University of Anbar/ Faculty of Engineering

Department of Mechanical Engineering

2nd Semester (2018/2019)

Subject: Engineering of Metallurgy

Course Code: ME2304

Stage: 2nd Year

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Lecture # 10

CHAPTER FIVE/PHASE DIAGRAMS

Definitions and basic concepts:

One reason that a knowledge and understanding of phase diagrams is important to the engineer relates to the design and control of heat-treating procedures; some properties of materials are functions of their microstructures, and, consequently, of their thermal histories.

- **Phase equilibrium diagram** is a graphic relationship between temperature and weight ratios of elements and alloys contribute to the built of the diagram.
- Phase diagrams provide information on the following:
  - Melting point .
  - Casting condition .
  - Crystallization condition .
  - phase transformations (changes).
- **Phase** is a uniform portion (part) of an alloy, and a homogeneous combination of mater having a certain chemical composition and structure, and uniform physical and chemical and mechanical properties. and which is

separated from other alloy constituents by phase boundary.[example: H_2O can exit as a ***gas, liquid*** *and* ***solid***. These are three different phases of water].

- **Component**: the element or compound which is present in the mixture (e.g., Al and Cu).
- **Solvent** - host or major component in solution, **solute** - minor component in solution.
- **Solubility Limit** - max. concentration of atoms to be dissolved in the solvent to form a **solid solution**.[example solubility of sugar in water]

  This solubility limit of sugar in water depends on the temperature of the water and may be represented in graphical form on a plot of temperature along the ordinate and composition.

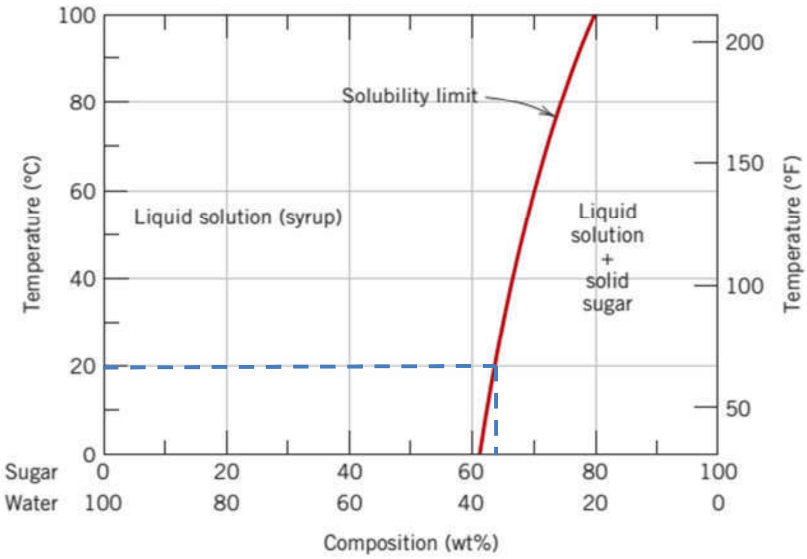


Figure 1. The solubility of sugar in a sugar–water syrup.

Example: What is the solubility limit at 20°C**?**

Answer: 65 wt% sugar.

If C_o < 65 wt% sugar at 20°C : syrup (1 phase)

If C_o > 65 wt% sugar at 20°C : syrup + sugar (2 phases)

- **Phases and solubility: [**Water and alcohol have complete solubility], [Salt and water have limited solubility], [Oil and water have no solubility].

ONE-COMPONENT (OR UNARY) PHASE DIAGRAMS

All curve from ***three curves*** in the **figure 2**. represent ***case equilibrium of two phases.***

From Phase Diagram of Water:

- **Triple point** – the point on a phase diagram at which the three states of matter: gas, liquid, and solid exist.
- **Critical point** – the point on a phase diagram at which the substance is indistinguishable between liquid and gaseous states (i.e., no separate interface between three phases).
- **Fusion(melting) (or freezing) curve** – the curve on a phase diagram which represents the transition between liquid and solid states
- **Vaporization (or condensation) curve** – the curve on a phase diagram which represents the transition between gaseous and liquid states
- **Sublimation (or deposition) curve** – the curve on a phase diagram which represents the transition between gaseous and solid states

