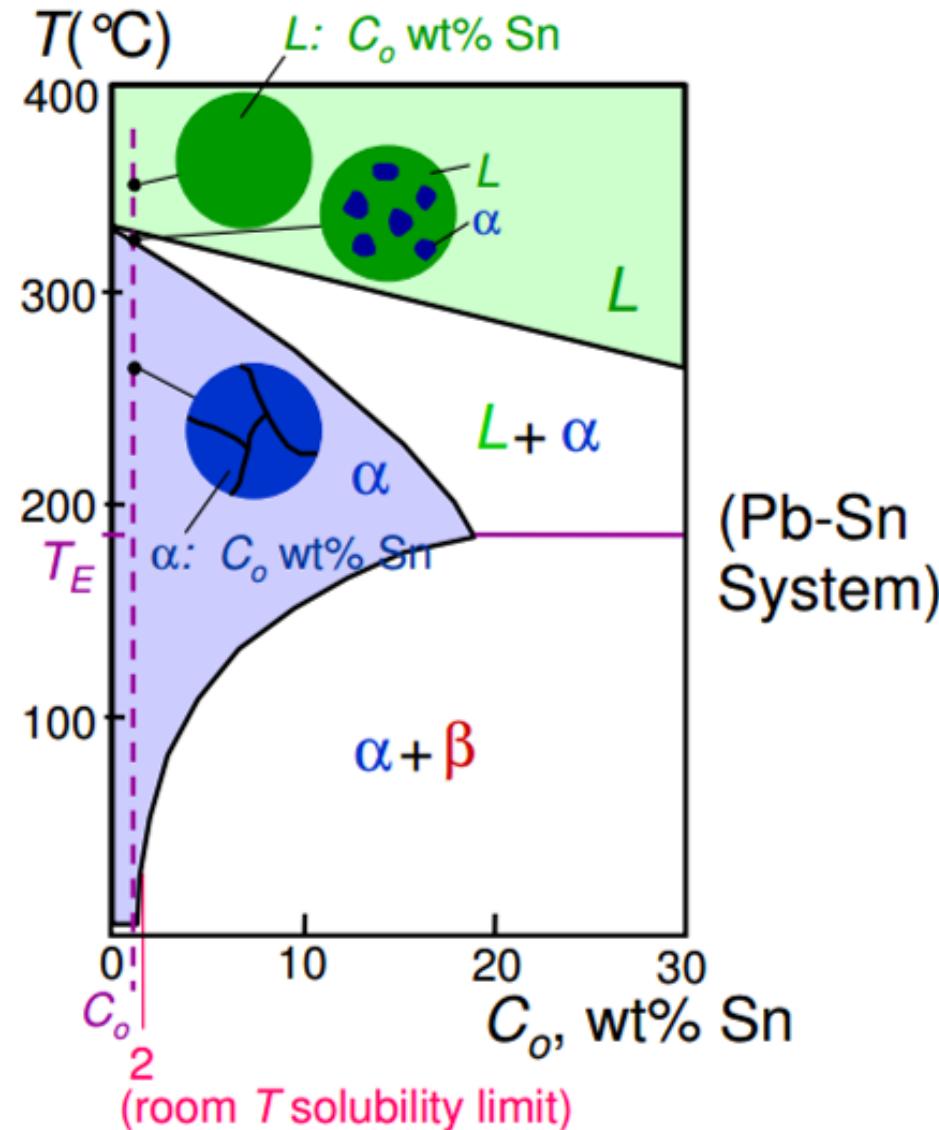
$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$
$$= \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$



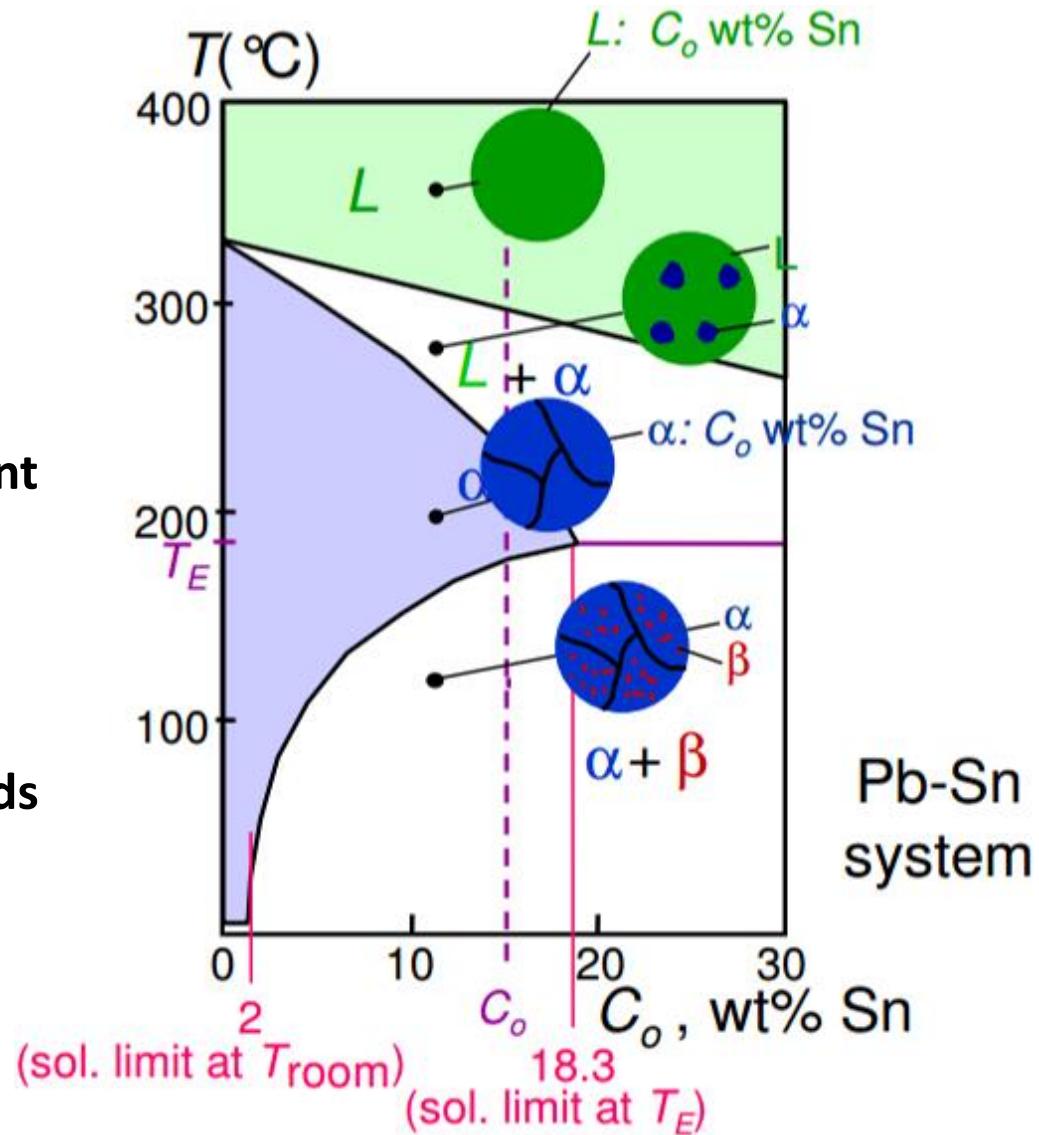
Microstructures in Pb-Sn Eutectic System – I

- $C_o < 2 \text{ wt\% Sn}$
- One component rich composition
- a:** start with homogeneous liquid
- b:** α -phase solids with liquid
Compositions and mass fractions can be found via tie lines and lever rule
- c:** α -phase solid solution only
- Net result: polycrystalline α solid
- Cooling at this composition is similar to binary isomorphous systems



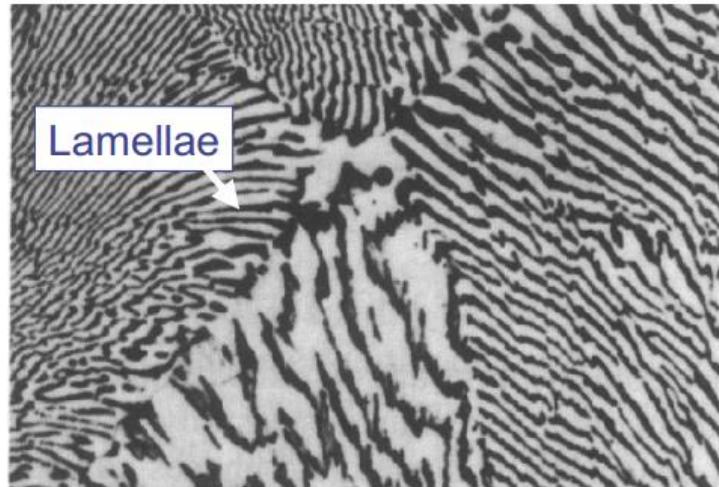
Microstructures in Pb-Sn Eutectic System – II

- $2 \text{ wt\% Sn} < C_o < 18.3 \text{ wt\% Sn}$
- One-component rich but cooling to $\alpha + \beta$ coexistence
- d:** homogeneous liquid
- e:** $\alpha + L$ phase (same as previous but at different compositions and mass fractions)
- f:** all α -phase solid solution
- g:** $\alpha + \beta$ phase (passing through solvus line leads to exceeding solubility limit and β phase precipitates out)
- Net result: polycrystalline α -solid with fine β crystals

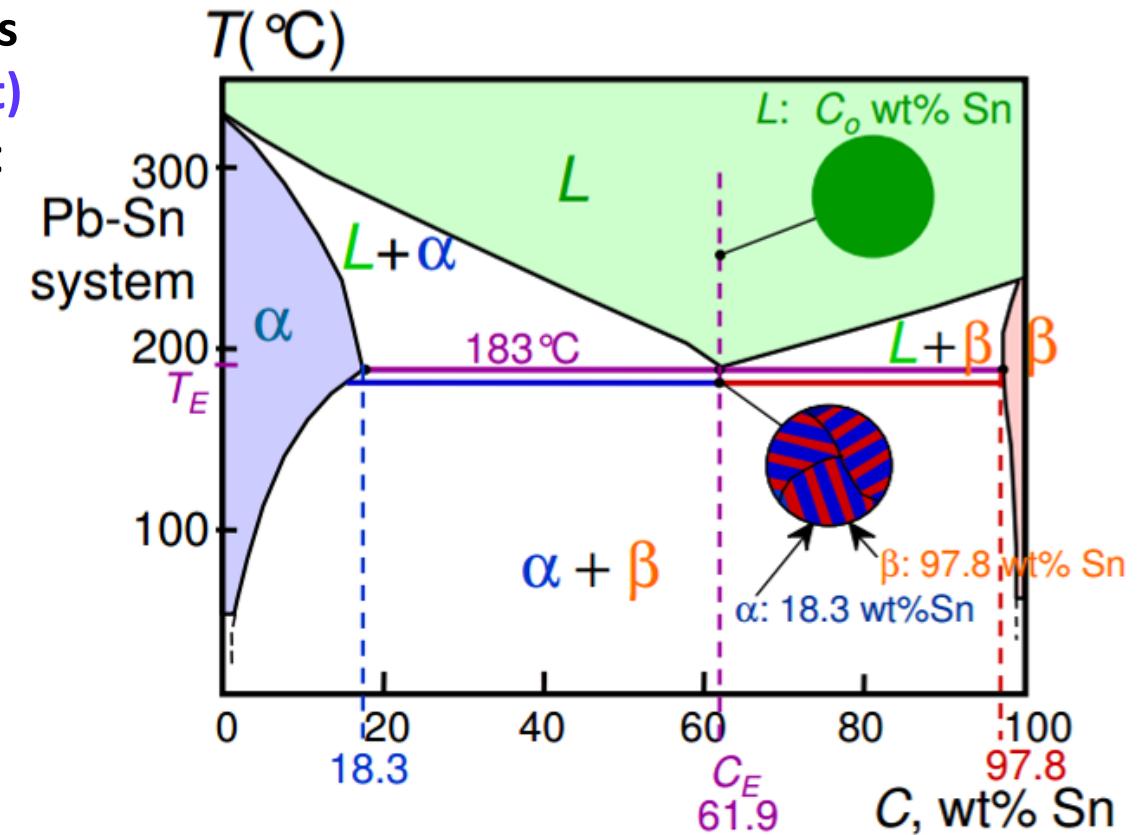


Microstructures in Pb-Sn Eutectic System – III

- $C_o = C_E$
 - Result: Eutectic microstructure (lamellar structure)**
 - alternating layers (lamellae) of α and β crystals
 - It forms when eutectic liquid freezes (loss of heat)**
 - Lamellar structure forms because relatively short diffusion lengths
 - In order to achieve large homogeneous regions, long diffusion lengths are required

