

4

Phase and Phase Equilibrium

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4.1 Introduction

- ▶ Phase diagrams, also known as Equilibrium Diagrams are a very important tool in the study of alloys.
- ▶ A phase diagram has temperature as its ordinate (Y-axis) & alloy composition as abscissa (X-axis).
- ▶ Ideally, the phase diagram will show the phase relationship under equilibrium conditions, in which there is no change with the time.
- ▶ Equilibrium conditions may be approached by extremely slow heating and cooling so that if a phase change is to occur, sufficient time is allowed.

4.2 Useful Terminology

- ▶ **System:** A system is a substance (or group of substances) so isolated from its surroundings that it is unaffected by these and is subjected to changes in the overall composition, temperature, pressure or total volume only to the extent allowed by the investigator.
- ▶ **Alloy System:** It is defined as a combination of two or more elements, forming alloys that are considered within a specified range of temperature, pressure, and concentration.
- ▶ **Component:** It is a unit of the composition variable of the system. A system having one component is called a Unary system and the system having two, three and four components are known as Binary, Ternary, and Quaternary systems, respectively.
- ▶ **Phase:** A phase can be defined as any part or portion of a chemical system that possesses distinctive physical characteristics, is limited by definite bonding surfaces, and may conceivably be mechanically separated from its surroundings.
- ▶ **Structural constituent:** The association of phases in a recognizably distinct fashion may be referred to as a structural constituent of the alloy.
- ▶ **Solid solution:** It consists of atoms of at least two different types where solute atoms occupy either substitutional or interstitial positions in the solvent lattice and the crystal structure of the solvent is maintained.
- ▶ **Solubility limit:** For almost alloy systems, at a specific temperature, a maximum of solute atoms can dissolve in the solvent phase to form a solid solution. The limit is known as the solubility limit. In general, solubility limit changes with temperature. If solute available is more than the solubility limit that may lead to the formation of different phases, either a solid solution or compound.
- ▶ **Phase equilibrium:** It refers to the set of conditions where more than one phase may exist. It can be reflected by the constancy with time in the phase characteristics of a system. In most metallurgical and materials systems, phase equilibrium involves just solid phases. However, the state of equilibrium is never completely achieved because of the very slow rate of approach of equilibrium in solid systems. This leads to non-equilibrium or meta-stable state, which may persist indefinitely and of course, has more practical significance than equilibrium phases. An equilibrium state of the solid system can be reflected in terms of characteristics of the microstructure, phases present and their compositions, relative phase amounts, and their spatial arrangement or distribution.

4.3 Cooling Curves

- ▶ A method to determine the temperature at which phase changes (liquid \rightleftharpoons solid) occur in an alloy system, consists of following the temperature as a function of time as different alloys in the system are very slowly cooled.

- ▶ The data obtained in this manner forms a cooling curve for each of the alloys. (Fig4.1)
- ▶ This method is useful in,
 - Studying the changes that occur during the solidification of alloys and also in determining transformations subsequent to solidification.

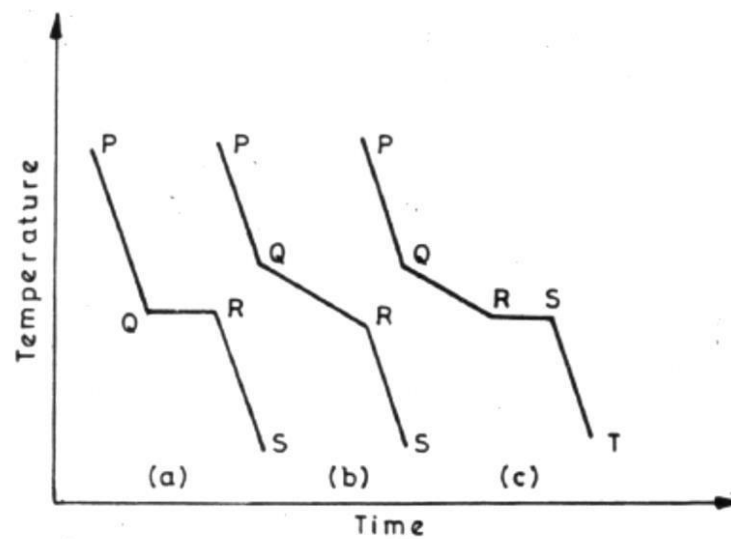


Fig.4.1 - Cooling curves for (a) Pure Metal or compound
(b) Binary solid solution
(c) Binary eutectic system

There are mainly three types of cooling curves.