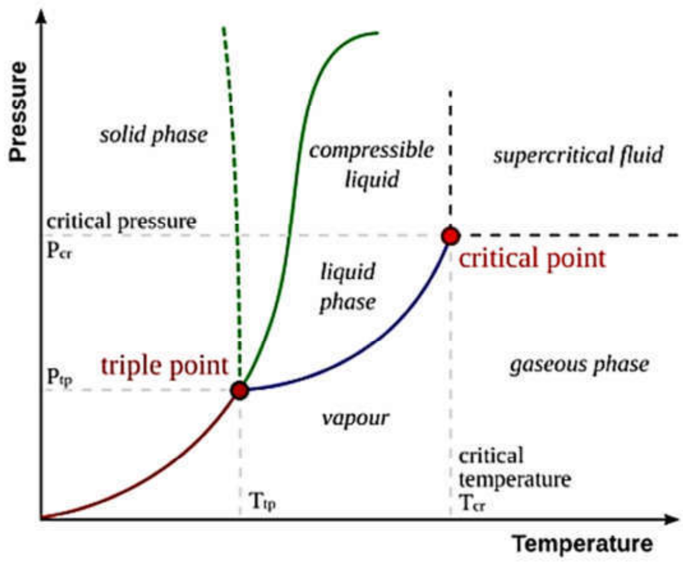


Figure 2. Pressure–temperature phase diagram for H_2O.

Note: the hidden green curve applied on water only, because the water expanded when transform to solid (ice), while all another materials converge when densification.

Alloying systems

There are many types of alloying systems which they are:

1) ***Binary system***: It means that alloying have two metals (2 components)only.
2) ***Ternary system:*** It means that alloying have three metals only.
3) ***Multi system:*** It means that alloying have three and more than that metals.

Binary Phase Diagrams

Binary Alloy: when two metals or a metal and a small amount of a nonmetal are mixed in their molten states and allowed to cool, the result is a binary alloy.

In general, binary alloys can be classified into the following types:

1) Solid solution type: The two components are completely soluble in each other both in the liquid state and in the solid state. [**example** of Solid solution; gold- silver alloy , cupper- nickel alloy].
2) Simple eutectic type: The two components are soluble in each other in the liquid state but not in the solid state. [**example** of eutectic are carbon steels].
3) Combination type: The two components are completely soluble in the liquid state, but are only partially soluble in the solid state (e.g. Pb-Sn)..

1) Solid solution system (Full Solubility) - (Cigar shaped diagram)

- Definition Solid solution alloy, types, and conditions of substitutional Solid solution [**See Chapter 4**].
- Solid solution formation usually causes increase of electrical resistance and mechanical strength and decrease of plasticity of the alloy.

  Simple solution system (e.g., Ni-Cu solution), Ni and Cu are totally soluble in all proportions (substitutional Solid solution); because of both have the same crystal structure (FCC) and have similar electronegativities and atomic radii.

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

In Solid solution system (Full Solubility diagram) there are three different regions:

1. Liquid (single phase)
2. Liquid + solid (double phase; L + α)
3. Solid solution (single phase α)

- **Liquidus**: the boundary line between the liquid region and the double phase region.
- **Solidus**: the boundary line between the solid solution region and the double phase region.