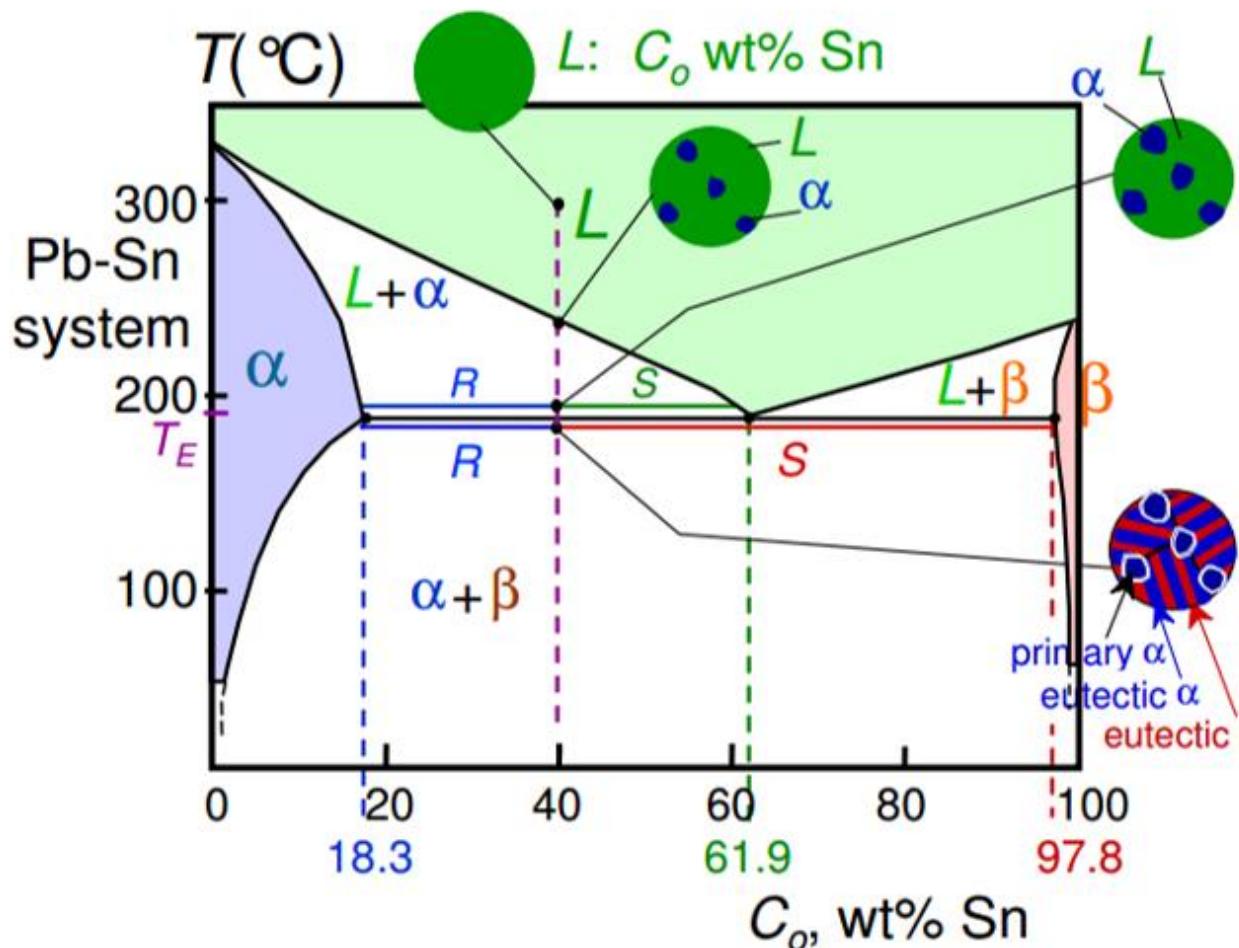


Alternating Pb-rich α -phase (dark layers) and a Sn-rich β -phase (light layers)



Microstructures in Pb-Sn Eutectic System – IV

- $18.3 \text{ wt\% Sn} < C_0 < 61.9 \text{ wt\% Sn}$
- Result: α crystals and a eutectic microstructure

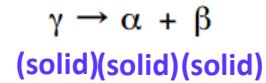


- Just above T_E :
 $C_\alpha = 18.3 \text{ wt\% Sn}$
 $C_L = 61.9 \text{ wt\% Sn}$
 $W_\alpha = \frac{S}{R + S} = 50 \text{ wt\%}$
 $W_L = (1 - W_\alpha) = 50 \text{ wt\%}$
- Just below T_E :
 $C_\alpha = 18.3 \text{ wt\% Sn}$
 $C_\beta = 97.8 \text{ wt\% Sn}$
 $W_\alpha = \frac{S}{R + S} = 73 \text{ wt\%}$
 $W_\beta = 27 \text{ wt\%}$

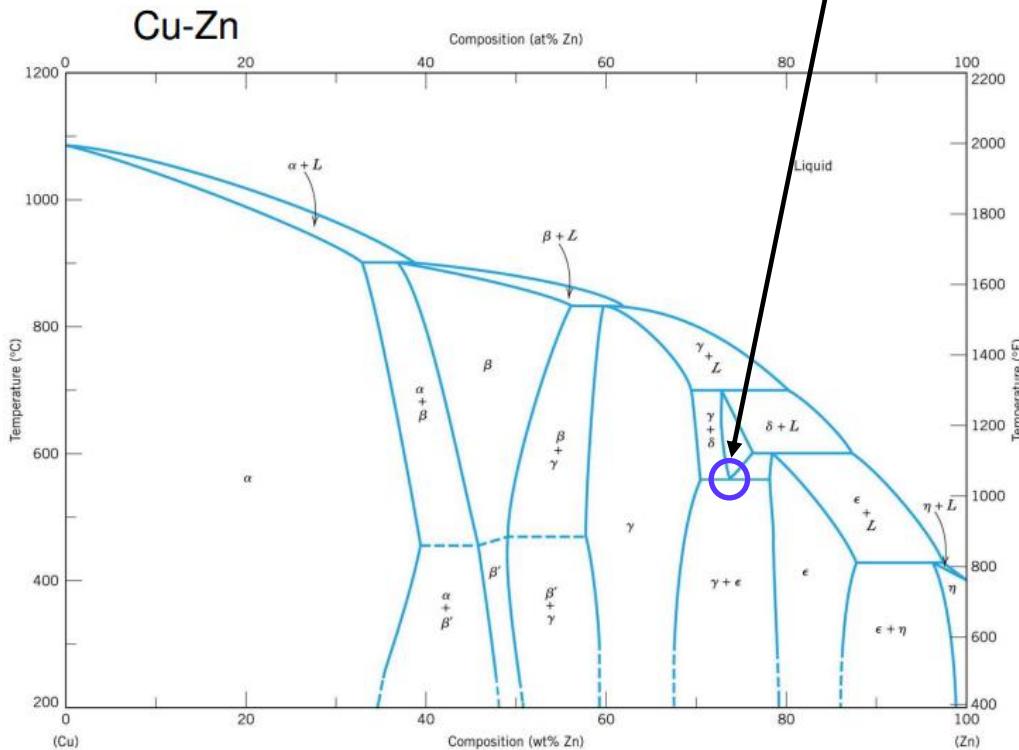
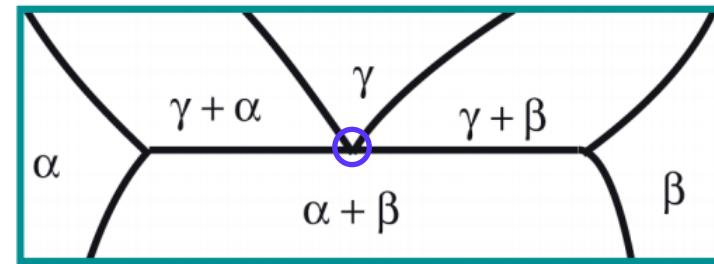


IV. Eutectoid Systems

Eutoctoid reaction:

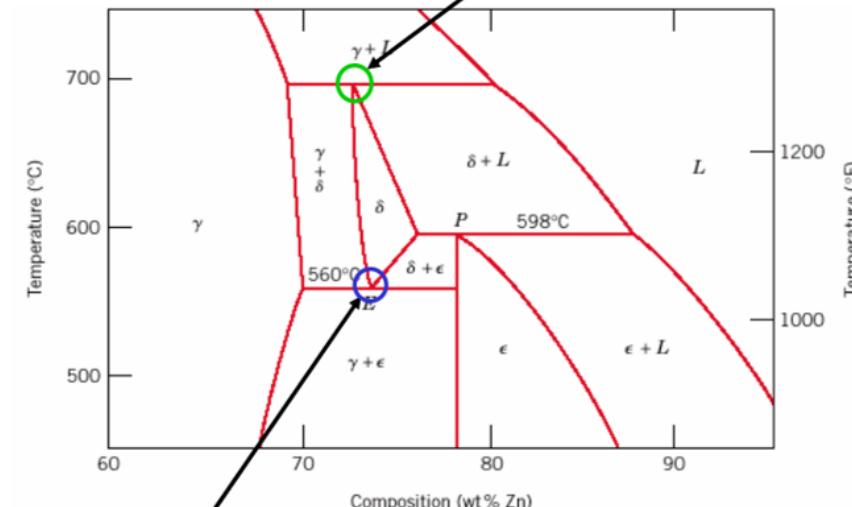


EUTECTOID



Cu-Zn Phase diagram

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

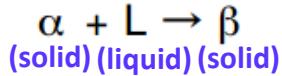


Eutectoid transition $\delta \rightleftharpoons \gamma + \epsilon$

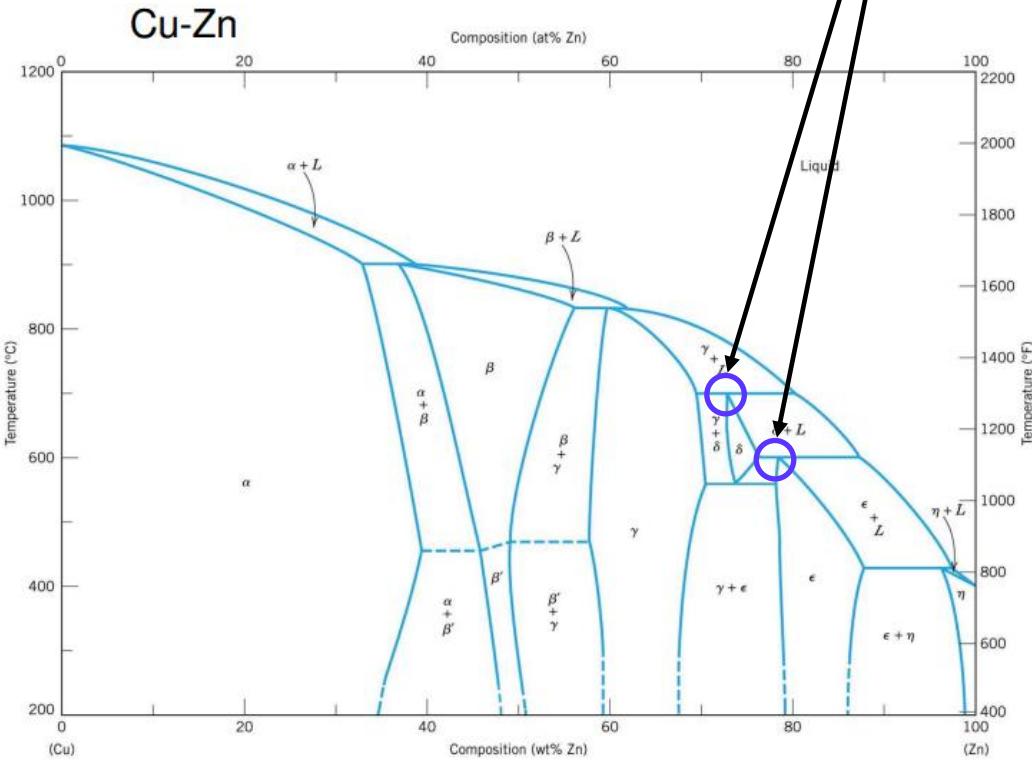
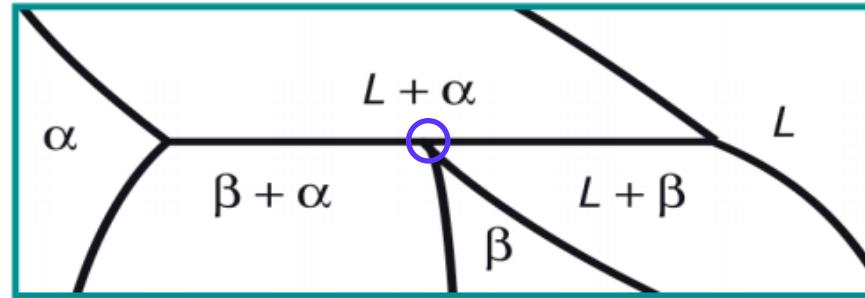


V. Peritectic Systems

Peritectic reaction:

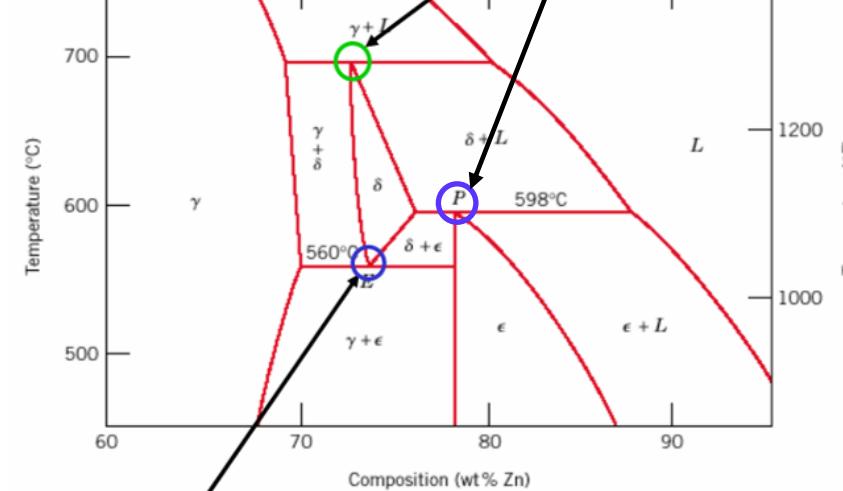


PERITECTIC



Cu-Zn Phase diagram

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

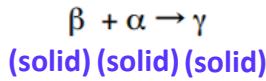


Eutectoid transition $\delta \rightleftharpoons \gamma + \epsilon$

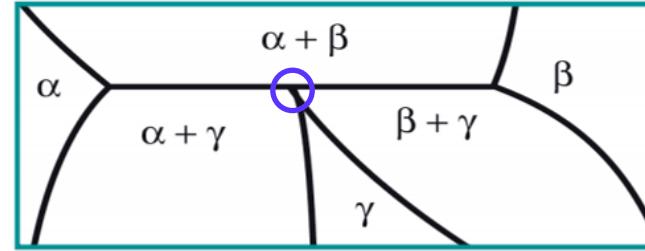


Peritectoid Systems

Peritectoid reaction:

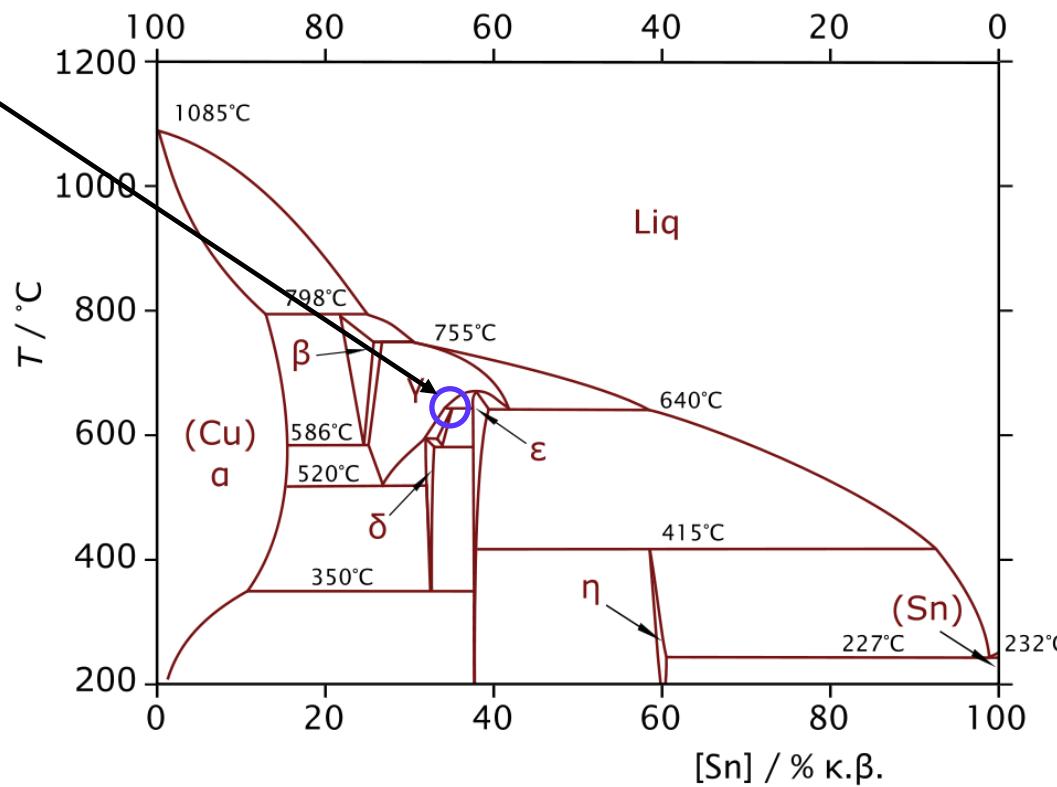


PERITECTOID



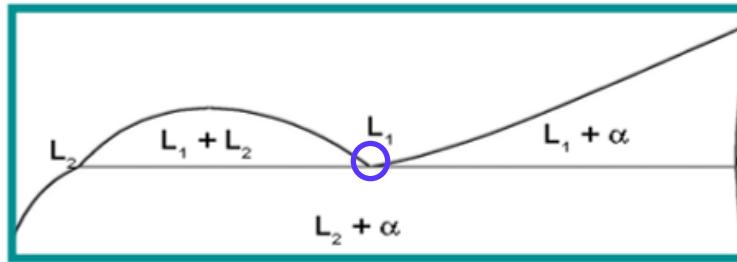
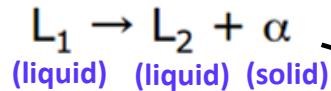
Two solid phases react to give a completely different solid phase
[Cu] / % κ.β.

Cu-Sn phase diagram

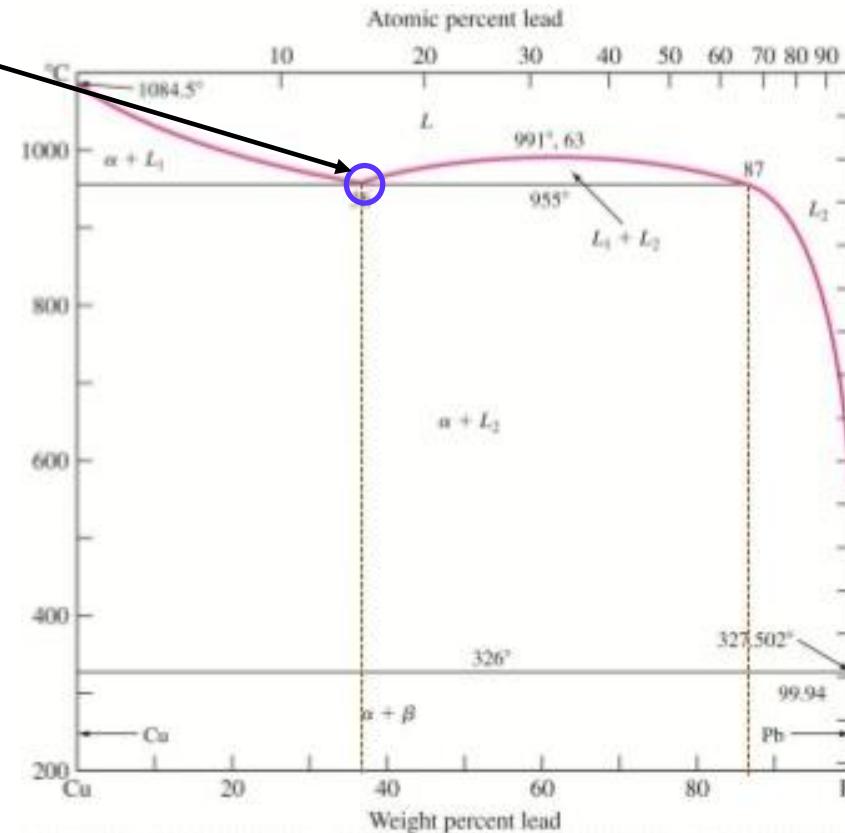


Monotectic Systems

Monotectic reaction :