a. Cooling curve of pure metal or compound

- ▶ The liquid metal cools from P to Q. First crystals begin to form at point Q.
- ▶ From Q to R, the melt liberates the latent heat of fusion in such amounts that the temperature from Q to R remains constant until the whole mass has entirely solidified (at point R). Between Q and R the mass is partly liquid and partly solid.
- ▶ On further cooling from R to S, the solid metal cools and tends to reach room temperature.
- ▶ The slopes of PQ and RS lines depend on the specific heats of liquid and solid metals respectively.

b. Cooling curve of a binary solid solution

- ▶ Curve portion PQ is similar no matter it is for a pure metal or for a binary system consisting of two metals forming a solid solution.
- ▶ However, in a binary system, during freezing (i.e.QR) period, the temperature does not remain constant, but it drops along line QR till the whole mass is solid at point R.
- ▶ The dropping trend of QR indicates that the alloy does not solidify at a constant temperature, but it possesses a freezing range which is due to the changes in the composition of the solid and liquid phases which naturally result in variable freezing (or melting) points.
- The solid cool along RS to attain the room temperature.

c. Cooling curve of a binary eutectic system

- ▶ In this system, the two components are completely soluble in the liquid state but entirely insoluble in solid-state.
- ▶ The liquid cools along PQ until the temperature Q is reached.
- ▶ At Q, one component that is in excess will crystalize and the temperature will drop along QR.

- ▶ At point R the liquid composition has been reached at which the two components crystallize simultaneously from the solution.
- ▶ The temperature remains constant until the whole mass is solid.
- ▶ Cooling from S to T is as usual.
- ▶ Fig 4.2 shows a series of cooling curves for different alloys in a completely soluble system (such as Cu-Ni system).
- ▶ The figure shows how a phase equilibrium diagram (shown dotted) can be constructed from the cooling curves of different alloys in the system.

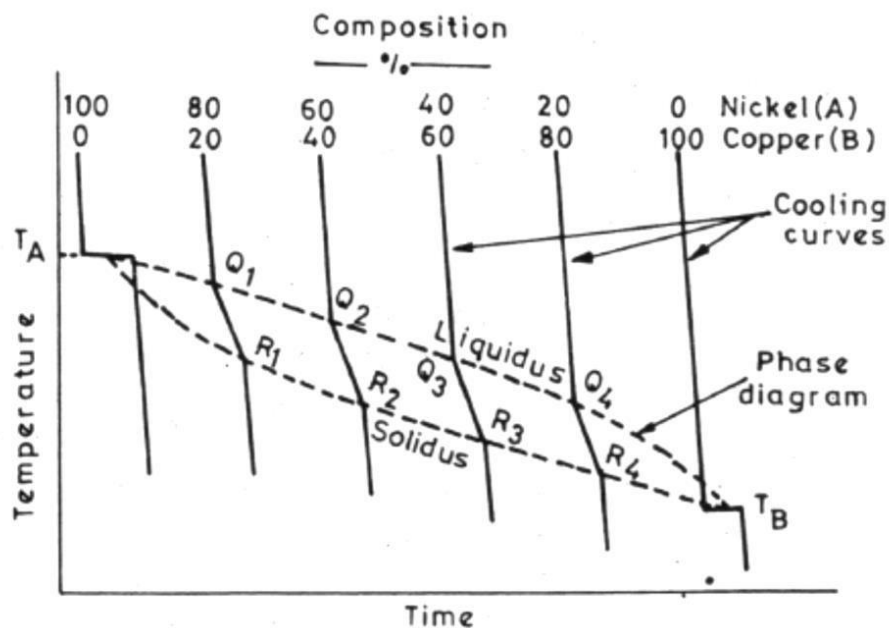


Fig.4.2 - Series of cooling curves giving rise to a phase diagram

4.4 Phase Diagram

- ▶ A huge amount of information concerning the phase changes in many alloys systems has been accumulated and the best way to record this data is in the form of the Phase diagram, which is also termed as Equilibrium diagram or Constitutional diagram.
- ▶ An equilibrium diagram shows the limits of composition and temperature within which the various constituents or phases of an alloy are stable.
- ▶ Changes of structure and the composition of the constituents in equilibrium at a fixed temperature can be determined from a phase diagram.
- ▶ If two metals of a binary solid solution (such as Cu-Ni) system are mixed in various proportions, melted and then cooled, and a cooling curve is constructed for each composition Fig .4.2 the resulting diagram obtain joining Q₁, Q₂, Q₃...and R₁, R₂, R₃...will be the phase diagram.
- ▶ Q₁, Q₂, Q₃... is the temperature at which solidification completed.
- ▶ This phase diagram shows two different and distinct phases; one is a liquid metal solution and the other is a solid solution.
- ▶ Within these two phases or within liquidus and solidus, the two phases i.e., liquid and solid exist together, which can be mechanically separated by decantation of the liquid phase.