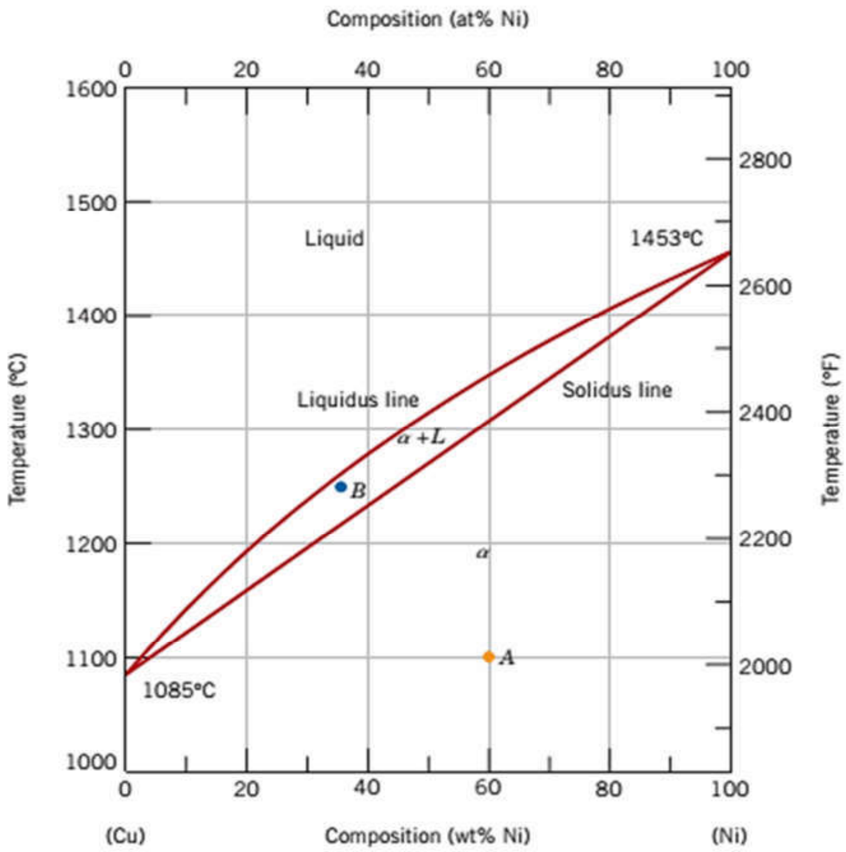


Figure 3. The copper–nickel phase diagram.

For a given temperature and composition we can use phase diagram to determine:

1) Phase presents: just locate the Temperature-Composition point and determine the phase(s)
2) Phase composition.
3) Phase amount (in the double phase region) – The Lever rule

At the point B:

1) **Phases presents:** 2 Phases (double phase; L + α)
2) **Phase composition:**

The Ni composition of the liquid phase is C_L

The Ni composition of the solid (α) phase is Cα

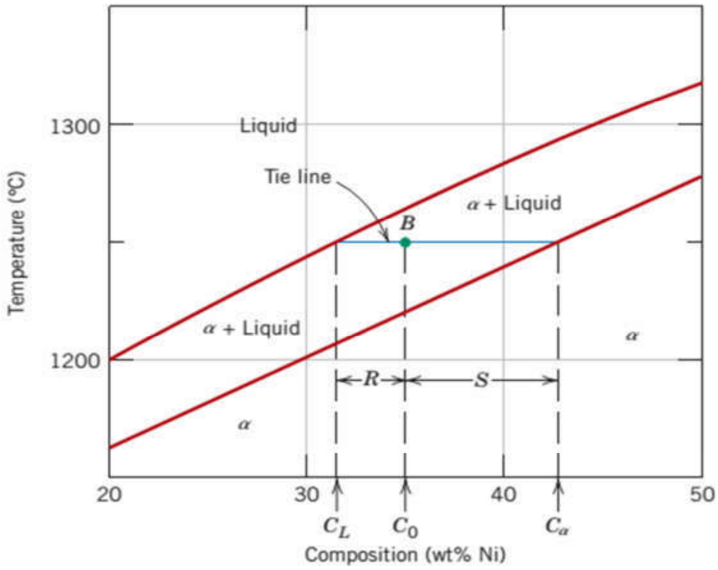
3) **Phase amount:**
   For two phases region, use the Lever Rule.

Amount of the liquid phase is:

$$W_L = \frac{S}{R + S}$$

Amount of the Solid phase is:

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



- **Rule 1**: If we know T and C_o, then we know: the numbers and type of phases present.
  Example: Point A (1100°C, 60wt%Ni): 1 phase: α
  Point B (1250°C, 35wt%Ni): 2 phases: L + α
- **Rule 2**: If we know T and Co, then we know: the composition of each phase.
  Example: from **Figure 3.**

Point A (1100°C, 60wt%Ni): Only Solid solution (α),
Cα = Co (= 60wt% Ni).

Point B (1250°C, 35wt%Ni): 2 phases: L + α;
C_L = Cliquidus (= 32wt% Ni)
Cα= Csolidus (= 43wt% Ni)

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

  Example: from **Figure 3.**

  Point A (1100°C, 60wt%Ni): 1 phase: α (only solid phase)

  $W_L = 0$, $W\alpha = 100$ wt%

The Lever Rule

<u>Finding the composition in a two phase region</u>:

1) Locate composition and temperature in diagram
2) In two phase region draw the tie line or isotherm.
3) Note intersection with phase boundaries. Read compositions at the intersections.