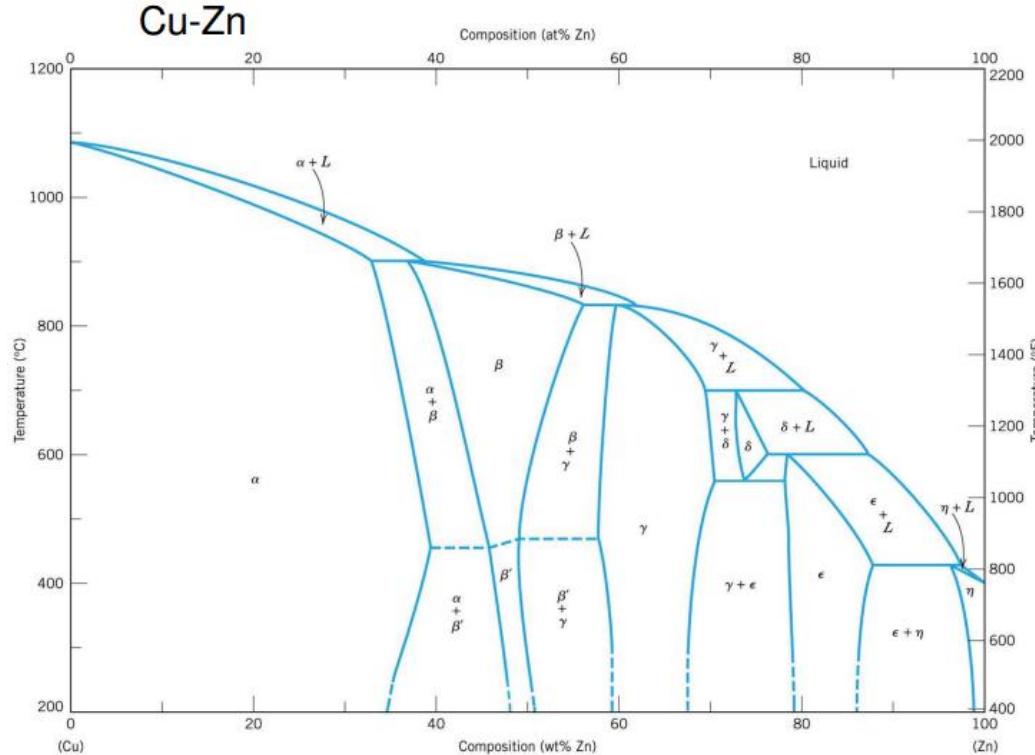
Cu-Pb phase diagram



- It occurs when there is a miscibility gap in the liquid phase
- Miscibility gap: two liquid phases co-exist



VI. Phase Diagrams With Intermediate Phases

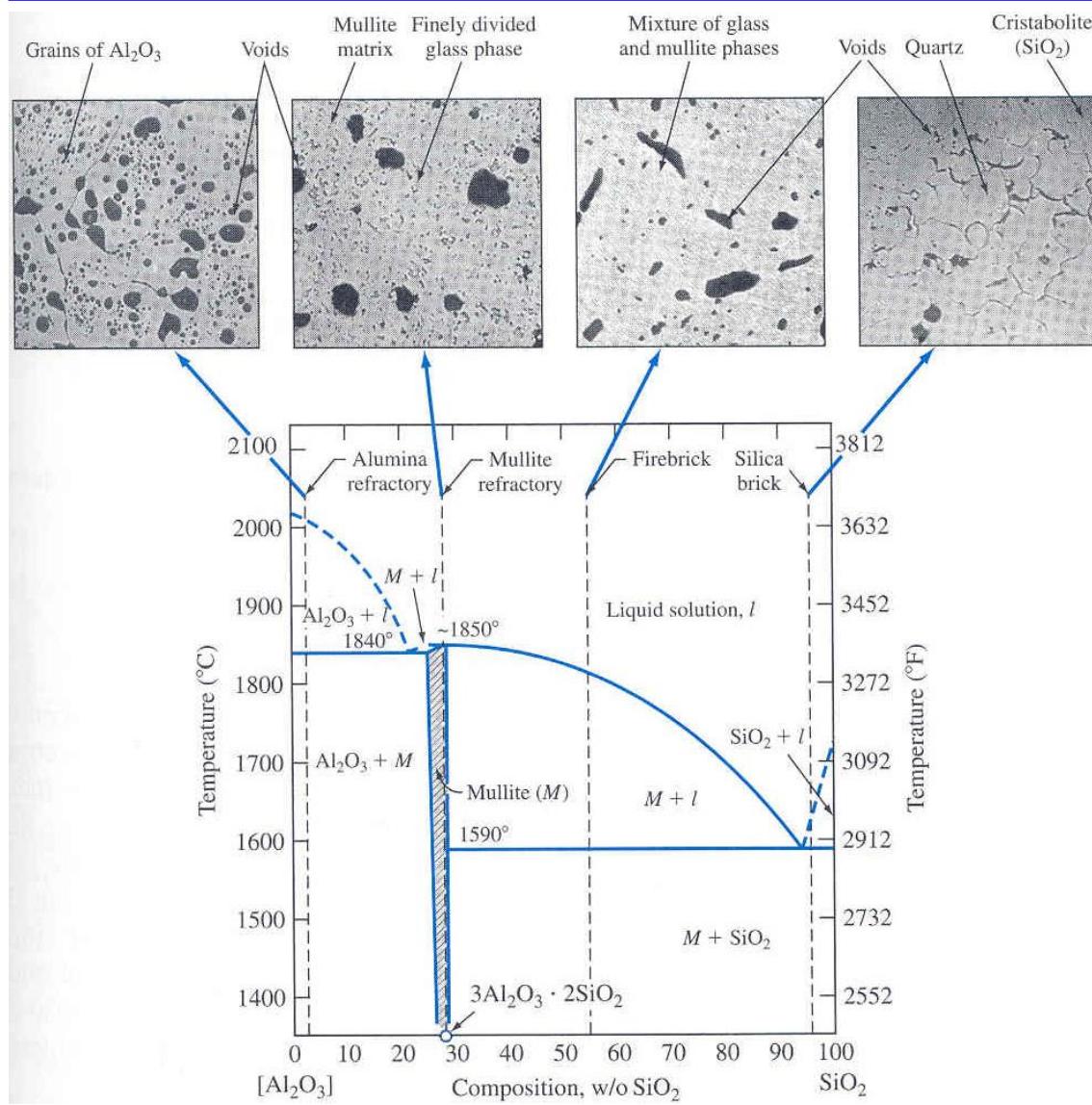


Cu-Zn phase diagram

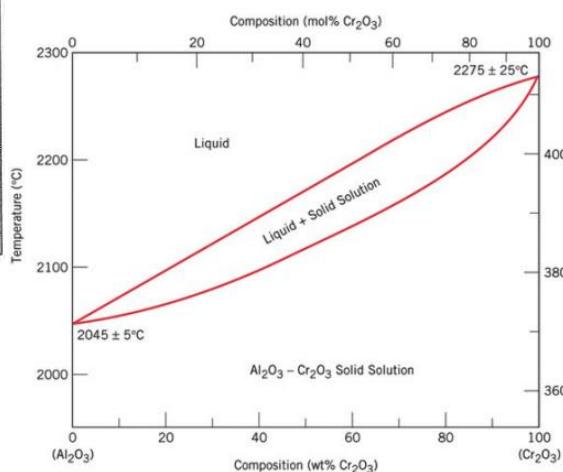
- **Terminal phases/solid solutions:** Phases occur at the end of phase diagrams (α and η)
- **Intermediate phases/solid solutions:** Phases occur in a composition range inside phase diagram (β , β' , γ , δ and ϵ)
- **Examples:** Cu-Zn diagram has both terminal and intermediate phases



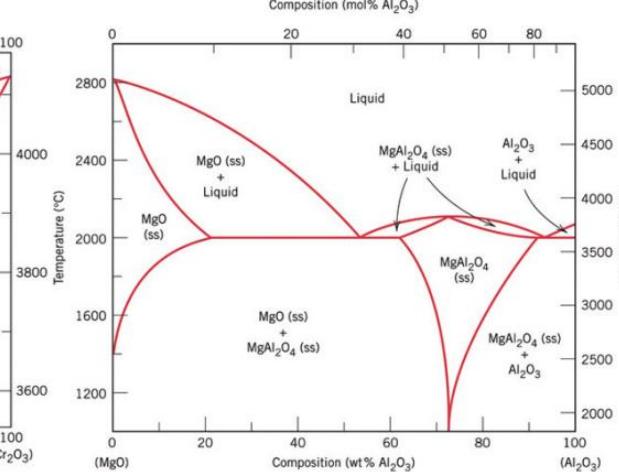
Ceramic Phase Diagrams and Intermediate Phases



$\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$



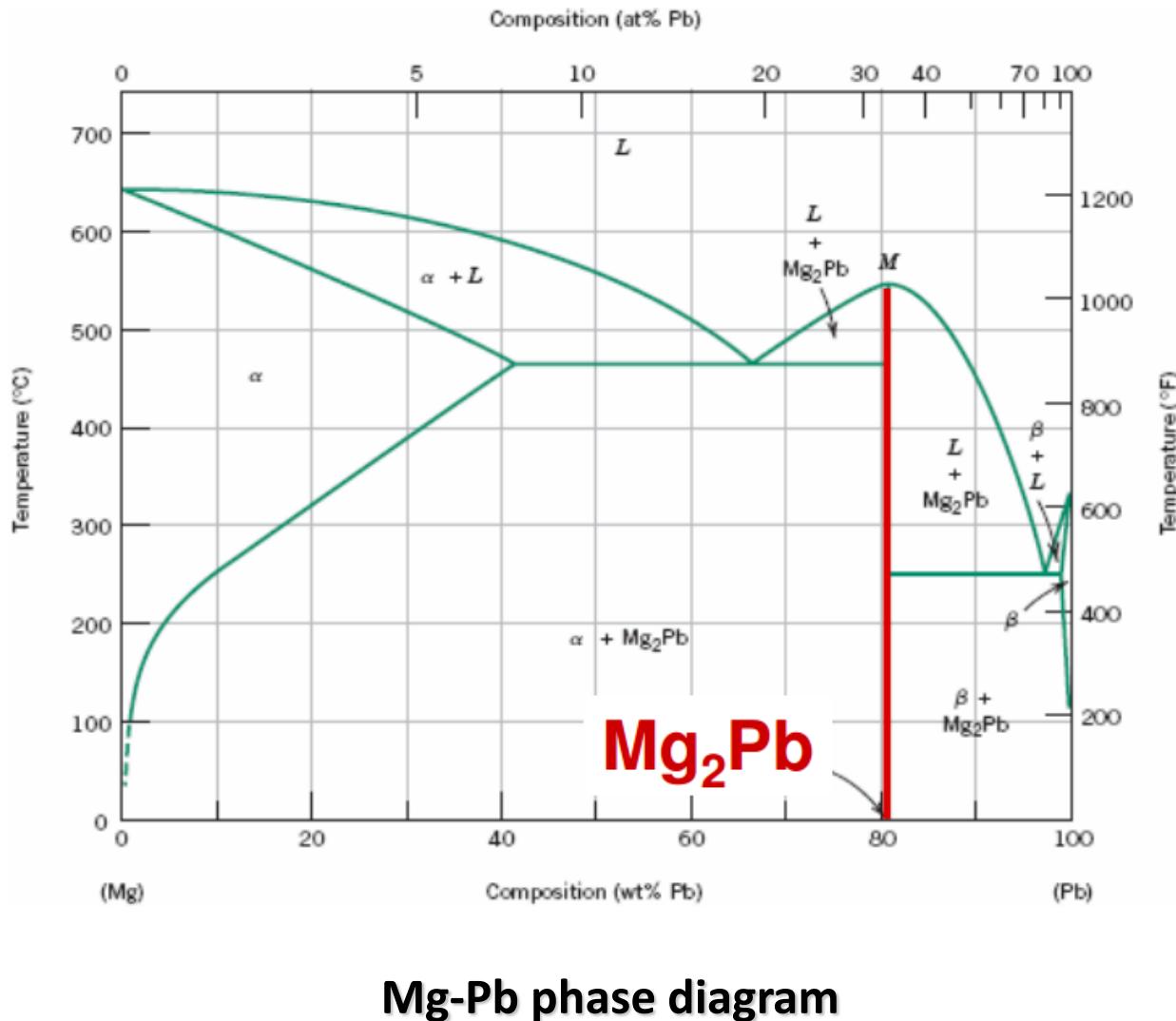
$\text{MgO-Al}_2\text{O}_3$



In $\text{Al}_2\text{O}_3 - \text{SiO}_2$ system, an intermediate phase called **Mullite** is formed, which includes the compound $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$



Phase Diagrams With Intermetallic Compounds



- Besides solid solutions, **intermetallic compounds**, that have precise chemical compositions can exist in some systems.
- Intermetallic compound forms a **discrete line** - not an area - because stoichiometry (i.e. composition) is exact.
- A **congruent transformation** involves no change in composition (e.g., allotropic transformation such as α -Fe to γ -Fe or melting transitions in pure solids).
- For an **incongruent transformation**, at least one phase changes composition (e.g. eutectic, eutectoid, peritectic reactions).