- ▶ Liquidus is the line above which the alloy is in a liquid state and from where the solidification starts.
- ▶ Solidus is that line below which the alloy is in solid-state and where solidification completes.
- ▶ If in a phase diagram adequate time is provided to attain equilibrium conditions, if equilibrium conditions are not achieved then the non –equilibrium solidification results in porous, dendritic material.

4.5 Interpretation of Phase Diagram

Rule-1: Prediction of Phases

- ▶ From a phase diagram, specific information can be obtained only if temperature and composition are specified.
- ▶ For example, the state of the alloy of composition 30% Bismuth can be determined only with reference to a certain temperature. Thus when this alloy is at 1200 °F, point
- ▶ It is located (Fig 5.3) and when it is at 900°F and 600°F, points 2 and 3 are located respectively.
- ▶ The next step is to determine the phase or phases present at points numbers 1, 2, and 3.
- ▶ Point-1: With 30% Bi 70% Sb alloy at 1200°F, the only liquid phase is present.
- ▶ Point-2: With the same alloy but at 900°F, two phases are present, i.e. Liquid solution and Solid solution.
- ▶ Point-3: With the same alloy, but at 600°F, only one phase, i.e. the solid solution is present.
- ▶ A similar analysis can be made for any other alloy composition and temperature in the phase diagram.

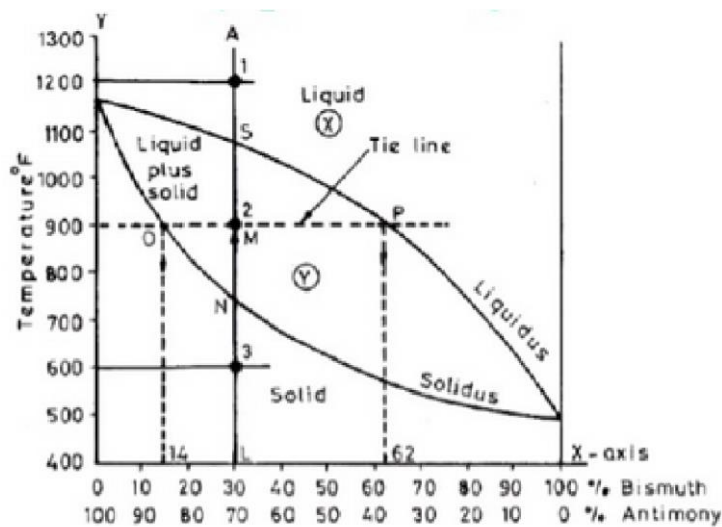


Fig.4.3 - Interpretation of phase diagram (Sb – Bi)

Rule 2: Phase Composition

- ▶ To find out the composition of phases which are stable at a given temperature (say 900°F, Fig 4.4), draw a horizontal (isothermal) line, OP at the given temperature.
- ▶ The projections upon the X-axis of the intersections (i.e. O & P) of the isothermally with the solidus and liquidus respectively, give the compositions of the solid and liquid, which co-exist in equilibrium at that temperature.

For Example,

- ▶ The liquid phase (point P) has a composition of roughly 62% Bismuth.
- ▶ Solid-phase (point O) has the composition roughly 14% Bismuth.

Rule 3: Lever Arm Principle

- ▶ Besides indicating the number of phases and phase composition, the phase diagram also tells the proportion of co-existing phases at any given temperature.
- ▶ To determine the relative amount of two phases, erect an ordinate at a point (say 30% Bi) on the composition scale which gives the total or overall composition of the alloy.
- ▶ The intersection of this composition vertical (AL) and a given isothermal line OP (i.e. point M) is the fulcrum of a simple lever system and OM and MP are lever arms,(fig 4.4).
- ▶ This is called as the lever rule because the amount of a given phase multiplied by its lever arm is equal to the amount of the other phase multiplied by its (i.e. other) lever arm.
- ▶ The lever rule or principle may be expressed mathematically as:
- ▶ The amount of solid phase,

$$\frac{MP}{OP} \times 100 = \frac{(62-30)}{(62-14)} \times 100 = 62.67\%$$

- ▶ The amount of liquid phase,

$$\frac{OM}{OP} \times 100 = \frac{(30-14)}{(62-14)} \times 100 = 33.33\%$$

4.6 Gibbs Phase Rule

- ▶ Phase rule, known as Gibbs Phase Rule, establishes the relationship between the number of degrees of freedom (F), the number of components (C), and the number of phases (P).
- ▶ It is expressed mathematically as follows:

$$P + F = C + 2$$

Where

P = Number of Phases (e.g. solid, liquid etc.)

