Crystal Imperfections:

These are the defects in the crystals. Variety defects are observed in the atomic/ionic arrangement of crystals and these defects influence many of the properties such as mechanical, electrical, magnetic etc. of material.

The various imperfections or crystalline defects are classified based on their geometry and dimensions. They are given below.

* point defects
* Line defects
* Surface defects
* Volume imperfections Ex: blowholes, cracks, etc.

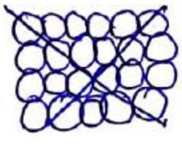
Point defects:

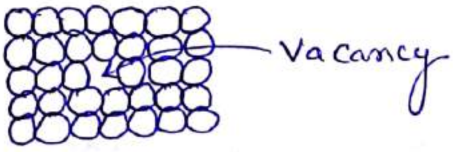
Point imperfections are also referred to as zero dimensional imperfections. As the name implies, they are imperfect point-like regions in the crystal.

Different kinds of point imperfections are described below.

Vacancy:

If an atom is missing from its regular site, the defect produced is called Vacancy.





Substitutional Impurity :

If a foreign atom or impurity atom occupies the position of parent atom, the defect produced is called Substitutional Impurity defect

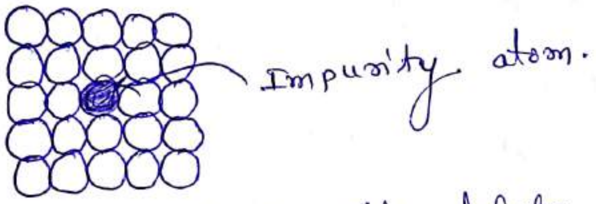
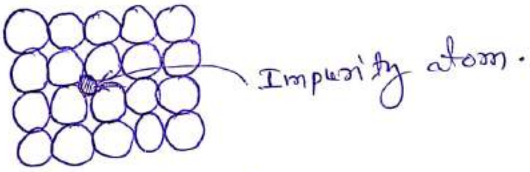


Fig. Substitutional impurity defect

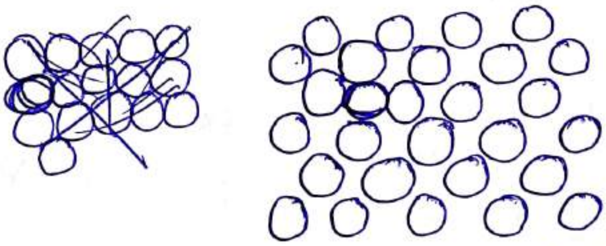
Interstitial Impurity :

If a foreign atom or impurity atom occupies the interstitial position of parent atom, then the defect produced is called Interstitial Impurity defect.



Self Interstitial defect :

If the parent atom occupies its own interstitial site then the defect produced is called Self Interstitial defect.



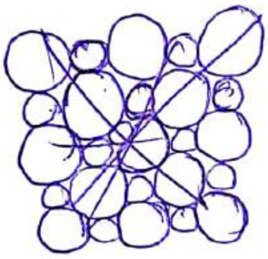
Self Interstitial defect.

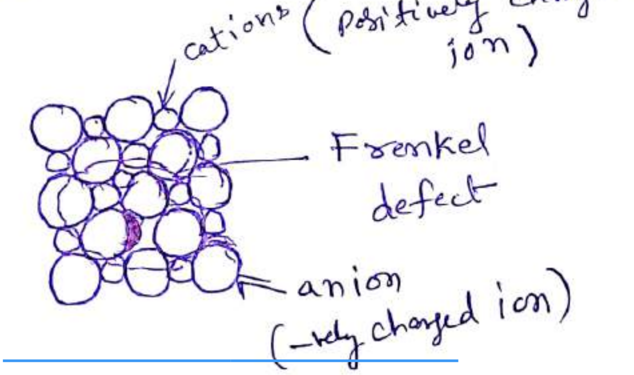
In addition to the above defects, di-vancies and tri-vacancies may exist in the crystals.

In Ionic crystals, Frenkel imperfections and schottky imperfections can be observed.

Frenkel defect:

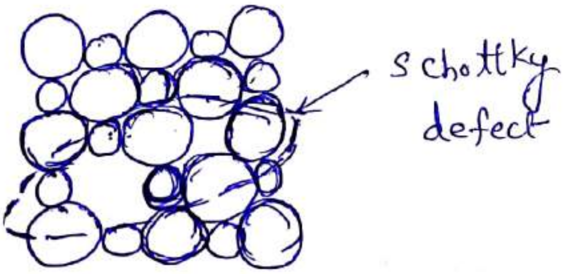
An ion may leave its regular position and may occupy nearby interstitial site of parent giving rise to two defects simultaneously i.e. one Vacancy and one self interstitial. These two defects together is called Frenkel defect. This can occur only for cations because of their smaller size as compared to the size of anions.





Schottky defect:

If one cation and one anion missing from their regular sites, then such a pair of vacant sites is called Schottky imperfections.



Line Imperfections or Line defects :

Line Imperfections are called dislocations. ~~these~~ This type of imperfections are generated in crystals because of a part of a line of atoms missing from its regular site. Line imperfections are one dimensional imperfections in the geometrical sense.

Edge dislocation :

The following fig ⓐ shows a perfect crystal, the top sketch depicting a three dimensional view and the bottom one showing the atoms on the front face. We can consider the perfect crystal to be made up of vertical planes parallel to one another and to the side faces. If one of these vertical planes does not extend from the top to the bottom of the crystal but ends part way within the crystal, as in fig ⓑ, a dislocation is present. In the lower sketch, notice the atomic arrangements on the front face.

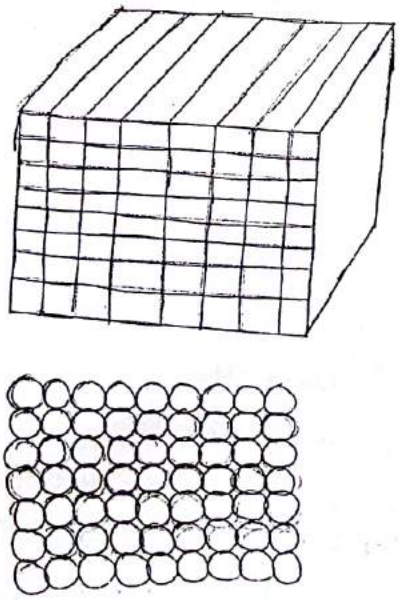


Fig ⓐ.