All material must be in one phase:

$$W\alpha + W_L = 1$$

Mass of a component that is present in both phases (Co):

$$W\alpha C\alpha + W_L C_L = Co$$

Solution of these equations gives us the lever rule:

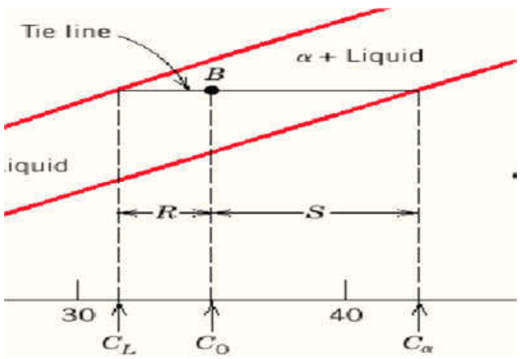
$$W_L = (C\alpha - Co) / (C\alpha - C_L)$$

$$W\alpha = (Co - C_L) / (C\alpha - C_L)$$

Or;

$$W_L = \frac{S}{R + S}$$

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



Example: at Point B Alloy (35wt%Ni) **at** temperature 1250°C;

- Phases present? 2 phases: L + α;
- Compositions of liquid and solid?

  C_L = Cliquidus (= 31.5wt% Ni)

  Cα= Csolidus (= 42.5wt% Ni)

- Phase amount (wt%)?
  Co = 35wt%Ni
  C_L = Cliquidus (= 31.5wt% Ni)
  Cα= Csolidus (= 42.5wt% Ni)

$W_L = (C\alpha - Co) / (C\alpha - C_L) = (42.5 - 35) / (42.5- 31.5) = 0.68$

$W\alpha = (Co - C_L) / (C\alpha - C_L) = (35 - 31.5) / (42.5- 31.5) = 0.32$

Or;

$W\alpha + W_L = 1; \quad W\alpha + 0.68 = 1; \quad W\alpha = 0.32$

Development of microstructure in isomorphous alloys

1) Equilibrium (very slow) cooling:

- Solidification in the solid + liquid phase occurs gradually upon cooling from the Liquidus line.
- The composition of the solid and the liquid change gradually during cooling (as can be determined by the tie-line method.)
- Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.

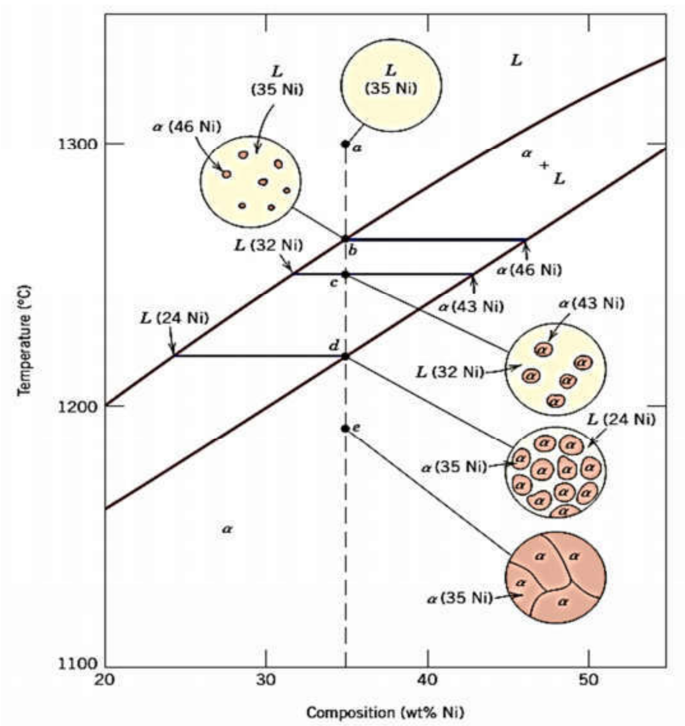


Figure 4. Schematic representation of the development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy

2) Non-equilibrium Fast cooling: (Coring in Solid Solutions)

- Compositional changes require diffusion in solid and liquid phases.

- **Diffusion in the solid is very slow** ⇒ new layers that formed on top of the existing grains have the equilibrium composition at that temperature but once they are solid their composition does not change. ⇒ Formation of layered (cored) grains.

- **Diffusion in the liquid is very fast** ⇒ tie-line method works ⇒ a greater proportion of liquid phase as compared to the one for equilibrium cooling at same T ⇒ Solidus line is shifted to the right (higher Ni contents), solidification is complete at lower T, the *outer part of the grains are richer in the low-melting component (Cu).*