F = Number of a degree of freedom or the number of physical variables (pressure, temperature, concentration) that can be independently changed without altering the equilibrium, i.e., without causing the disappearance of a phase or the formation of new phase in the system.

C = number of components in the system; for example, Pb and Sn

are the components of the Pb and Sn equilibrium diagram (fig 5.7).

- ▶ In metallurgical systems where pressure is regarded as remaining fixed at one atmosphere, the pressure variable is often omitted and the equation is simplified in to,

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

- ▶ Since the degree of freedom cannot be less than zero,
- ▶ So, $C + 1 - P \geq 0$, or $P \leq C + 1$
- ▶ This means the number of Phases (P) in a system cannot exceed the number of components plus one.
- ▶ Therefore in a Binary system having value $C=2$, not more than $2+1=3$ phases may be in equilibrium.

- ▶ Considering the figure 5.4, it is required to determine the number of degrees of freedom using the phase rule.
 1. Point X, in the region above the liquidus
 Number of components $C=2$, since it is a binary system of Bi and Sb,
 Number of phases $P=1$ (liquid)
 Applying the rule, $F = C + 2 - P$

$$= 2+2-1$$

$$= 3 \text{ degrees of freedom}$$
 2. Point Y, between the liquidus and solidus
 Number of components $C=2$
 Number of phases $P=2$ (liquid and solid)
 Applying the rule, $F = C + 2 - P$

$$=2+2-1$$

$$=2 \text{ degrees of freedom}$$

4.7 Classification of Equilibrium Diagrams

- ▶ An equilibrium diagram has been defined as a plot of the composition of phases as a function of temperature in any alloy system under equilibrium conditions.
- ▶ Equilibrium diagram may be classified according to the relation of the components in the liquid and solid states as follows:
 1. Components completely soluble in the liquid state,
 - a. and also completely soluble in the solid state,
 - b. but partially soluble in the solid-state (eutectic reaction)
 - c. but insoluble in the solid-state(eutectic reaction)
 - d. The peritectic Reaction
 2. Components partially soluble in the liquid state,
 - a. but completely soluble in the solid-state,
 - b. And partly soluble in the solid-state.
 3. Components are completely insoluble in a liquid state and completely insoluble in the solid-state.

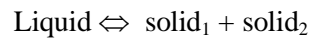
4.8 Two Metals Completely Soluble In the Liquid and Solid-State

Solid States

- ▶ A system that illustrates an equilibrium diagram in which there is complete solubility in the liquid and solid states is that of Antimony – Bismuth system shown in figure 4.4.
- ▶ Since the two metals are completely soluble in the solid-state, the only type of solid solution formed will be a substitutional solid solution.
- ▶ Actually, the solidification of a liquid alloy of this type consists of two processes :
 - i. a. Formation of crystals in the melt (at say point S),
 b. Growth of crystals (just as at point M).
 - ii. Homogenization of the composition in various parts of each crystal:
 - a. By diffusion between core and encasement.
 - b. By diffusion between core and melt.

4.9 Eutectic System

- ▶ In a eutectic reaction, when a liquid solution of fixed composition, solidifies at a constant temperature, forms a mixture of two or solid-phase without an intermediate pasty stage. This process reverses on heating.



- ▶ In the eutectic system, there is always a specific alloy, known as eutectic composition (fig 4.4), that freezes at a lower temperature than all other compositions.
- ▶ Under conditions approaching equilibrium (slow cooling), it (specific alloy) freezes at a single temperature like pure metal.
- ▶ In other respects, the solidification reaction of this composition is quite different from that of a pure metal since it freezes to form a mixture of two different solid phases.
- ▶ At the eutectic temperature, two solids form simultaneously from a single liquid phase.
- ▶ The eutectic temperature and composition determine a point on the phase diagram called a eutectic point.