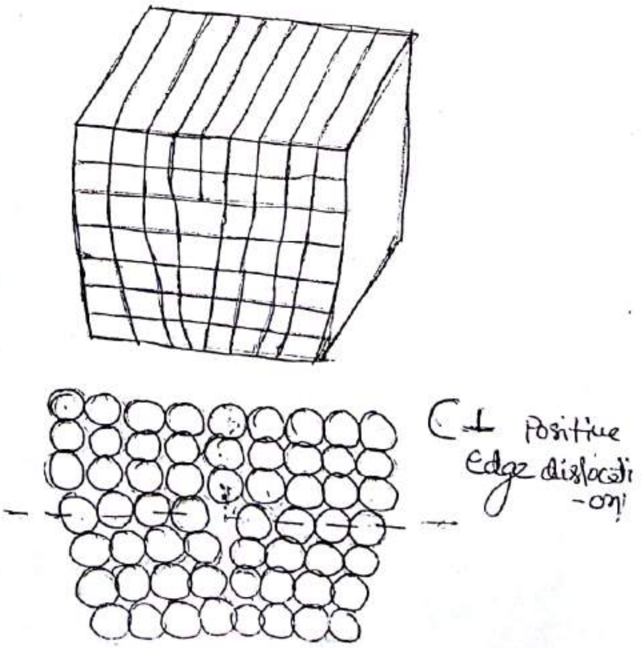


Fig ⓑ

the Perfect crystal, the atoms are in equilibrium positions and all the bond lengths are of equilibrium value. In the imperfect crystal on the right, just above the edge of the incomplete plane, the atoms are squeezed together and are in a state of compression. The bond lengths have been compressed to smaller than the equilibrium value. Just below the edge, the atoms are pulled apart and are in a state of tension. The bond lengths have been stretched to above the normal values. This distorted configuration extends all along the edge into the crystal.

Edge dislocations are symbolically represented by ⊥ or T depending on whether the incomplete plane starts from the top or from the bottom of the crystal. The first symbol represented for positive edge dislocation and next one is ~~for~~ negative edge dislocation.

Burgers vector is perpendicular to the edge dislocation line.

Consider the Perfect crystal shown in fig 2(a) below starting from the point P, if we go up by x number of steps (x=4 in fig 2(a)). then take y steps to the right (y=5 in fig 2(a)), then x steps down and finally y steps to the left, we end up ~~at~~ the starting point. we have now traced a Burgers circuit ~~to~~ in taking these steps. If we now do the same

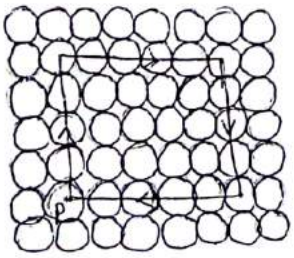


fig 2(a)

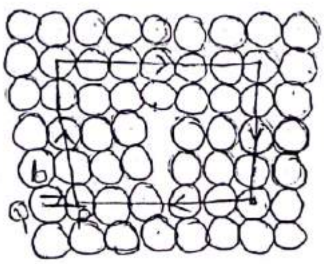


fig 2(b).

operation which has a dislocation in it as shown in fig 2(b), starting from point P, we end ~~at~~ up at Q. We need an extra step to return to point P (or to close the Burgers circuit). The magnitude and the direction of this step defines the Burgers vector (B.V).

$$B.V = \vec{QP} = b$$

This Step $\vec{QP}$ is perpendicular to the edge dislocati lin

Screw dislocation

Screw dislocation exists which may be thought of as being formed by a shear stress that is applied to produce the distortion.

The following fig shows a simple example of a screw dislocation. The upper part of the crystal to the right of AD has moved relative to the lower part in the direction of slip vector. No slip has taken place to the left of A.D. and there fore A D is a dislocation line.

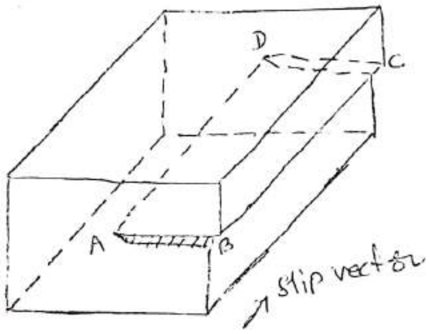
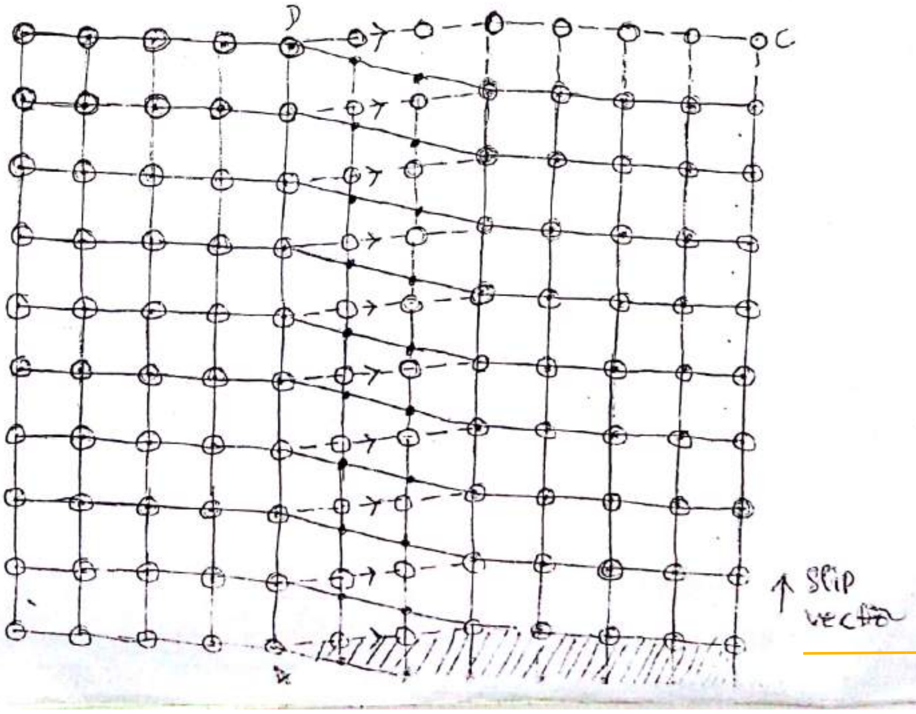


Fig Ⓐ

The arrangement of atoms around a screw dislocation is shown in fig below. In this figure we are looking down on the slip plane of fig above (i,e fig A). The open circles represent atoms just above the slip plane, and the solid circles are atoms just below the slip plane. The screw dislocation derives its name from the spiral or



helical path or ramp that is traced around the dislocation line by atomic planes of atoms. ↻ symbol is used to designate the screw dislocation.

The atomic distortion in screw dislocation (burgers' vector) is parallel to the dislocation line.