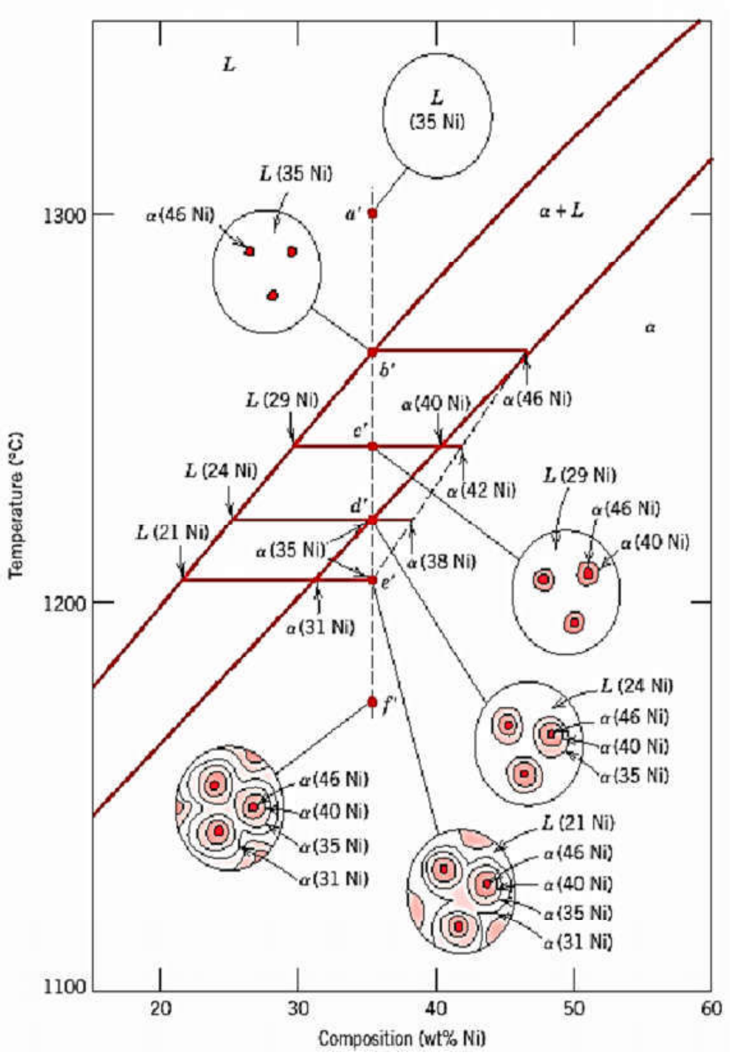
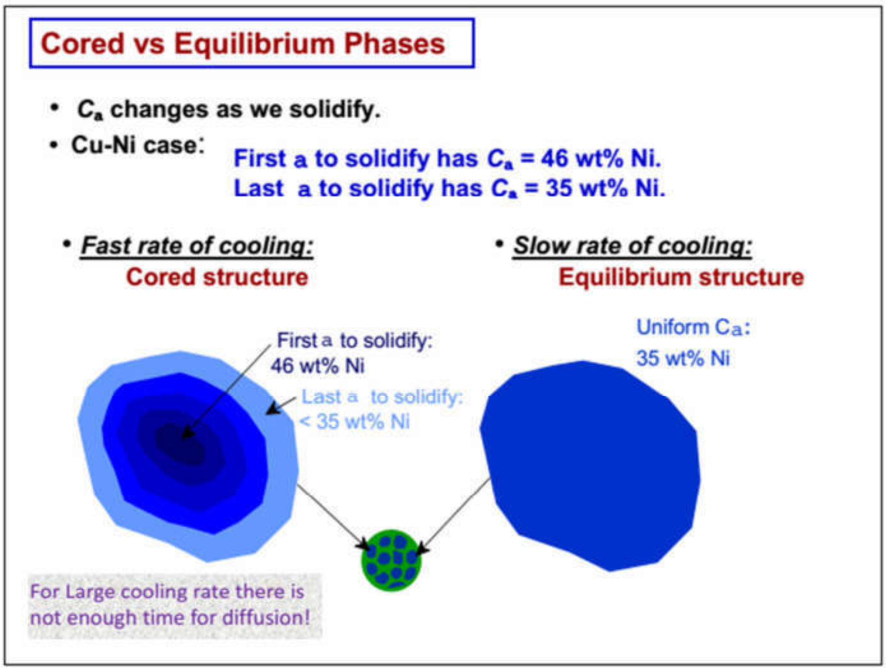


Figure 5. Schematic representation of the development of microstructure during the nonequilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy

- As a casting having a cored structure, upon heating grain boundaries will melt first. This can lead to premature mechanical failure.
- **Coring** may be **eliminated by a homogenization (annealing) heat treatment** carried out at a temperature below the solidus point for the particular alloy composition. During this process, **atomic diffusion occurs**, which produces **compositionally homogeneous grains**.



Example - Equilibrium Cooling:

A copper–nickel alloy of composition 35wt% Ni – 65wt% Cu is slowly cooled from 1300°C;

(a) At what temperature does the first solid phase form?