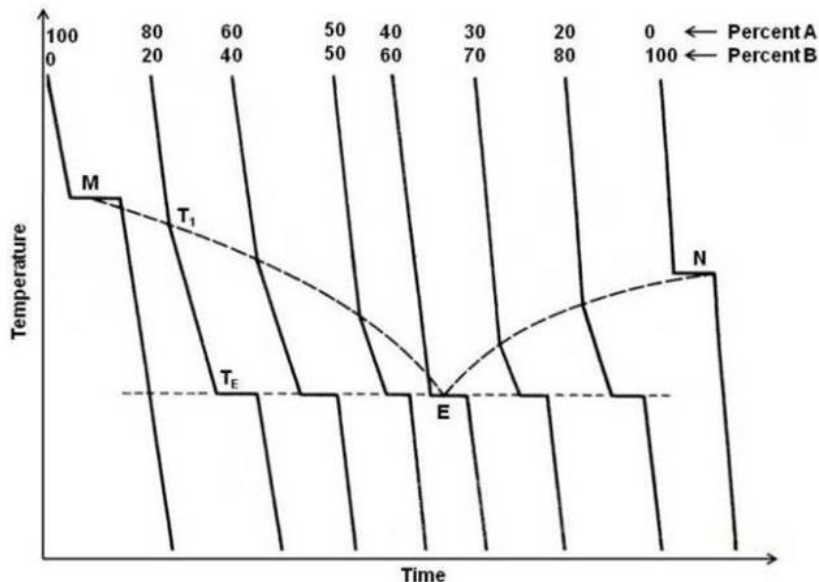


Fig.4.4 - Cooling curves for two metals insoluble in solid-state

- ▶ Binary alloy eutectic system can be classified as:
 - a. One in which, two metals are completely soluble in the liquid state but are insoluble in each other in solid-state.
 - b. The other in which, two metals are completely soluble in the liquid state but are partly soluble in each other in the solid-state.
- a. **Two metals are completely soluble in the liquid state but completely insoluble in the solid-state.**
 - ▶ Technically, no two metals are completely insoluble in each other. However, in some cases the solubility is so restricted that for practical purposes they may be considered insoluble, e.g. Tin – Zinc or Bismuth – Cadmium.
 - ▶ Fig 5.5 shows cooling curves for a series of two metals that are insoluble in the solid-state such as Bismuth and Cadmium. The figure also shows, how by joining a1b1, a1b2... the point, the equilibrium diagram for such a system can be obtained.

- ▶ To explain this type of system it is necessary to consider the cooling and solidification of three compositions 1, 2 and 3.(fig 4.5)

Alloy-1: 20% Cd and 80% Bi

- ▶ Contrary to alloy 3, in this case, a crystal of pure Bi form first, enriching the melt with Cd.
- ▶ The composition of the melt (or liquid) moves to the right until ultimately the point E is reached and the remaining liquid solidifies as eutectic (40% Cd and 60% Bi).

Alloy-2: 40% Cd and 60% Bi (Eutectic alloy)

- ▶ No solidification occurs until the melt reaches the eutectic temperature (140°C)
- ▶ At the eutectic temperature, the two pure metals crystallize together to give a characteristically fine aggregate [Fig. 4.5 (C)] known as a eutectic.
- ▶ Eutectic consists of alternate layers of Cd and Bi which form at the eutectic temperature (140°C in this case).

Alloy-3: 80% Cd and 20% Bismuth.

- ▶ As the temperature falls to T1, crystal nuclei of pure Cd begin to form. Since pure Cd is deposited, it follows that the liquid becomes richer in Bi; the composition of liquid moves to left 3 and as indicated by the diagram, no further Cd deposits until the temperature falls to T2.
- ▶ At T2 more Cd is deposited and dendrites begin to develop from the already formed nuclei (Fig. 4.5 (D)).
- ▶ The growth of the Cd dendrites, on the one hand, and the consequent enrichment of the remaining liquid in Bi, on the other, continues until the temperature has fallen to 140°C, the eutectic temperature in this case.
- ▶ The remaining liquid then contains 40% Cd and 60% Bi, the eutectic composition.

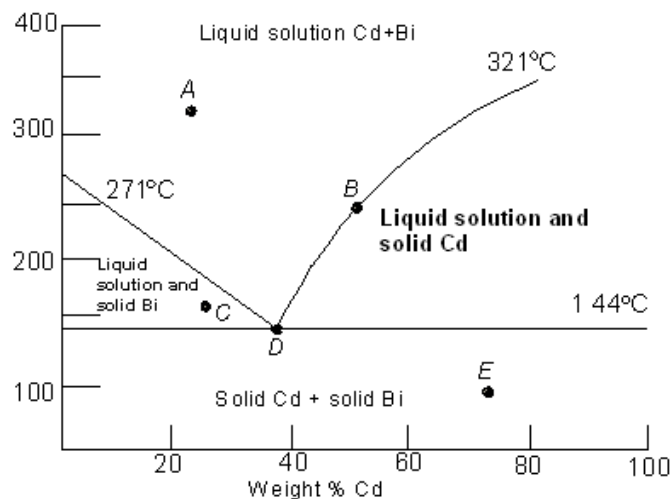


Fig.4.5 - The Bismuth – Cadmium Equilibrium Diagram

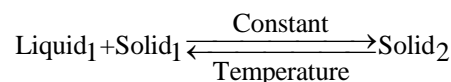
4.10 Two Metals Completely Soluble In The Liquid State, But Only Partly Soluble In The Solid-State

- ▶ Since most metals show some solubility for each other in the solid-state, this type is the most common and, therefore, the most common alloy system.
- ▶ Metals such as Pb-Sn and Pb-Sb are partly soluble in each other in the solid-state.