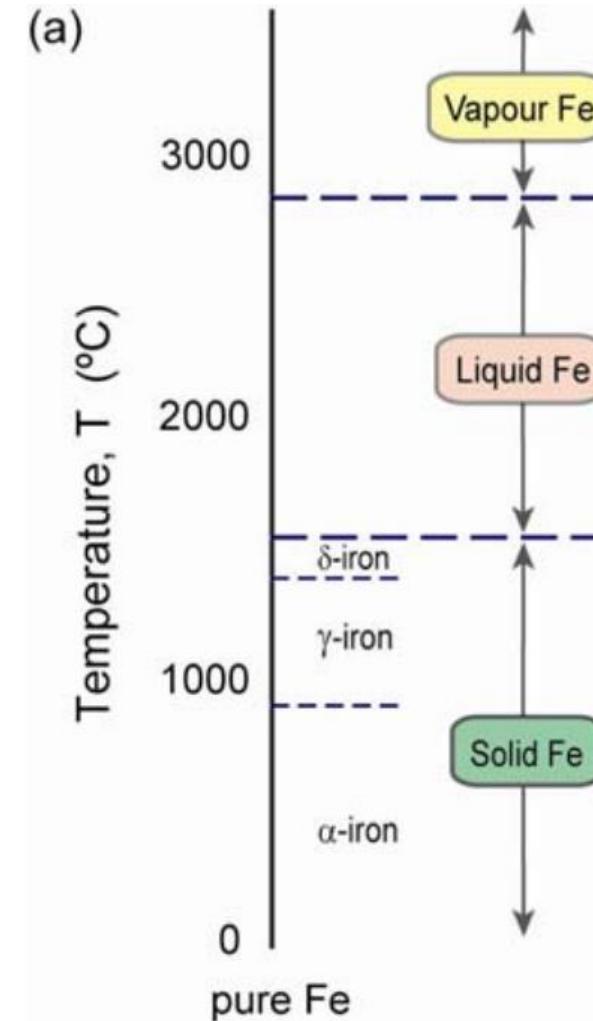
Iron-Carbon Phase Diagram – Introduction

- The iron-carbon phase diagram is important in engineering as it provides the basis for understanding all **cast irons** and **carbon steels** and their **heat treatment**. For structural and mechanical applications, steels and other alloys based on **iron (the ferrous alloys)** are the dominant engineering alloys. They are intrinsically stiff, strong and tough, and mostly low cost.
- In the phase diagram, temperature is plotted against composition. Any point on the diagram therefore represents a definite composition and temperature. The phase diagram indicates the phases present and the phase changes that occur during heating and cooling. The relative amounts of the phases that exist at any temperature can also be estimated with the help of **lever rule**.
- A portion of the Fe-C diagram – the part from pure Fe to 6.67 wt.% carbon (*corresponding to cementite, Fe_3C*) – *is technologically very relevant*. Part of the diagram after 6.7 wt% C is ignored as it has little commercial significance.
- It is **not a true equilibrium phase diagram** because **iron carbide is not a stable phase**. Cementite would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.
- Compositions up-to 2.1% C are called steels and beyond 2.1% are called cast irons.



Pure Iron – Phase Changes With Temperature

- First, consider pure iron.
- Figure a shows the phases found in pure iron (i.e. the phase diagram becomes a single temperature axis).
- The low temperature form of iron is called ferrite (or α -iron), which has a BCC lattice (body-centered cubic).
- On heating pure iron changes to austenite (or γ -iron) at 910 °C, and switches to a face-centered cubic (FCC) lattice.
- Pure austenite is stable up to 1394 °C, when it changes back to BCC δ -iron, before melting at 1539 °C, and boiling at 2860 °C.

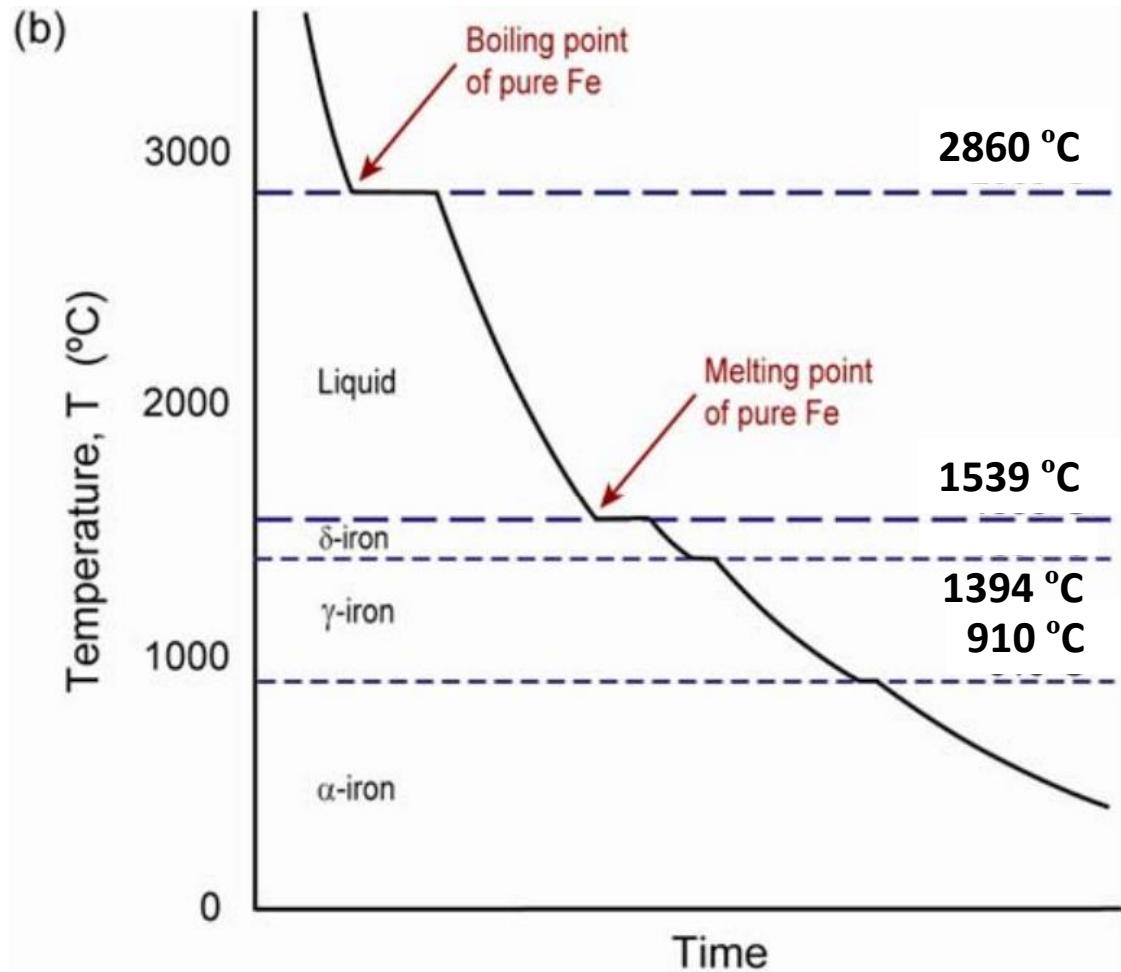


(a) one-dimensional phase diagram
for pure iron



Pure Iron – Cooling Curve

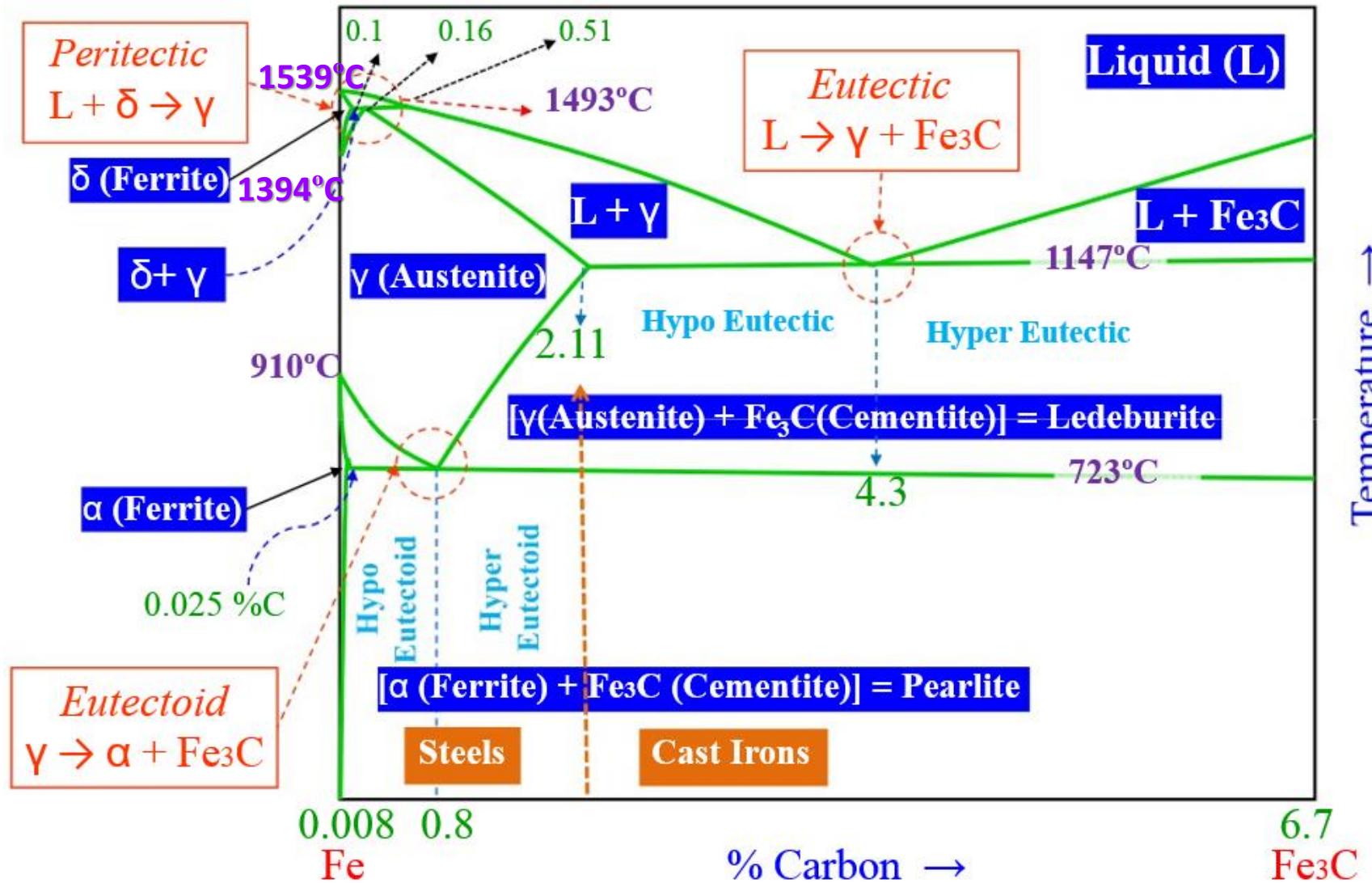
- Figure b shows the cooling curve, i.e., cool iron slowly from above its boiling point, the temperature as a function of time.
- Pure iron solidifies initially to BCC δ -iron, but undergoes further solid-state phase transformations on cooling, first to FCC γ -iron at $1394\text{ }^{\circ}\text{C}$, and then back to BCC α -iron at $910\text{ }^{\circ}\text{C}$.
- These transformations also release latent heat, but the amount is much smaller.