Differences between edge dislocation and screw dislocation

Edge dislocation	Screw dislocation.
1. In the case of edge dislocation, an edge of an atomic plane (or extra plane of atoms) is formed internal to the crystal	1. In the case of screw dislocation only a distortion of the lattice cells in the immediate vicinity is produced.
2. An edge dislocation lies perpendicular to its Burgers vector	2. A screw dislocation lies parallel to its Burgers vecto
3. A edge dislocation moves (in its slip plane) in the direction of the burgers vector (slip direction)	3. A screw dislocation moves (in the slip plane) in a direction perpendicular to the Burgers vector (slip direction).
4. An edge dislocation involves an extra row/plane of atoms either above (positive sign) or below (negative sign) the slip plane. Symbols : ⊥ or T.	4. In the screw dislocation, the distortion follows a helical or screw path and both right hand and left hand senses are possible. Symbols : ↻ (or) ↺
5. The forces required to form and to move an edge dislocation are smaller ~~than~~ in their values	5. The forces required to form and move a screw dislocation are greater in their values
6. Speed of movement of an edge dislocation is greater	6. Speed of movement of a screw dislocation is less
7. The edge dislocation is particularly useful in explaining slip in plastic flow during mechanical working	7. Screw dislocation is especi useful in explaining crystal growth as well as slip in plastic deformation.

Surface Imperfections / Defects :

Surface defects or imperfections are two - dimensional irregularities at the regions of materials that have different crystal structures or crystallographic orientations. ~~Such~~ Different types of Surface Imperfections are given below.

- * Grain boundaries
- * Twin boundaries
- * External Surfaces
- * tilt boundaries.
- * stacking defects.

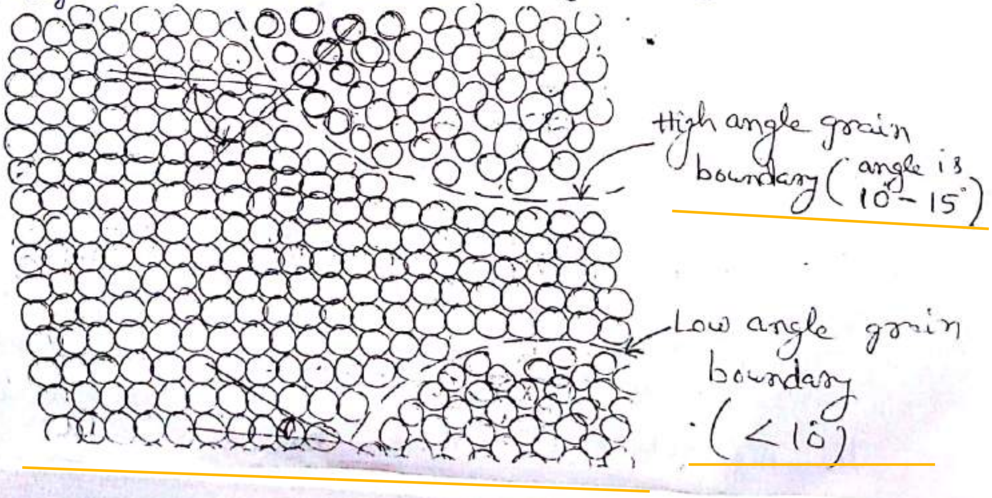
Grain boundaries :

[most crystalline solids are composed of a collection of many small crystals or grains. such materials are termed Polycrystalline.]

The grain boundary is the boundary seperating two small gains or crystals having different crystallographic orientations in polycrystalline materials.

A grain boundary is repesented schematically from an atomic ~~representation~~ Perspective in fig below. within the boundary region, which is probably just several atom distances wide, there is some atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one.

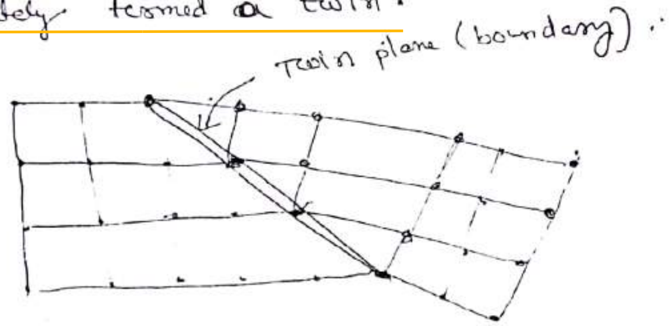
Various degrees of crystallographic misalignment between adjacent grains are possible (fig below). when this orientation mismatch is slight, on the order of a few degrees, then the term small or low angle boundary is used.



Note: When the orientation of grains differ by only few degrees a low angle boundary is formed b/w the two grains.

Twin Boundaries:

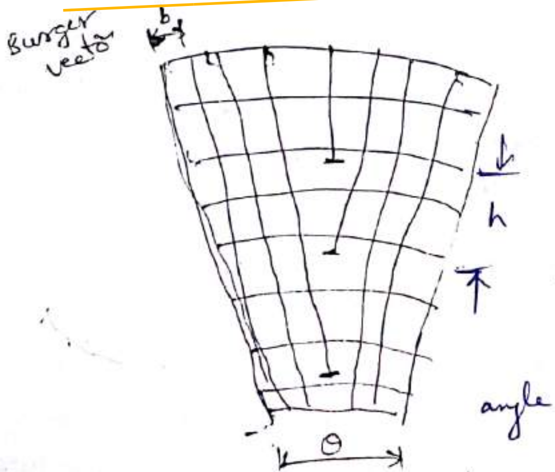
A Twin Boundary is special type of ~~boundary~~ grain boundary across which there is a specific mirror latice symmetry. i,e atoms on one side of the boundary are located in mirror image positions of the atoms on the other side (shown in fig below). The region of material between these boundaries is appropriately termed a twin.



(Twin plane or boundary)

Tilt Boundary:

Grain boundaries can also be described in terms of dislocation arrays; one simple small-angle grain boundary is formed when edge dislocations are aligned in the manner of fig (A). This type is called a tilt boundary.



angle of tilt $\theta = \frac{b}{h}$

Fig (A): Tilt boundary having an angle of misorientation θ results from an alignment of edge dislocation.

b = magnitude of the Burger's vector; h = avg. vertical distance b/n the dislocations

Solidification

Solidification is the process of transformation of metals from liquid phase to the solid phase.

In this process, an unstable system with high free energy is converted into a more stable thermodynamic state with less free energy.

Solidification is a reverse process of melting.

Mechanism of solidification:

Solidification process starts when the molten metal temperature reaches its freezing point temperature. During this process, initially small stable particles called "Nuclei" or "seed" crystals will form inside the molten metal. Infact, Nuclei by itself are the solidified points which acts as centres for further solidification. As cooling continues, more atoms tend to freez and attach themselves to the existing nuclei or form new nuclei of their own. Each Nucleus grows by the attraction of atoms from the liquid metal into its space lattice.

This Nucleus growth or crystal growth continues in three dimensions by the attachment of atoms in certain preffered directions, usually along the axes of the crystal. This gives rise to a characteristic tree like structure which is called dendrite (in Greek dendron means tree). Since Nuclei - formation is spontaneous the crystal axes are oriented randomly and hence the dendrite grow in different directions in each crystal.