Answer: Around 1250°C

(b) What is the composition of this solid phase?

Answer: 46 wt% Ni

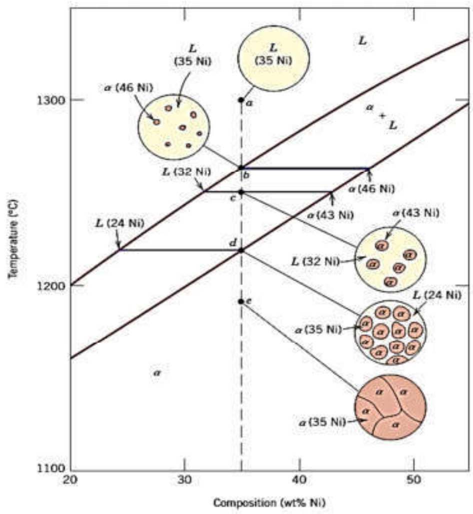
(c) At what temperature does complete solidification of the alloy occur?

Answer: Around 1210°C

(d) What is the composition of the last liquid remaining prior to complete solidification?

• 24 wt% Ni

(e) What is the amount of the solid phase at point c?



$W\alpha = (C_o - C_L) / (C\alpha - C_L) = (35 - 32) / (43 - 32) = 27\%$

$W\alpha + W_L = 1 \Rightarrow W_L = 73\%$

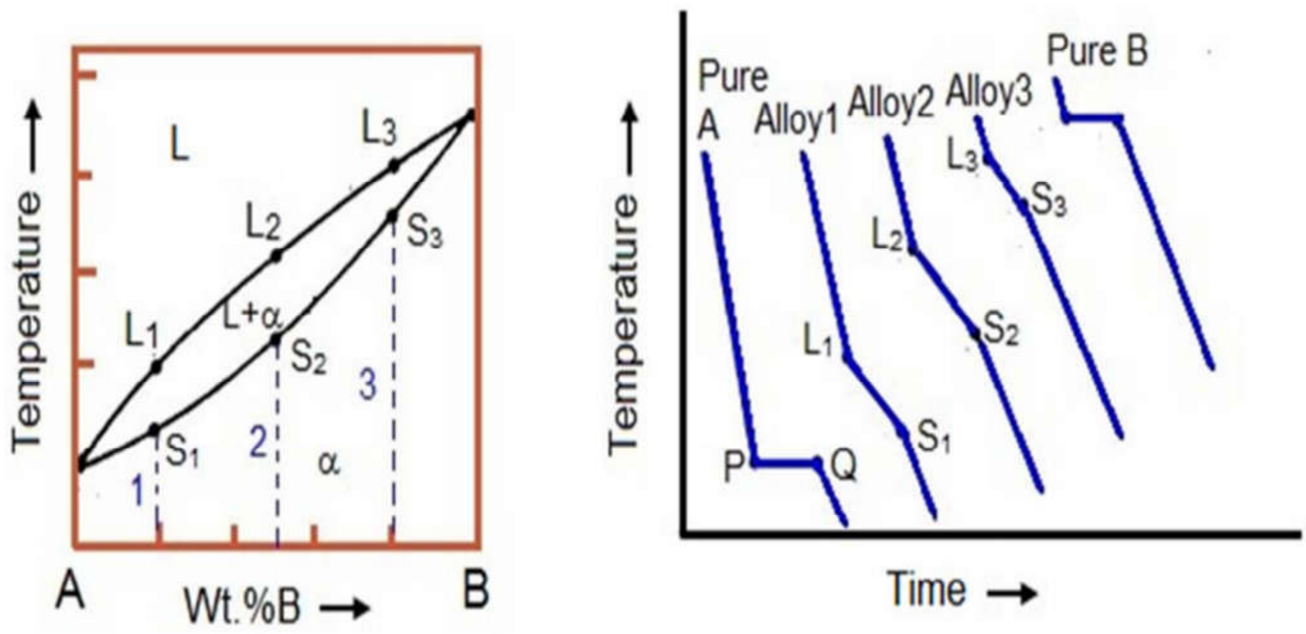
Cooling Curves

Pure Metal

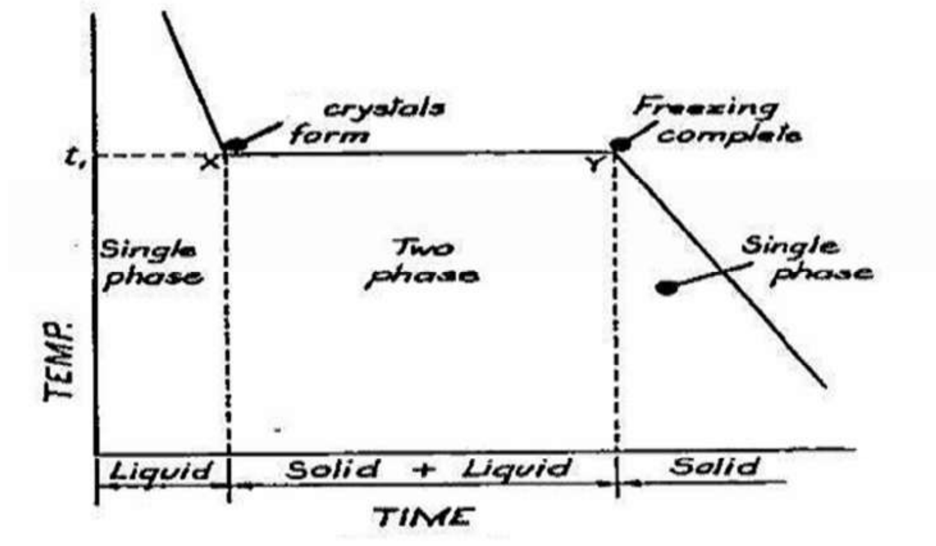
Upon cooling from liquid state, the temperature of the pure metal (A or B) drops continuously till melting point at which solidification starts. Solidification