- ▶ Fig. 4.6 shows the Tin-Lead equilibrium diagram with microstructure obtained under the non-equilibrium condition of solidification.
- ▶ The figure shows that:
 - ▶ (i) The tin will dissolve up to a maximum of 2.6% Pb at the eutectic temperature, forming the solid solution α .
 - ▶ (ii) The lead will dissolve up to a maximum of 19.5% at the eutectic temperature, giving the solid solution β .
 - ▶ (iii) The slope of AB and CD indicates that the solubility of Pb into sn(α) and that of sn into Pb(β) decrease as the temperature falls.
- ▶ Consider an alloy of composition Z (70%Pb – 30%Sn). As the melt temperature falls to T₁, dendrites of composition Y will deposit.
- ▶ The alloy solidifies as a solid solution until at 183° C, the last layer of solid to form is of composition C (80.5% Pb – 19.5% Sn).

4.11 Peritectic Reaction

- ▶ It is the reaction that occurs during the solidification of some alloys where the liquid phase reacts with a solid phase to give a solid phase of different structures.
- ▶ The reaction reverses on melting.



- ▶ Like solid solution formation and eutectic reaction, the peritectic reaction is also a mechanism of solidification shown by various metal systems, but it is comparatively less common.
- ▶ A peritectic reaction is, actually, just the opposite of the eutectic reaction.
- ▶ Refer to Fig. 4.6 showing the peritectic reaction.
- ▶ Assuming very slow rates of cooling, the peritectic reaction will occur only in those Pt-Ag alloys that contain between 12 and 69% silver (Ag).
- ▶ Consider a liquid (melt) of composition Z, i.e., containing 25% Ag. Solidification commence at T₁ and dendrites of α , initially of composition W, being forming
- ▶ Selective crystallization of α continues down to T_p, the peritectic temperature; when the alloys reach this temperature, it is composed of solid α -dendrites of composition B and liquid of composition D in the proportion α : liquid = RD: RB.

$$\frac{\text{Weight of } \alpha \text{ (composition B)}}{\text{Weight of } \delta \text{ (composition C)}} = \frac{RC}{BR}$$

- ▶ Consider another alloy Y.
- ▶ The first stage in the solidification of alloy Y is the same as in alloy Z: solidification begins at T₂ and when the peritectic is reached, the alloy consists, similarly, of dendrites of α , of composition B and liquid of composition D, but in the proportions, α : liquid = Y₁D: Y₁B

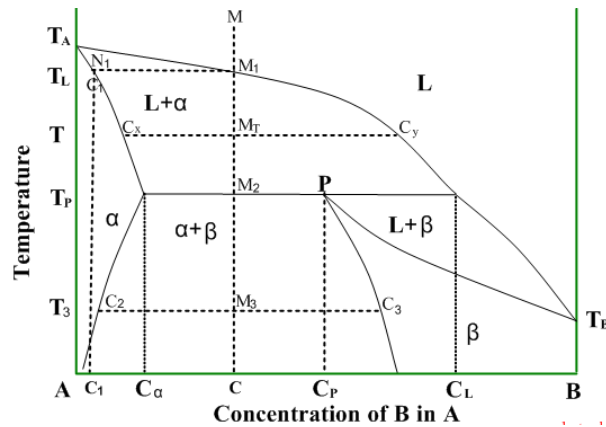
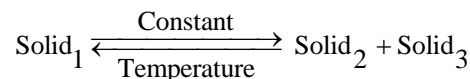


Fig.4.6 - Peritectic Reaction

- ▶ At peritectic temperature all the α reacts with some of the liquid to form δ of composition C, the proportion of δ to remaining liquid is $Y_1D: Y_1C$.
- ▶ After the peritectic reaction has occurred, the temperature falls and the remaining liquid tends to solidify as δ which changes in composition along CY_2 . At Y_2 solidification will be completed and the structure will consist of crystal of uniform δ (of the same composition as that of the original liquid).
- ▶ In actual practice, fast cooling tends to produce heterogeneous grains and may cause some α to be retained in the center of the (δ) grains.

4.12 Eutectoid Transformation (Reaction)

- ▶ Unlike Eutectic or Peritectic transformations which are liquid-solid transformations, Eutectoid involves a solid-solid transformation.
- ▶ Eutectoid reaction is an isothermal reversible reaction in which a solid phase (usually a solid solution) is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system.