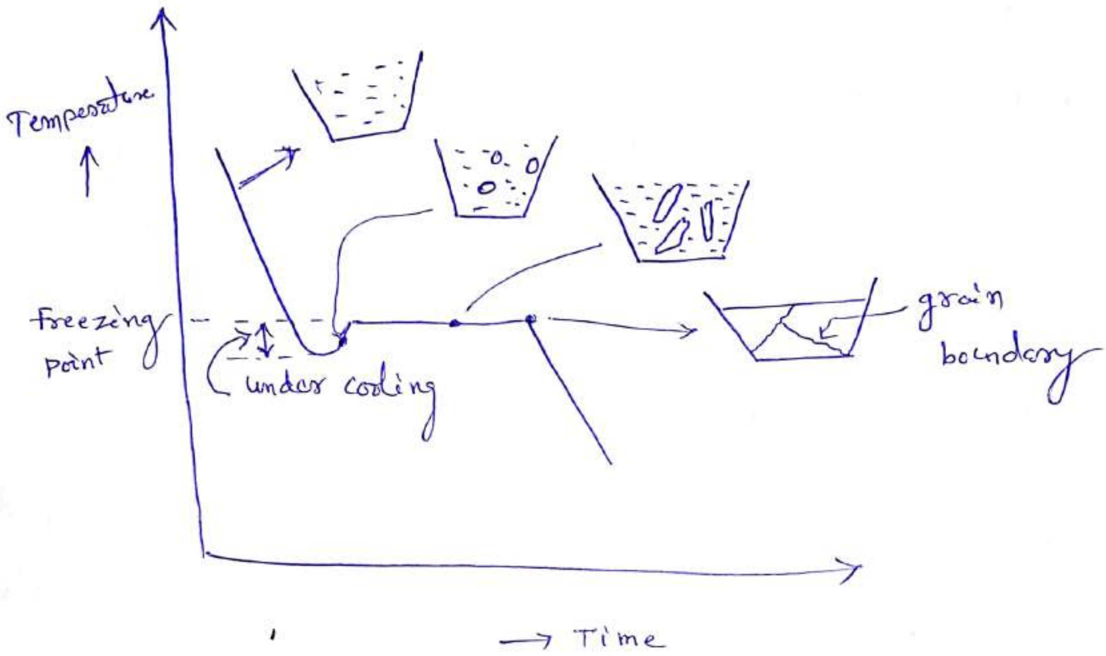
Fig: Stages in solidification.

The dentrites grow outwards and contact is made with neighbouring growths, this contact surface becomes the boundary of the crystal or grain.

Solidification of a pure metal:

Solidification occurs by the Nucleation and growth of crystals in the molten metal.

In pure metal, the Nuclei formation will not start exactly at its freezing point temperature but it starts when it is cooled below to its freezing point. So when the pure molten metal cooled below its freezing point temperature, nuclei begin to form in many parts of the molten metal at the same time.



The rate of Nuclei formation depends on under cooling or super cooling. After start of the Nucleation process, the molten metal temperature increased to its freezing point temperature because of release of latent heat of fusion and the remaining Solidification process Continues at its freezing point temperature only ~~fo~~ ~~Nucleation~~ ~~go~~ ~~and~~ i.e Nucleus growth and grain boundary formation.

latent heat of fusion : Heat released because of occurance of phase change.

Sensible heat : because of temperature difference

Solid solutions:

When homogeneous mixture of two or more kinds of metals or atoms occur in the solid state, they are known as solid solutions.

The more abundant atomic form is referred as solvent or base metal or parent metal and the less abundant atomic form is referred as solute or alloying element.

Example of solid solutions : sterling silver (92.5% Si, 7.5% Cu)

Brass (64% Cu and 36% Zinc)

Types of solid solutions :

(1) substitutional solid solutions

(2) Intecostitial solid solutions.

Substitutional solid solutions:

If the atoms of the solvent or parent metal are replaced in the crystal lattice by atoms of the solute metal then the solid solution is known as substitutional solid solutions.

Ex : copper atoms may substitute for nickel atoms without disturbing the FCC structure of nickel.

In the substitutional solid solutions, the substitution can be either ordered or disordered.

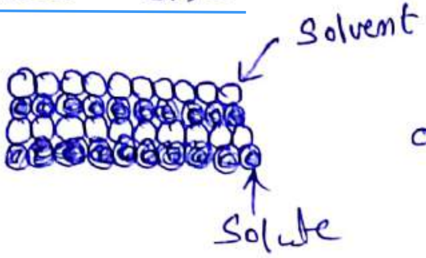
Substitutional solid soltions are two types :

ⓐ ordered substitutional solid solutions.

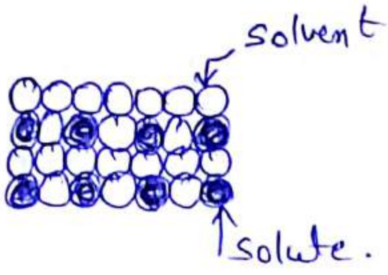
ⓑ Disordered substitutional solid solutions.

Ordered substitutional solid solutions:

Here the solute atoms have substituted in an orderly manner for the solvent atoms on their lattice site.

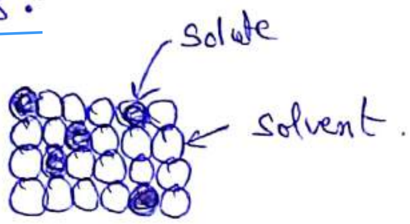


or



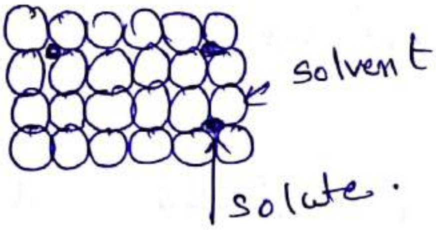
Disordered substitutional solid solutions:

Here the solute atoms have substituted disorderly for the solvent atoms on their lattice sites.



Interstitial solid solutions:

In Interstitial solid solutions, the solute atom doesnot displace a solvent atom but rather it enters one of the ~~holes, voi or~~ gaps interstitial position. between the solvent atoms.



Hume - Rothery Rules for the formation of Substitutional solid - solutions :

By studying a number of alloy systems, Hume - Rothery formulated certain rules which govern the formation of substitutional solid solutions. They are

① Crystal structure factor :

For complete solid solubility, the elements should have the same type of crystal structure i,e both elements should have either FCC or B.CC or HCP structures etc.

② . Relative size factor :/ Atomic size factor

If the sizes of two metallic atoms differ by less than 15% , the metals are said to have a favorable size factor for substitutional solid solution formulation.

If the size factor is greater than 15% , solid ~~solution~~ ~~formulation or~~ solubility is 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.