(b) corresponding cooling curve for condensing then solidifying iron from vapor to liquid to solid



Iron-Cementite Phase Diagram – Features



Classification Scheme of Ferrous Alloys

✓ Iron

Pure iron contains less than 0.008 wt% C

✓ Steel

0.008-2.11 wt% C, in practice, <1.0 wt% C

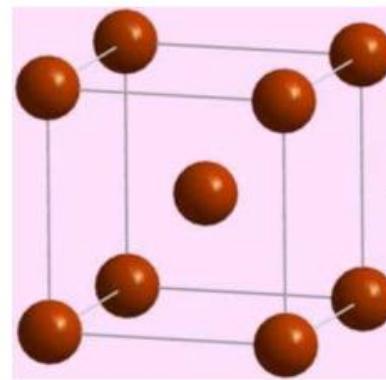
✓ Cast Iron

2.11-6.70 wt% C, in practice, <4.5 wt% C

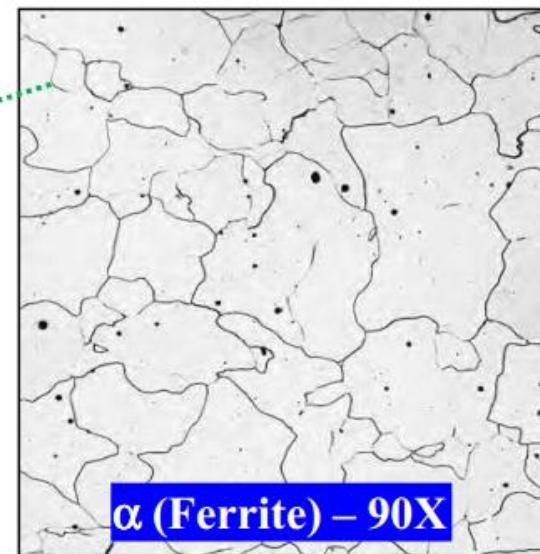


Ferrite (α)

- It is an interstitial solid solution of a small amount of carbon dissolved in α iron. The maximum solubility is 0.025% C at 723 °C and it dissolves only 0.008% C at room temperature. *It is the softest structure that appears on the diagram.*
- Ferrite is ferromagnetic at low temperatures but loses its magnetic properties with the rise of temperatures with major loss at curies temperatures, 768 °C and above this temperature, it becomes non magnetic (paramagnetic).
- The crystal structure of ferrite (α) is B.C.C
- Tensile strength - 245 Mpa, Yield strength 118 Mpa
- Elongation - 40-50% in 2 in.
- Hardness - 95 VPN



α (Ferrite) contains
B.C.C structure

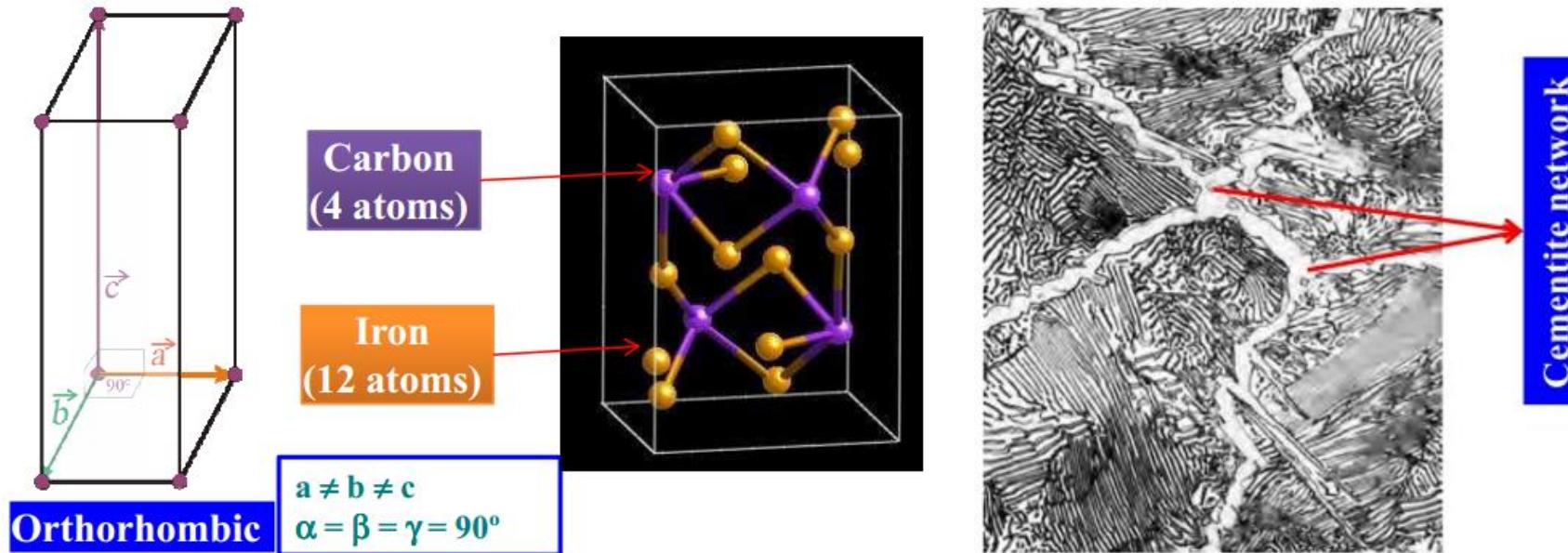


α (Ferrite) – 90X



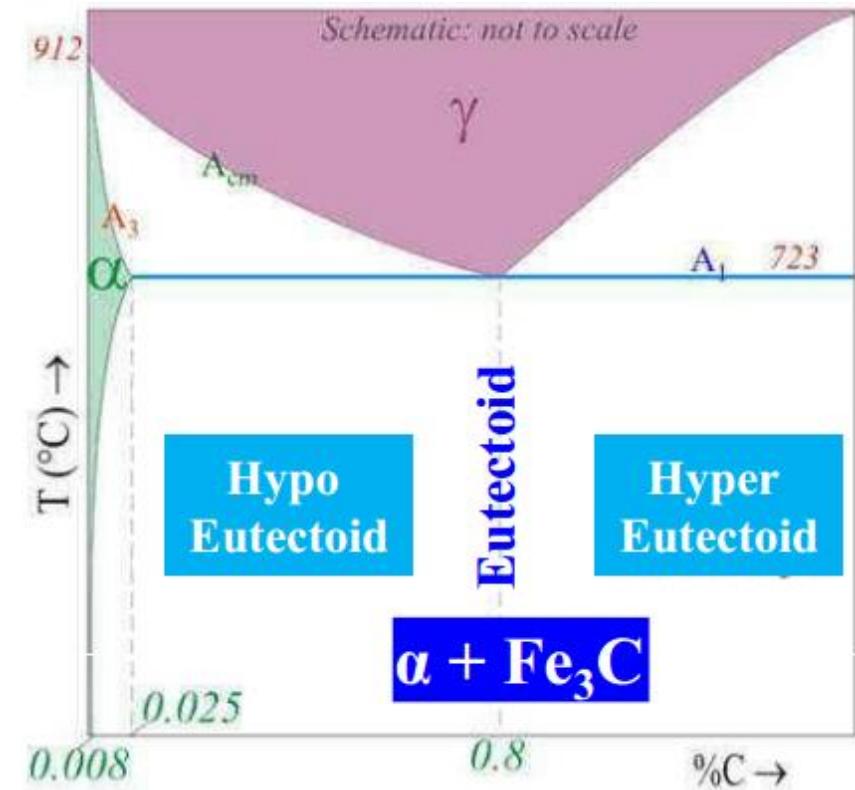
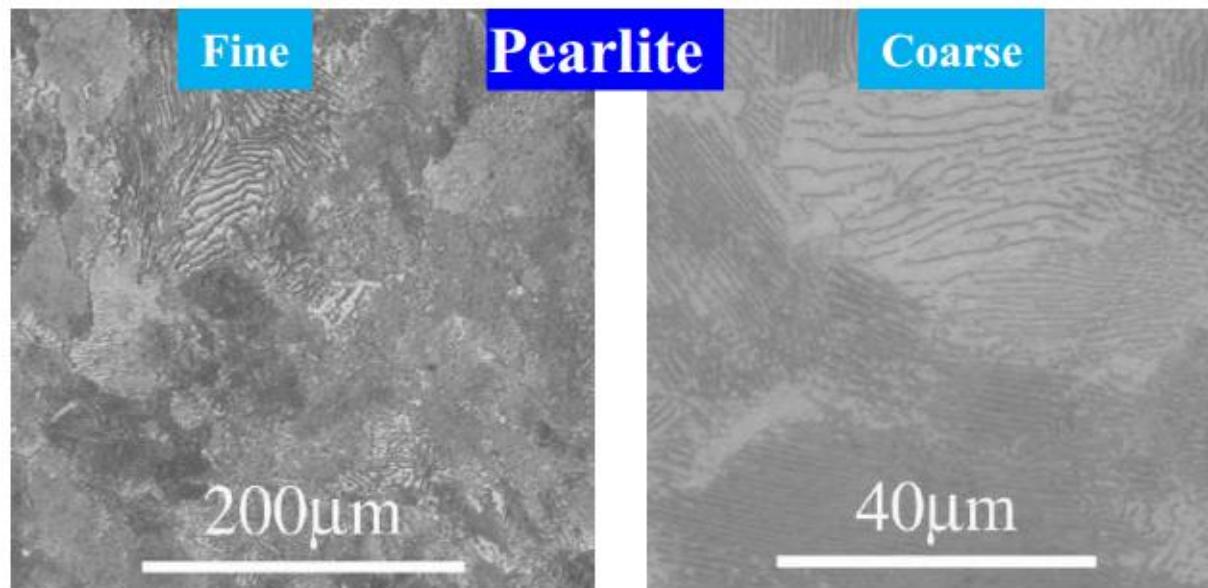
Cementite (Fe_3C)

- Cementite or iron carbide, chemical formula Fe_3C , contains 6.67% C by weight and it is a **metastable phase**.
- Any **metastable phase** is a phase with momentary stability or in other words, which give enough time, will change.
- It is typically hard and brittle interstitial compound of low tensile strength (35 MPa) but high compressive strength and high hardness ~800 VPN.
- It is the hardest structure that appears on the diagram.
- It has a complex orthorhombic crystal structure with 12 iron atoms and 4 carbon atoms per unit cell.
- It is slightly ferromagnetic up to 210 °C and paramagnetic above it. Melting point around 1227 °C.