- ▶ Eutectoid point: The point in the equilibrium diagram indicating the composition of the eutectoid and its temperature of transformation.
- ▶ Eutectoid structure: The structure, frequently lamellar, produced by the simultaneous precipitation of the components of the eutectoid from the solid solution.
- ▶ Eutectoid reaction is found in many systems such as Cu-Al, Cu-Zn, Al-Mn, Cu-Be, etc.
- ▶ Fig. 4.7 shows an eutectoid-diagram.
- ▶ Consider the alloy-1 As it is slowly cooled by γ solid solutions formed when the liquidus line cross at Y_1 . More and more γ is formed until the solidus line is cross at Y_2 . it remains a uniform solid solution until the solvents line cross at Y_3 . The pure metal A must now be started to undergo an allotropic change, forming the α solid solution.
- ▶ The composition of γ is gradually moving down and along the line ME; γ solution becomes richer in metal B.
- ▶ When alloy reaches the eutectoid temperature T_e , the reaches eutectoid point E.

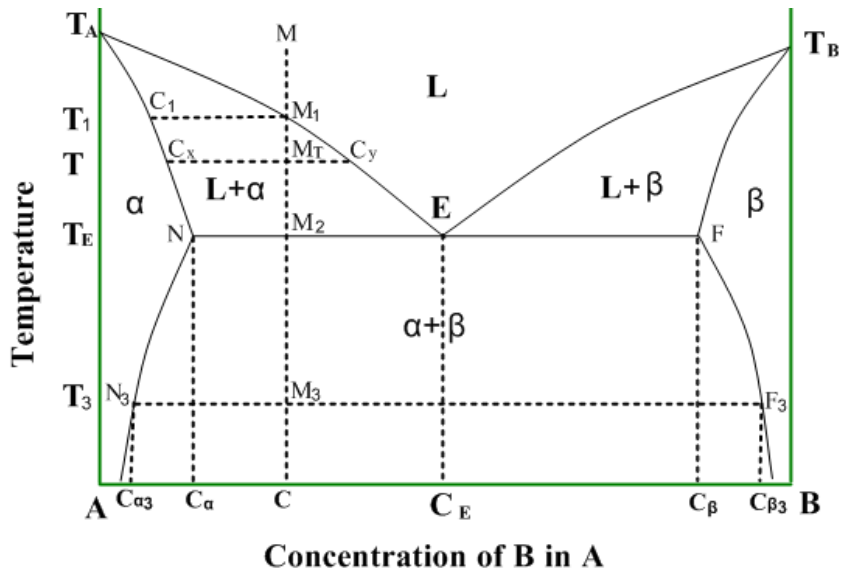
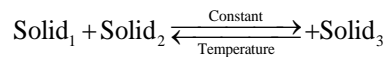


Fig.4.7 - Eutectoid diagram

- ▶ The microstructure at room temperature consists of primary α of pro eutectoid α which was formed between Y_3 and Y_4 surrounded by the eutectoid mixture of $\alpha + \beta$.

4.13 Peritectoid Transformation (Reaction)

- ▶ The peritectoid reaction is the transformation of two solids into a third solid.
- ▶ It is an isothermal reversible reaction in which a solid phase reacts with a second solid phase to produce yet a third solid phase on cooling.



- ▶ Fig. 4.8 shows a Peritectoid Diagram, which can be explained on lines similar to those for the eutectoid diagram (Refer section 4.12).
- ▶ L is the liquid phase.
- ▶ γ , α and β are solid phases.
- ▶ A and B are two metals.
- ▶ E_p is the peritectoid point.
- ▶ T_p is the peritectoid temperature.