Solid solubility is favoured when two metals have lesser chemical affinity.

④. Relative Valancy factor:

It is found that a metal of lower valence tends to dissolve more of a metal of higher valance. A metal of higher valancy can dissolve only a small amount of lower valency metal.

Ex: Aluminium – nickel alloy system:

Nickel (lower Valance) dissolves 5% aluminium but aluminium (higher valance) dissolves only 0.04% nickel.

Intermediate phase:

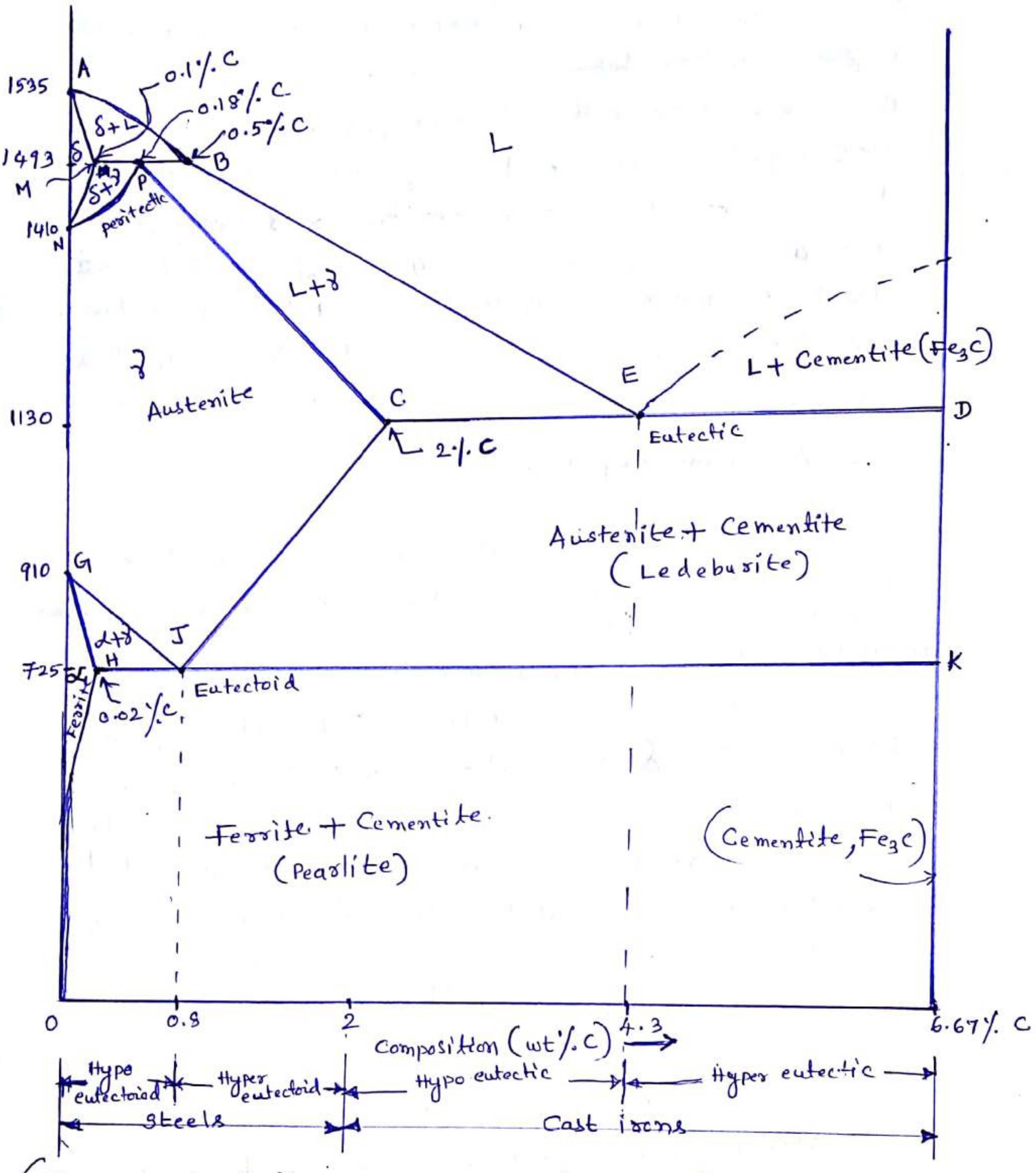
when an alloying element is added in a given metal in such (solvent) in such an amount that the limit of solid solubility is exceeded, a second phase appears along with the primary solid solution. More often the second phase that appears is an "Intermediate phase".

This second phase may be the primary solid solution of the base metal in the alloying element. This differs in both crystal structure and properties from either primary solid solutions. Intermediate phases may range between the ideal solid solution on one hand and the ideal ~~solid solution on the~~ chemical compound on the other hand.

Some intermediate phases have a fixed composition and they are called intermetallic compounds. In general intermetallic compounds are hard and brittle and have high melting point.

The intermediate phases in which the ratio of no. of free electrons to the no. of atoms is constant are called electron compounds.

Iron – Iron Carbide phase diagram ($Fe-Fe_3C$)



(Hypo means less than or below)

Iron– Iron carbide phase diagram

A Portion of Iron – Carbon diagram is shown in Fig above. This is the part between pure iron and an interstial compound, iron carbide (Fe_3C), Containing 6.67 % Carbon by weight. Therefore, we call this portion as the iron – Iron Carbide phase/equilibrium diagram.

The melting point of pure iron is 1535°C. If we heat pure iron, it experiences two changes in crystal structure before it melts. At room temperature the stable form, called ferrite, or α iron, has a BCC crystal structure. Ferrite experiences a polymorphic transformation to FCC austenite, or γ iron, at 910°C. This austenite persists to 1410°C, at which temperature the FCC austenite reverts back to a BCC phase known as δ ferrite, which finally melts at 1535°C. All these changes are apparent along the left vertical axis of the phase diagram.

The phase diagram shows three horizantal lines which indicate isothermal reactions ~~and~~ or phase transformations.

PERITECTIC TRANSFORMATION:- The portion of the diagram in the upper left-hand corner is known as the delta region because of the δ solid solution present in that region. The first horizantal line in the phase diagram can be considered as line MB at 1493°C and a peritectic reaction takes place at this temperature. The equation of the peritectic reaction may be written as

$$\text{Liquid} + \delta \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \text{Austenite}\,(\gamma)$$

The maximum solubility of carbon in BCC, δFe is 0.1% (Point M), while in FCC, γFe the solubility is much greater. The peritectic transformation range is from 0.1% C to 0.5% C. All the steels containing carbon between 0.1 and 0.5% exhibit peritectic transformation when cooled from the liquid state. Other steels (i,e steels containing carbon from 0.008 to 0.1% and 0.5 to 2%) do not undergo peritectic transformation.