Pearlite (α + Fe_3C)

- Pearlite is the eutectoid mixture containing 0.80 % C and is formed at 723 °C on very slow cooling.
- It is very fine plate like or lamellar mixture of ferrite and cementite. The fine finger print mixture called pearlite is shown in below figure.
- The weight % of these two phases are thus in ratio 8:1
- Tensile strength - 120,000 psi or 825 Mpa Elongation - 20 percent in 2 in.
- Hardness - HRC 20, HRB 95-100, or BHN 250-300



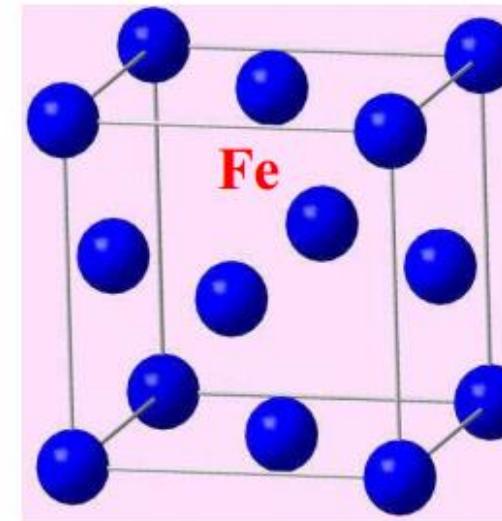
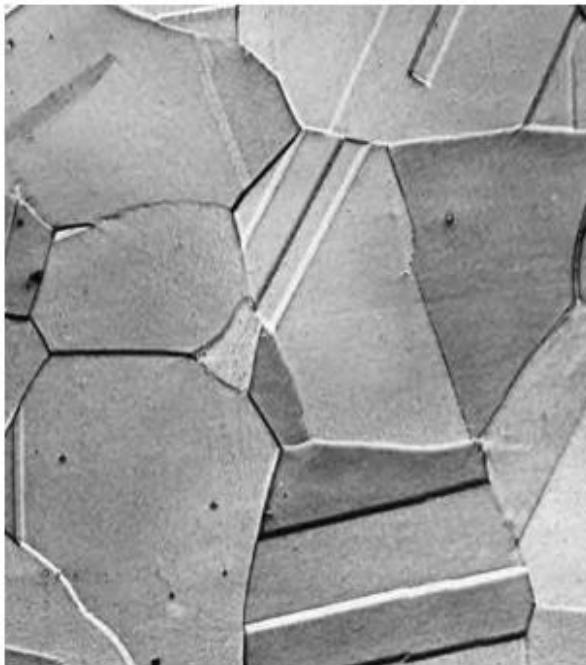
Remember...!

Pearlite is a not a phase but combination of two phases (ferrite + cementite)



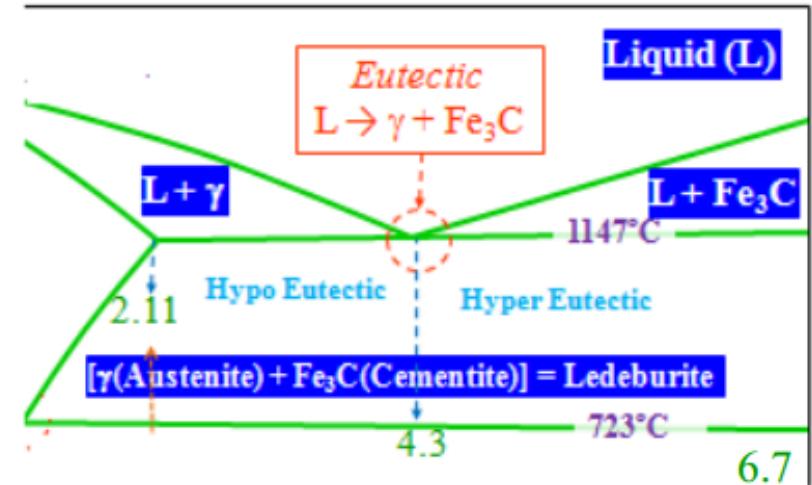
Austenite (γ)

- It is an interstitial solid solution of a small amount of carbon dissolved in γ iron and has FCC crystal structure. The maximum solubility is 2.1% C at 1147 °C.
- Austenite is soft, ductile tough and malleable (FCC structure) and non magnetic (paramagnetic).
- Steels are commonly rolled and forged above about 1100 °C when they are in austenite state due to its high ductility and malleability, which is also due to its FCC structure.
- Tensile strength - 150,000 psi or 1035 Mpa
- Elongation - 10% in 2 in.
- Hardness - 395 VPN and Toughness is high.



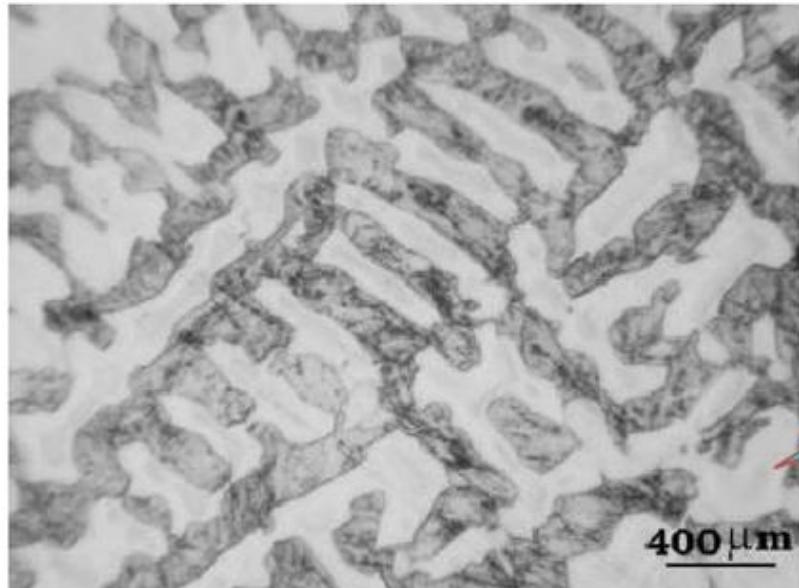
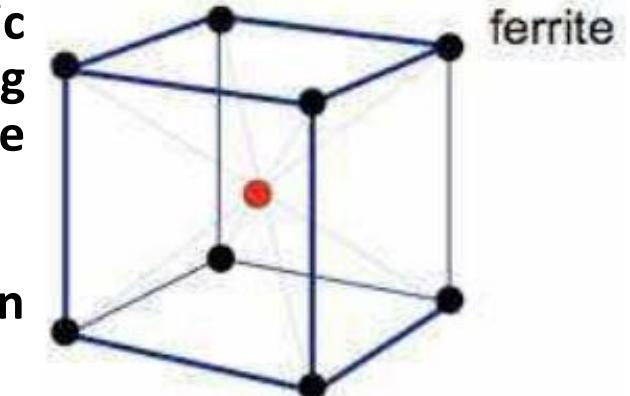
Ledeburite (γ + Fe_3C)

- Ledeburite is the eutectic mixture of austenite and cementite.
- It contains 4.3% C and is formed at 1147 °C.
- Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
- Not stable at room temperature



Ferrite (δ)

- Interstitial solid solution of carbon in iron of body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89 \AA) having solubility limit of 0.1 wt% at 1493 °C with respect to austenite. The stability of the phase ranges between 1394-1539 °C.
- It is a high temperature phase and is a high temperature manifestation of α ferrite.
- This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel specially duplex stainless steel.



δ -ferrite in dendrite form
in as-cast
 $\text{Fe-0.4C-2Mn-0.5Si-2Al0.5Cu}$

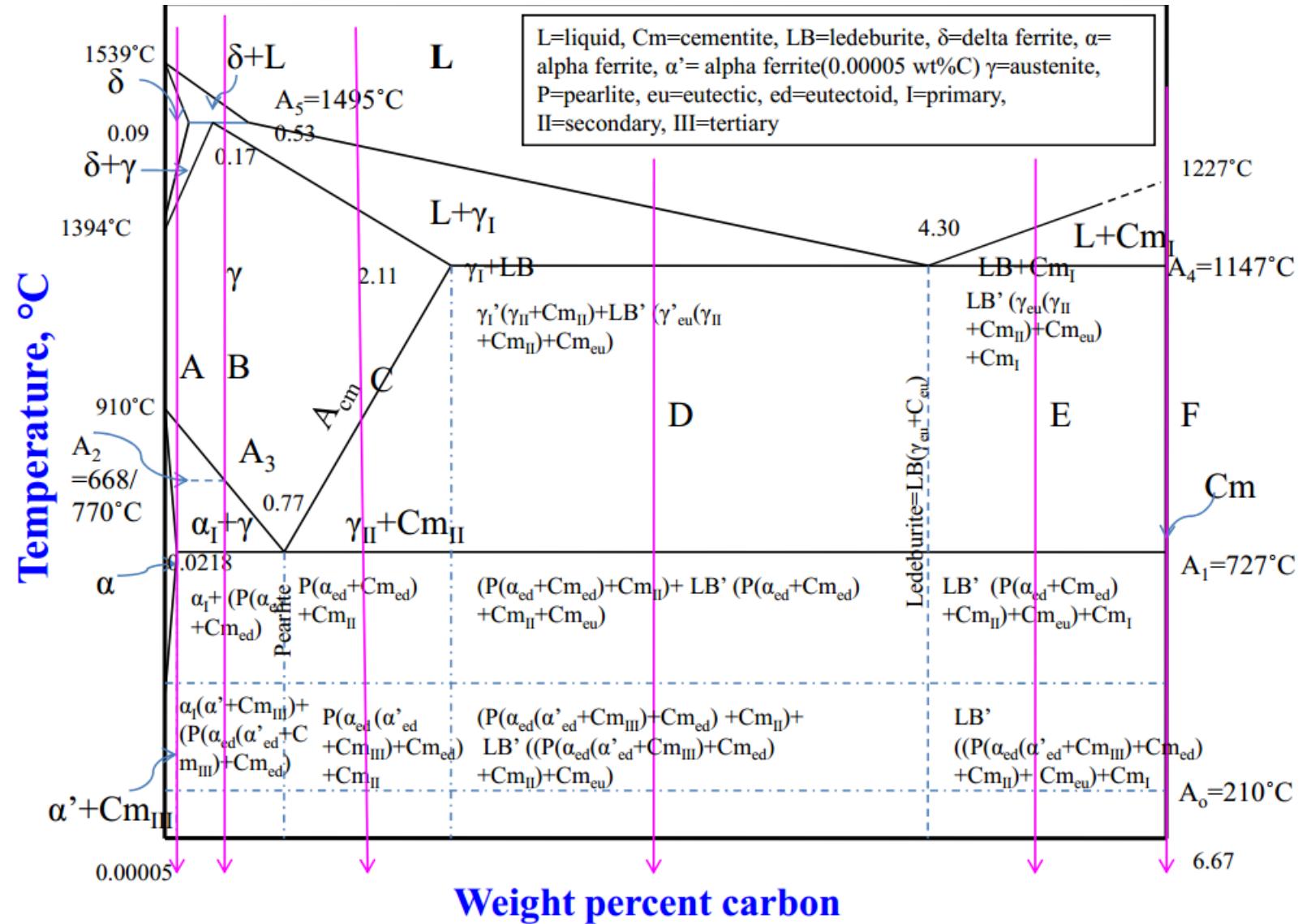


Limitations on Fe-Fe₃C Phase Diagram

- Fe-Fe₃C diagram represents behavior of steels under equilibrium conditions, whereas the actual heat treatments of steels are normally under non-equilibrium conditions.
- The diagram does not indicate the character of transformation of austenite such as to bainite, or martensite.
- The diagram does not indicate the presence of metastable phases like martensite, or bainite.
- It does not indicate the temperature of start of martensite M_s or bainite B_s.
- It does not indicate the kinetics of the transformation of austenite to martensite, bainite or even pearlite.
- It does not indicate the possibilities of suppressing the pearlitic or bainitic transformations.