happens at a constant temperature (line PQ) as a result from formation of crystals and loss of latent heat. The temperature drops again on completion of solidification.

Alloy

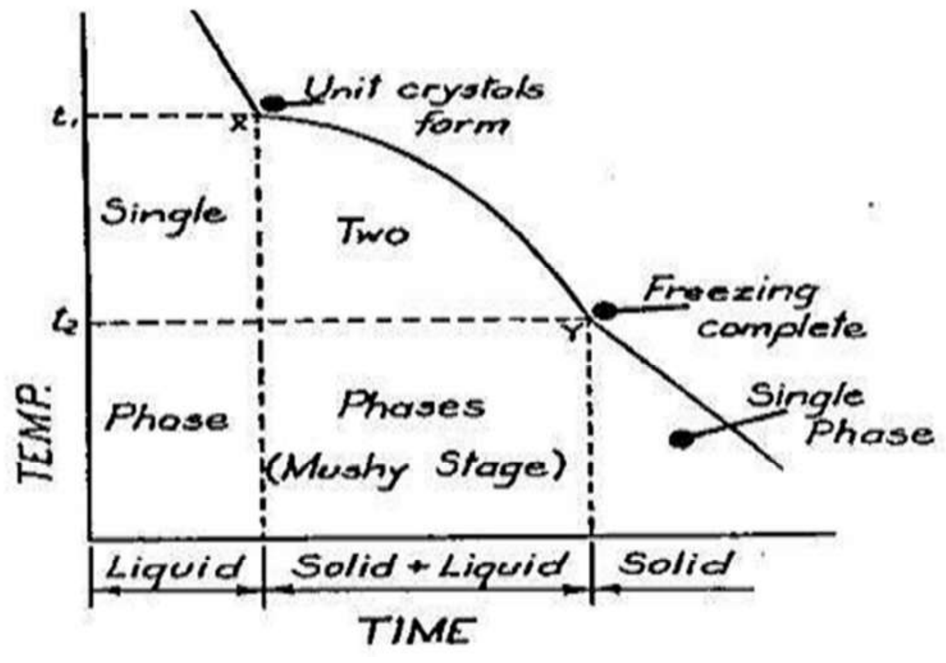
For any alloy (1, 2, 3) temp temperature drops till the Liquidus (L1, L2, L3). However, in this case, solidification proceeds over a range of temperature. Once solidification completes at the solidus (S1, S2, S3) the temp temperature drops again.



Cooling Curves describe creation of Cu-Ni solid solution phase diagram



Cooling Curve of Pure Metal



Cooling Curve of solid solution alloy.

Sample question:

Metal A melts at 1400ºC, Metal B melts at 600ºC. Thermal arrest data is obtained from cooling curves for the alloy of AB and is shown below.