Eutectic transformation:

In general, eutectic transformation is denoted as:

$$L \longrightarrow S_1 + S_2$$

where S_1, S_2 are two different solids and L is liquid.

In Fe-C. system, this reaction occurs at 1130°c and gives an eutectic mixture of austenite and Cementite. This eutectic mixture of austenite and Cementite is called ledeburite. Austenite from the ledeburite is not stable at low temperatures and gets transformed to pearlite with slow rates of cooling at 725°c, and hence at room temperature, structure consists of pearlite and cementite. This mixture is called transformed ledeburite.

Cementite is hard and pearlite is also fairly hard and therefore, transformed ledeburite is also hard and subsequently brittle.

Eutectoid transformation:

In general, eutectoid transformation is denoted as $S_1 \rightleftharpoons S_2 + S_3$

where S_1, S_2, and S_3 are different solid phases.

Eutectoid transformation in Fe-C phase diagram occurs at point J and is as below:

$$\gamma \rightleftharpoons \alpha + Fe_3C$$

Austenite ⇌ ferrite + Cementite

Austenite of 0.8% C decomposes at constant temperature of 725°c and forms a mixture of ferrite and cementite. This eutectoid mixture of ferrite and cementite is called pearlite, due to its pearly appearance under the optical microscope. It consists of alternate lamellae of ferrite and cementite.

The properties of pearlite depend upon its interlamellar spacing. Smaller the spacing, higher are the mechanical properties. The interlamellar spacing depends on the cooling rate and within limit, the spacing becomes less and less with increasing cooling rates.

The interlameller spacing of a pearlite is defined as the distance from the centre of a ferrite (or cementite) lamella to the centre of the next adjacent ferrite (or cementite) lamella.

The various phases existing in the diagram are below:

(i) α (Ferrite): Ferrite is an interstitial solid solution of carbon in low temperature B.C.C α-iron. It is almost a pure iron and the name ferrite comes from the Latin word ferrum which means iron. The solubility of carbon in α-iron at room temp. is 0.008% and increases with increasing temperature to about 0.02% at 725°c.

It is relatively soft and ductile phase. It can be extensively cold worked without cracking. It is strongly ferromagnetic upto 768°c and becomes paramagnetic at 768°c during heating. This temperature (768°c) at which ferrite becomes paramagnetic is called Curie temperature.

(ii) γ (Austenite): Austenite is an interstitial solid solution of carbon in FCC γ-iron. The phase is called Austenite in honour of Sir Austin, who was one of the first metallographer to study its properties. It can dissolve upto 2%·C at 1130°c. This phase is only stable above 725°c. It is soft, ductile, malleable and non-magnetic (~~paramagnetic~~ Paramagnetic) phase.

(iii) δ (δ-ferrite) :

It is an interstitial solid solution of Carbon in high temperature BCC δ- iron. It is similler to α- ferrite. except its occurance at high temperature.

(iv) Fe_3C (Cementite) :

It is an intermetallic compound of iron and Carbon with a fixed carbon content of 6.67% by weight Cementite has a complex orthorhombic crystal structure with 12 iron atoms and 4 carbon atoms in a unit cell. It is ~~extreamly~~ extreamly hard and brittle phase. It is ferromagnetic upto 210°C and paramagnetic above this temperature. It is also called Iron carbide or simply carbide in the discussion of Fe-C system.

~~maintain equilibrium during cooling, sufficient time must be allowed at each temperature for the appropriate compositional readjustments.~~

~~In virtually all practical solidification situations, cooling rates are much too rapid to allow these compositional readjustments and maintenance of equilibrium; Consequently, microstructures other than those shown is~~ Phase diagrams develop.

Gibbs phase Rule :

The Gibb's phase rule states that under equilibrium conditions, the following relation must be satisfied.

$$P+F=C+2$$

where P = No. of phases existing in a system under consideration

F = No. of Degree of freedom i,e the number of externally controlled variables such as temperature, pressure or concentration (i,e composition) that can be changed independently without changing the number of phases that coexist at equilibrium.

and C = Number of components in the System.

2 represents any two variables out of the above three variables i,e temperature, pressure and composition.

Most of the studies are done at Constant pressure i,e one atmospheric pressure and hence pressure is no more a variable. For such cases Gibbs phase rule becomes :

$$P+F=C+1$$

Construction/ploting of phase diagrams or Equilibrium diagrams:

Equilibrium diagrams can be plotted by using several techniques such as thermal analysis, dilatometry, optical and electron microscopy, X-ray and electron difraction, thermodynamic data analysis, electrical resistivity and magnetic measurements. Each method has certain advantages and limitations.

Most of the times, equilibrium or phase diagrams are plotted by the method of thermal analysis using the data obtained from cooling curves; and other methods are generally used to eliminate the ambiguities existing in the diagram plotted by the above method.

Therefore, the basic method of plotting the diagrams by the use of cooling curves is explained below:

Let us consider a binary Cu–Ni system. Cu and Ni have 100% solubility in the liquid and solid states and they form a series of solid solutions. Following steps are used to obtain the equilibrium diagrams.

(i) Prepare a large Number of alloys of varying compositions, say with a variation of 10% Ni and mark them as below.

% Cu	100	90	80	70	60	50	40	30	20	10	0
% Ni	0	10	20	30	40	50	60	70	80	90	100
Material No.	1	2	3	4	5	6	7	8	9	10	11

Material No 1 and 11 are pure metals and No. 2 to 10 are alloys.

(ii) plot cooling curves of the above materials. This is shown in Fig ⓶①.