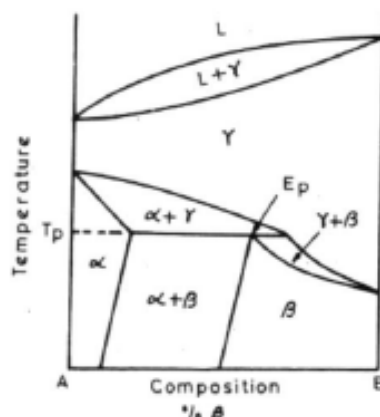


Fig.4.8 - Peritectoid diagram

4.14 Types of Solid Solutions

Solid solutions occur in either of two distinct types, namely

Substitutional solid solution

1. Disordered
 2. Ordered
 3. Interstitial solid solution.
- ▶ **Substitutional Solid Solution:** In substitutional solid solution, there is a direct substitution of one type of atom for another so that solute atoms (Cu) enter the crystal to take positions normally occupied by solvent atoms (e.g., nickel atoms); In other words, in substitutional solid solution, the atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent. Substitutional solid solution forms when the solute and solvent atoms possess equal or approximately equal (within $\pm 7.5\%$) diameters; for example, an atomic diameter of copper is 2.551 Å and that of nickel is 2.487 Å, and the two (i.e., Cu and Ni) form a substitutional solid solution. The great majority of the solid solutions are of a substitutional type.
 - ▶ **Disordered Substitutional Solid Solution:** In the formation of a substitutional solid solution the solute atoms do not occupy any specific position but are distributed at random in the lattice structure of the solvent. This alloy is said to be in a disordered condition. In the disordered condition, the concentration of solute atoms can vary considerably throughout the lattice structure.
 - ▶ When a disordered substitutional solid solution crystallizes from the melt, there is a natural tendency for the core of the dendrite to contain rather more atoms of the metal with a higher melting point, whilst the outer fringes of the crystal will contain correspondingly more atoms of the metal of the lower melting point.
 - ▶ **Ordered substitutional solid solution:** The alloy in the disordered condition, if it is cooled slowly, undergoes a rearrangement of the atoms because of the diffusion that takes place during cooling. Diffusion tends to produce a uniform distribution of solute and solvent atoms. The solute atoms move into definite orderly positions in the lattice.
 - ▶ This structure is now known as ordered substitutional solid solution or superlattice. Prolonged annealing tends to produce still more uniform and ordered solid solution. Cu- Zn, Au-Cu, Cu₂MnAl are some examples of ordered structures.
 - ▶ **Interstitial Solid Solution:** Interstitial solid solution forms when solute atoms are very small as compared to the solvent atoms, they are unable to substitute solvent
 - ▶ atoms (because of the large difference in diameters of solvent and solute atoms) and can only fit into the interstices or spaces in the crystal lattice of solvent atoms
 - ▶ Those atoms which have atomic radii less than 1 angstrom (1 Å) are likely to form interstitial, solid solutions. Such atoms are carbon (0.77 Å), nitrogen (0.71 Å), hydrogen (0.46 Å), oxygen (0.6 Å), etc. Actually, atomic size is not the only factor that determines whether or not an interstitial solid solution will form.
 - ▶ Small interstitial solute atoms dissolve much more readily in transition metals (such as Fe, Ni, Mn, Mo, Cr, W, etc.) than in other metals. Carbon forms an interstitial solid solution with F.C.C. iron during the solidification of steel but it can also be absorbed by solid iron provided the latter is heated to a temperature at which the structure is F.C.C. This is the basis of carburizing steels. Nitrogen also dissolves interstitially in solid steel, during the nitriding process.

4.15 Factors Governing Substitutional Solubility (Hume-Rothery Law)

Several factors are now known, largely through the work of Hume-Rothery that controls the range of solubility in alloy systems. The different rules or factors are:

1. Crystal Structure Factor

- ▶ The crystal lattice structure of the two (metal) elements should be the same (i.e., both should be of b.c.c., f.c.c, or h.c.p. structure) for complete solubility, otherwise the two solutions would not merge into each other. Also, for complete solid solubility, the size factor must usually be less than 8%.

2. Relative Size Factor

- ▶ If two metals are to exhibit extensive solid solubility in each other it is essential that their atomic diameters shall be fairly similar, since it is essential that their atomic diameters shall be fairly similar, since atoms differing greatly in size cannot be accommodated readily in the same structure (as a substitutional solid solution) without producing excessive strain and corresponding instability. This is what is referred to when the term size-factor is employed and extensive solid solubility is encountered only when the two different atoms differ in size by less than 15%, called a favorable size factor (e.g., Cu-Ni). If the relative size factor is between 8% and 15%, the alloy system usually shows a minimum and if this factor is greater than 15%, substitutional solid solution formation is very limited.

3. Chemical-affinity Factor

- ▶ The greater the chemical affinity of two metals, the more restricted is their solid solubility. When their chemical affinity is great, two metals tend to form an intermediate phase rather than a solid solution. Generally, the farther apart the elements are in the periodic table, the greater is their chemical affinity.

4. Relative Valence (Valency) Factor

- ▶ Consider two atoms, one with large valence electrons and the other with a small number of valence electrons. It has been found that the metal of high valence can dissolve only a small amount of a lower valence metal, while the lower valence metal may have good solubility for the higher valence metal. For example, in the Al-Ni alloy system, both metals have f.c.c. structure. The relative size factor is approximately 14%. However; Ni is lower in valence than Al and thus solid nickel dissolves 5% aluminum, but the higher valence Al dissolves only 0.04% Ni.

4.16 References

Sidney H Avner " Introduction to Physical metallurgy 2nd Edition 2011 Tata Mc Graw- Hill Publication.

O. P. Khanna "Material Science and Metallurgy" Dhanpat Rai Publications.