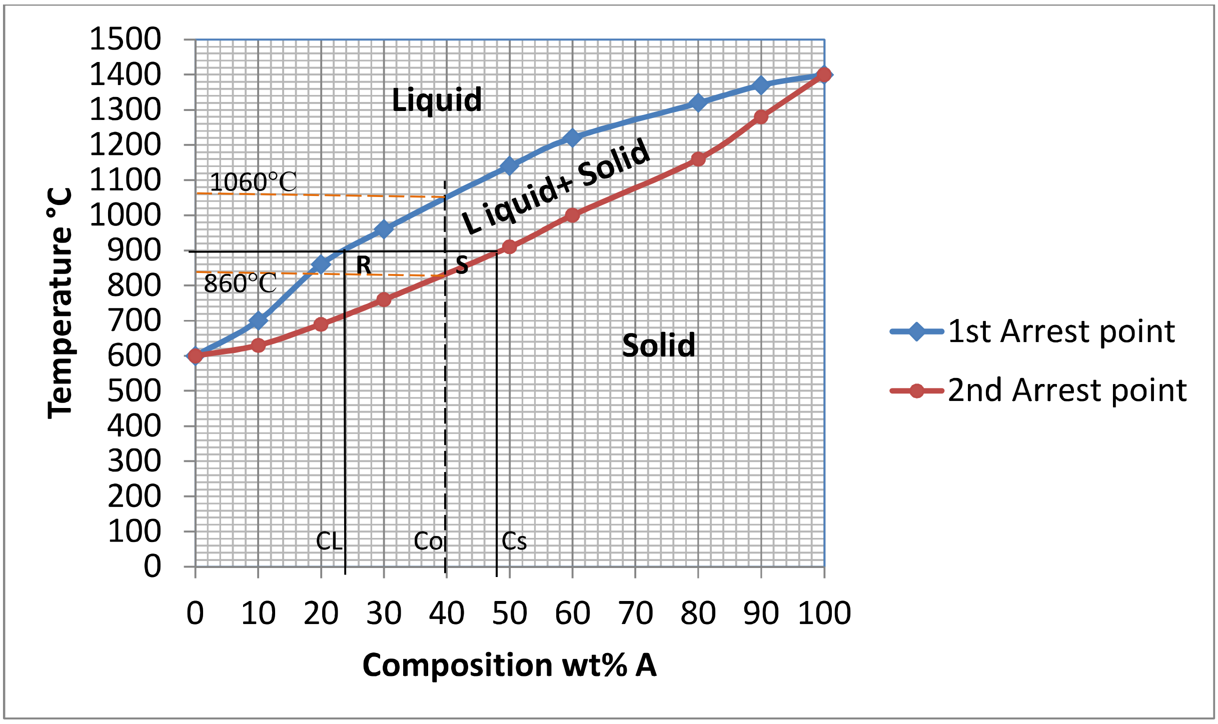
%A	0	10	20	30	50	60	80	90	100
1st Arrest point	600	700	860	960	1140	1220	1320	1370	1400
2nd Arrest point	600	630	690	760	910	1000	1160	1280	1400

1st Arrest point: Freezing Start temperature ºC.
2nd Arrest point: Freezing End temperature ºC.

(i) plot and label the equilibrium diagram
(ii) for an alloy containing 40% of A and 60% B state
(a) solidification start temperature
(b) solidification ending temperature
(c) composition of phases at 900ºC
(d) the amount of phases
(e) the ratio of phases

Solution:

(i) plot and label the equilibrium diagram



(ii) for an alloy containing 40% of A and 60% B state

(a) Solidification start at 1060ºC.

(b) Solidification ending at 840ºC

(c) Composition of phases at 900ºC,

Liquid Point (C_L) = 24% A 76% B

Solid point (C_s)= 48% A and 52% B.

(d) Amount of the phases is determined by Law of Lever rule:

$W_L = (Cs - Co) / (Cs - C_L) = (48 - 40) / (48- 24) = 0.33$

$Ws = (Co - C_L) / (Cs - C_L) = (40 - 24) / (48- 24) = 0.67$

Or;

$Ws + W_L = 1$; $Ws + 0.33= 1$; $W\alpha = 0.67$

(e) Ratio of the phases:

$W_L = 0.33$, $Ws = 0.67$

Ratio = $Ws/W_L = 0.67/0.33 = 2$

Example: Nickel, Aluminum & Copper have face cantered cubic structure yet Ni is soluble in copper whereas Al has only a limited solubility. Explain why it is so?

Answer: Both the metals must have same crystal structure, valence & nearly same atomic diameter. Both Ni & Cu have the same crystal structure (FCC) and have similar electronegativities and atomic radii as well as valence. Aluminum has larger atomic radius, and higher valence. Therefore its solubility of Al in Cu is limited.