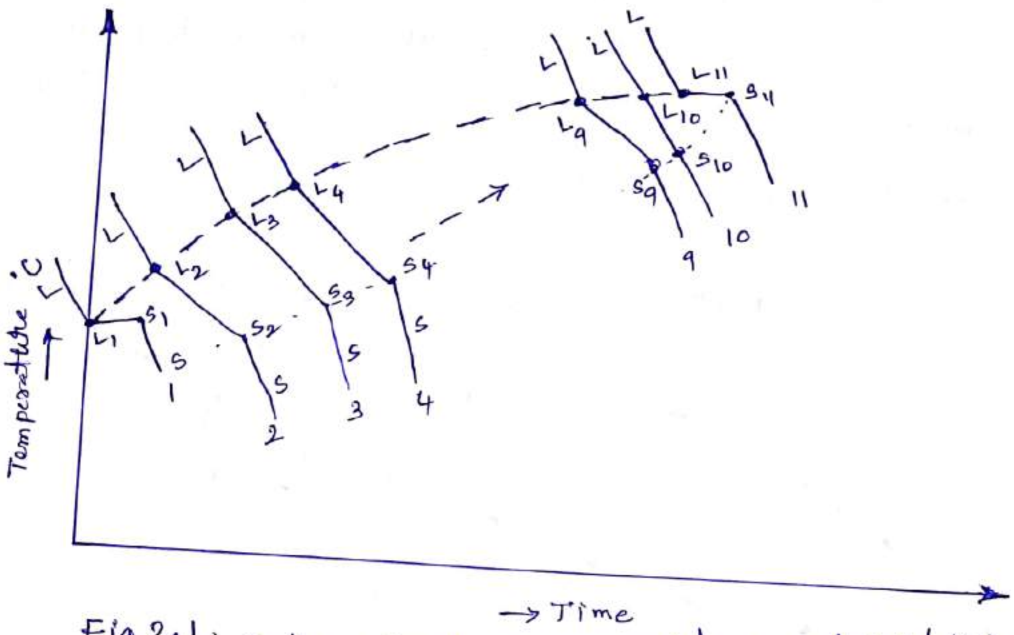


Fig 2.1: Cooling Curves of pure metals and solid solution alloys

(iii) Note down the liquidus and solidus temperatures of these materials. Liquidus temperatures are marked ~~by~~ as $L_1, L_2, L_3, L_4 \ldots\ldots L_9, L_{10}, L_{11}$ and solidus temperatures are marked by $S_1, S_2, S_3 \ldots\ldots S_9, S_{10}\ S_{11}$ respectively. Since material No. 1 and 11 are pure metals, they solidify at constant temperature and hence their liquidus and solidus temperatures are Same i,e $L_1 = S_1$ and $L_{11} = S_{11}$.

(iv) Transfer these temperatures to a temperature Vs Composition graph as shown in Fig 2.2. corresponding to materials 1 and 11 i,e for pure Cu and Ni, we get only one point and for others we get two points because solid solution alloys solidify over a range of temperature.

(v) Draw smooth curves through the points L_1 to L_{11} and S_1 to S_{11}. which represent liquidus and solidus of the diagram. Above liquidus temperatures, all the materials are in the ~~solid~~ ~~state~~ liquid state and below the solidus temperatures they are in the solid state. Between the liquidus and solidus temperatures, the alloys are in the liquid plus solid state.

The resulting loop type of curve is called as the phase or equilibrium diagram. Steps for plotting of equilibrium diagram of any other system are similar to that explained above.

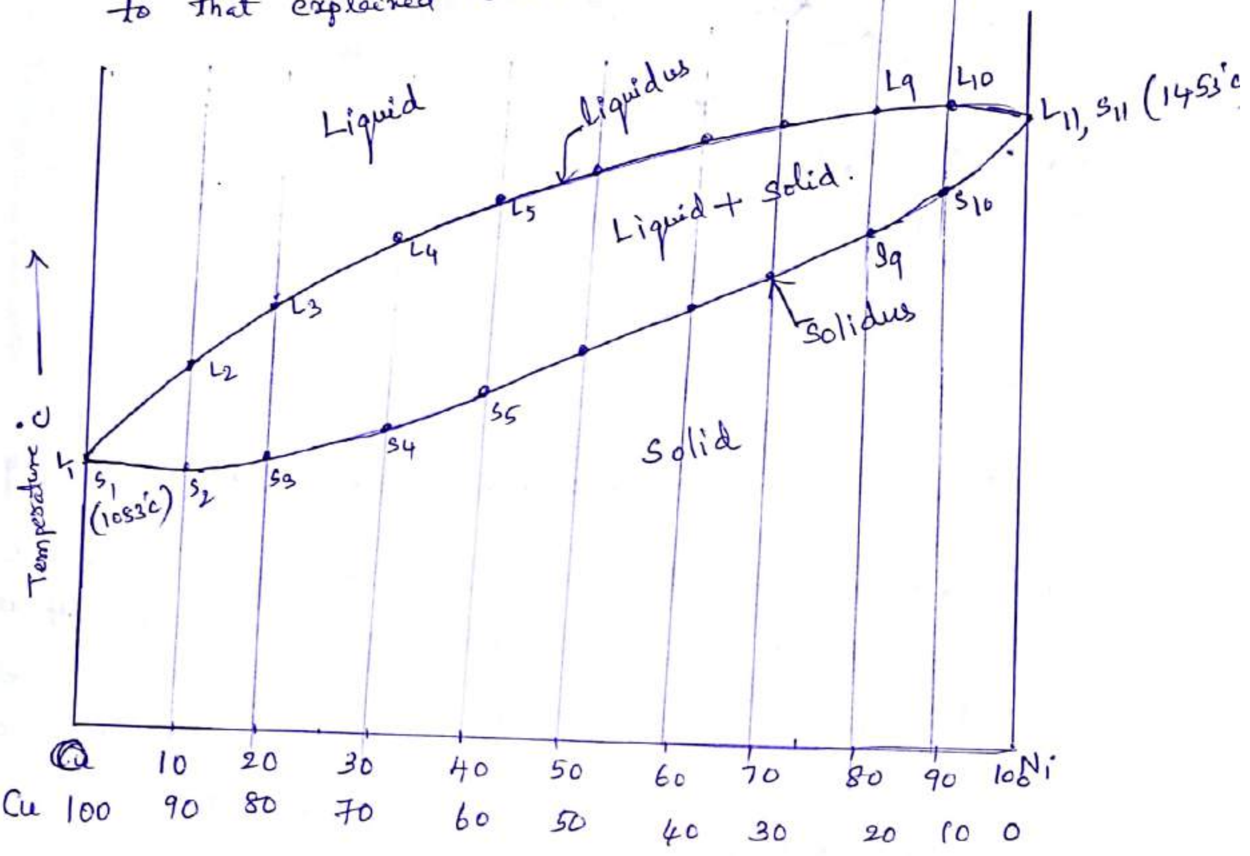


Fig 2.2: Equilibrium diagram of Cu-Ni System.

Note: Two-component systems have binary phase diagrams. Apart from temperature and pressure, we have one composition variable for each of the phases in equilibrium. We then need a three-dimensional diagram to plot the variations in pressure, temperature and composition. In order to simplify the representation of the phase relationships on paper, binary phase diagrams are usually drawn at atmospheric pressure, showing variations in temperature and composition only. Pressure changes often produce no significant effect on the equilibrium and ~~thefte~~ therefore, it is customary to ignore the pressure variable and the vapour phase.

$$P + F = C + 1$$

Interpretation of phase diagrams :

For a binary system of known composition and temperature at least three kinds of information are available: (1) the phases that are present ② the composition of these phases ③ the percentages or fraction of the phases.

Lever Rule :

This Rule is used to find the relative amounts (the percentage or fraction) of phases present ~~at equilibrium~~. ~~may~~ in a binary system for a given alloy at any temperature under consideration.