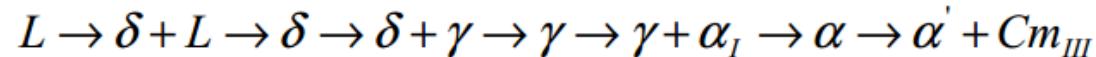
Fe- Fe_3C Phase Diagram (Microstructural Aspects)



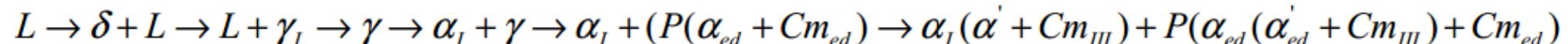
Evolution of Microstructures on Equilibrium Cooling

- Sequence of evolution of microstructure can be described by the projected cooling on compositions A, B, C, D, E, F.

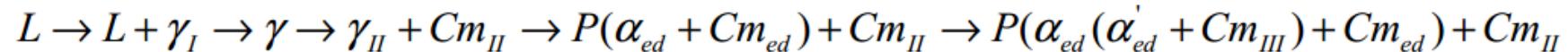
- At composition A**



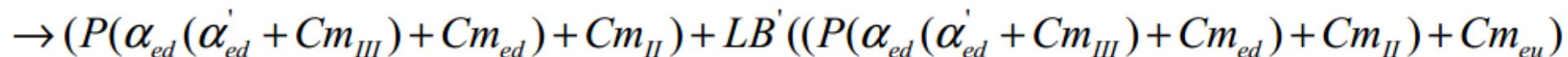
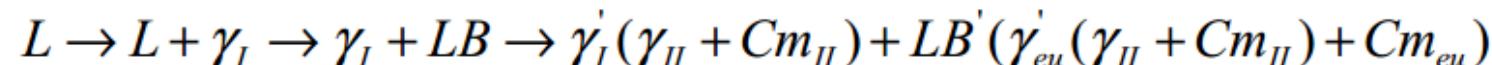
- At composition B**



- At composition C**



- At composition D**

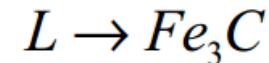


Contd...

□ At composition E

$$\begin{aligned}L &\rightarrow L + Cm_I \rightarrow LB(\gamma_{eu} + Cm_{eu} + Cm_I) \rightarrow LB'(\gamma_{eu}(\gamma_{II} + Cm_{II}) + Cm_{eu}) + Cm_I \\&\rightarrow LB'(P(\alpha_{ed} + Cm_{ed}) + Cm_{II}) + Cm_{eu} + Cm_I \\&\rightarrow LB'((P(\alpha_{ed}'(\alpha_{ed}' + Cm_{III}) + Cm_{ed}) + Cm_{II}) + Cm_{eu}) + Cm_I\end{aligned}$$

□ At composition F



Example – 3

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

- Composition of Fe_3C and ferrite (α)
- The amount of Fe_3C and ferrite (α)
- The amount of pearlite and proeutectoid ferrite (α)
- Composition of Fe_3C and ferrite (α)

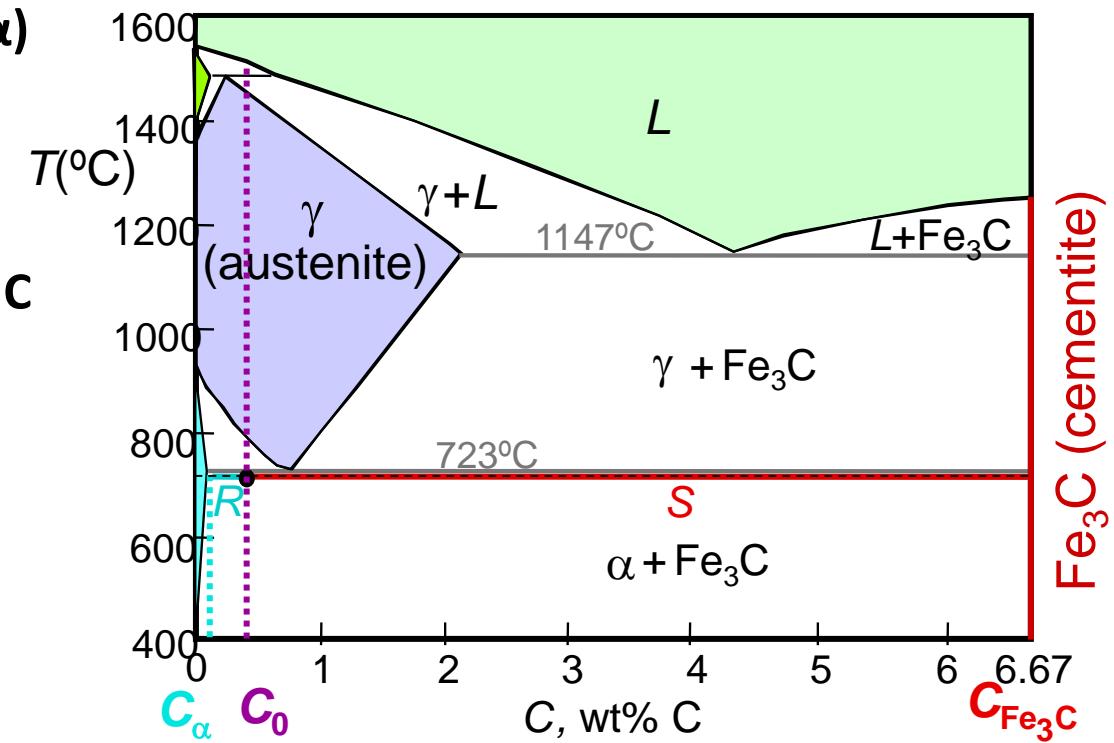
$$C_\alpha = 0.025 \text{ wt\% C}$$

0.025
Ferrite

0.4

$$C_{\text{Fe}_3\text{C}} = 6.67 \text{ wt\% C}$$

6.67
Cementite



Contd...

b) The amount of Fe_3C and ferrite (α)

$$C_\alpha = 0.025 \text{ wt% C}$$

0.025

0.4

Ferrite

$$C_{\text{Fe}_3\text{C}} = 6.67 \text{ wt% C}$$

6.67

Cementite

$$C_0 = 0.4 \text{ wt% C}$$

$$\text{Percentage of } \text{Fe}_3\text{C} = \frac{0.4 - 0.025}{6.67 - 0.025} * 100$$

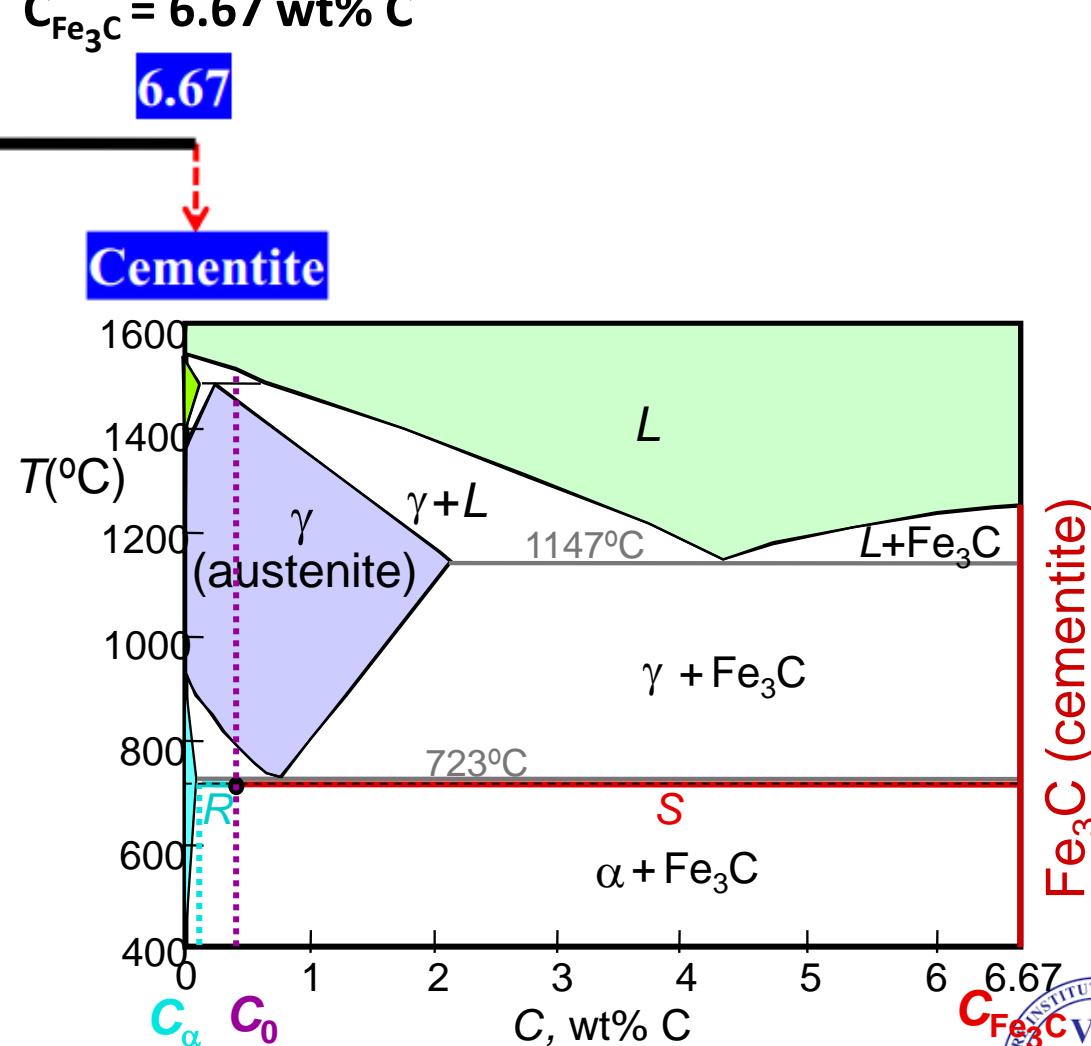
Percentage of Fe_3C in 0.4 %C steel is 5.64 %

Percentage of Ferrite (α) in 0.4 %C steel = $(100 - 5.64)\%$

Percentage of ferrite in 0.4 %C steel = 94.36%

or

$$\text{Percentage of ferrite} = \frac{6.67 - 0.4}{6.67 - 0.025} * 100 = 94.36\%$$



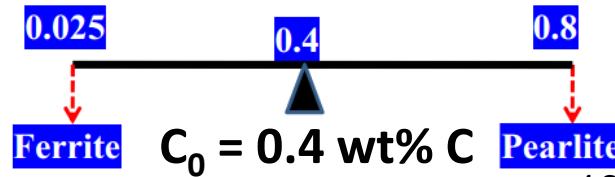
Contd...

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

$$\text{Percentage of pearlite} = \frac{0.4 - 0.025}{0.76 - 0.025} * 100$$

$$C_\alpha = 0.025 \text{ wt% C} \quad C_{\text{pearlite}} = C_\gamma = 0.8 \text{ wt% C}$$

Percentage of pearlite = 48 %



Percentage of proeutectoid ferrite (α) in 0.4 %C steel = (100 - 48)%

Percentage of proeutectoid ferrite (α) = 52 %

or

$$\text{Percentage of proeutectoid ferrite} = \frac{0.76 - 0.4}{0.76 - 0.025} * 100 = 52\%$$

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