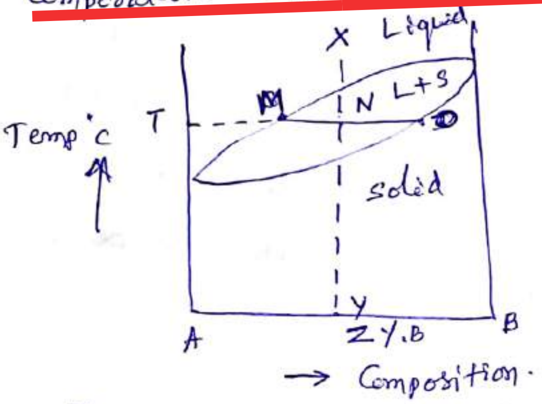


Fig 2.3. Isomorphous System

~~Draw~~

Let us consider an isomorphous system of two metals A and B (Fig 2.3)

Let Z be the Composition of the alloy under consideration and T be the temperature at which the amounts of phases are to be found out.

Procedure :

* Draw a Horizontal line at given temperature T. (i.e MNO)

* Draw a vertical line XY for given Composition Z%.B.

MNO in the above Fig 2.3 is a Tie line.

N is acting as a Fulcrum.

$$\%\ \text{Solid} = \frac{\text{Length of MN}}{\text{Length of MO}} \times 100$$

$$\%\ \text{liquid} = \frac{\text{Length of NO}}{\text{Length of MO}} \times 100.$$

~~pressure experiments have shown that, when a pressure of about 15 GPa is applied at room temperature, the BCC iron transforms to the HCP (ϵ) phase, as illustrated in Fig 2.4~~

Binary PHASE DIAGRAMS :

Two - component systems have binary phase diagrams. Apart from temperature and pressure, we have one composition variable for each of the phases in equilibrium. we then need a three-dimensional diagram to plot the variations in pressure, temperature and Composition. In order to simplify the representation of the phase relationships on paper, binary phase diagrams are usually drawn at atmospheric pressure, showing variations in temperature and composition only. Pressure changes often produce no significant effect on the equilibrium and therefore, it is customary to ignore the pressure variable and the vapour phase.

(i) Isomorphous system :

This is the simplest binary phase diagram and is obtained for a system exhibiting complete liquid solubility as well as solid solubility. The two components dissolve in each other in all proportions both in the liquid and the solid states. For complete solid solubility, the two components must have the same crystal structure and ~~other~~ must satisfy other Hume Rothery rules. Examples of this type of systems are Cu – Ni, Ag – Au, (Aurum) gold, Au – Cu etc.

latin: Argentum (silver) Latin word.

widely used in Specialized jewelry. (Pink gold or red gold or Russian gold)

Au-Si is Eutectic-2

A typical diagram for an Isomorphous system is shown in Fig 2.5.

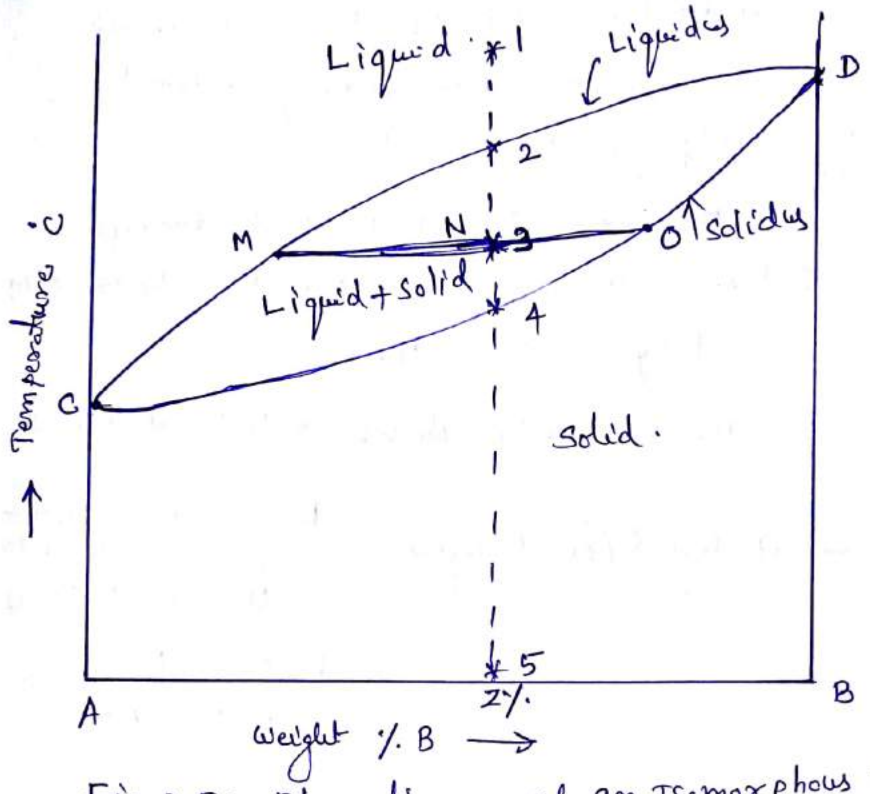


Fig 2.5: Phase diagram of an Isomorphous system.

In the above Fig 2.5, C and D are the melting ~~points of C and D~~ temperatures of of metal A and B respectively. The phase boundary between the liquid and the two-phase region is called the liquidus. The boundary between the solid and the two-phase region is called the Solidus.

The cooling of an alloy with Z% B from liquid state to room temperature is explained below.

(i) From 1 to 2, the alloy is in the liquid state and no change occurs.

(ii) At just below 2, solidification starts and solid phase starts separating out from the liquid. As the temperature decreases, the amount of solid increases and this continues upto 4 where last liquid freezes to solid. Between 2 and 4, the alloy contains liquid and solid phases. At any temperature between 2 and 4, the average composition of existing solid is indicated by the solidus line while that of liquid by the liquidus line. At the temperature of consideration, amounts of solid and liquid can be obtained by applying the lever rule.

For example, at point 3, average composition of the existing liquid is given by the point M and that of Solid by the point N.

The amounts of phases will be as below:

$$\text{Amount of liquid (or \% liquid)} = \frac{\text{length on the opposite sides of the line}}{\text{the total length of tie-line}} \times 100$$

$$= \frac{\text{length of } NO}{\text{length of } MO} \times 100$$

$$\text{Amount of solid (or \% Solid)} = \frac{\text{length of } MN}{\text{length of } MO} \times 100$$

(iii) No change occurs in the solidified alloy from 4 to 5.

(ii) Eutectic Systems.

These diagrams are obtained for two metals having complete solubility in the liquid state and complete insolubility in the solid state.

Titanium Arsenic gold
Examples: Bi–Cd, Th–Ti, Pb–As and Au–Si

A Typical phase diagram for such a system is shown in Figure 2.6.

Note: Eutectic: an alloy or mixture whose melting point is lower than that of any other alloy or mixture of the same ingredients. (OR) An alloy having the lowest freezing point of all possible mixtures of the substances.
Greek – eutektos — melting readily.

Eutectic is defined as the composition of a given mixture that has the lowest freezing point of all possible compositions of that mixture.

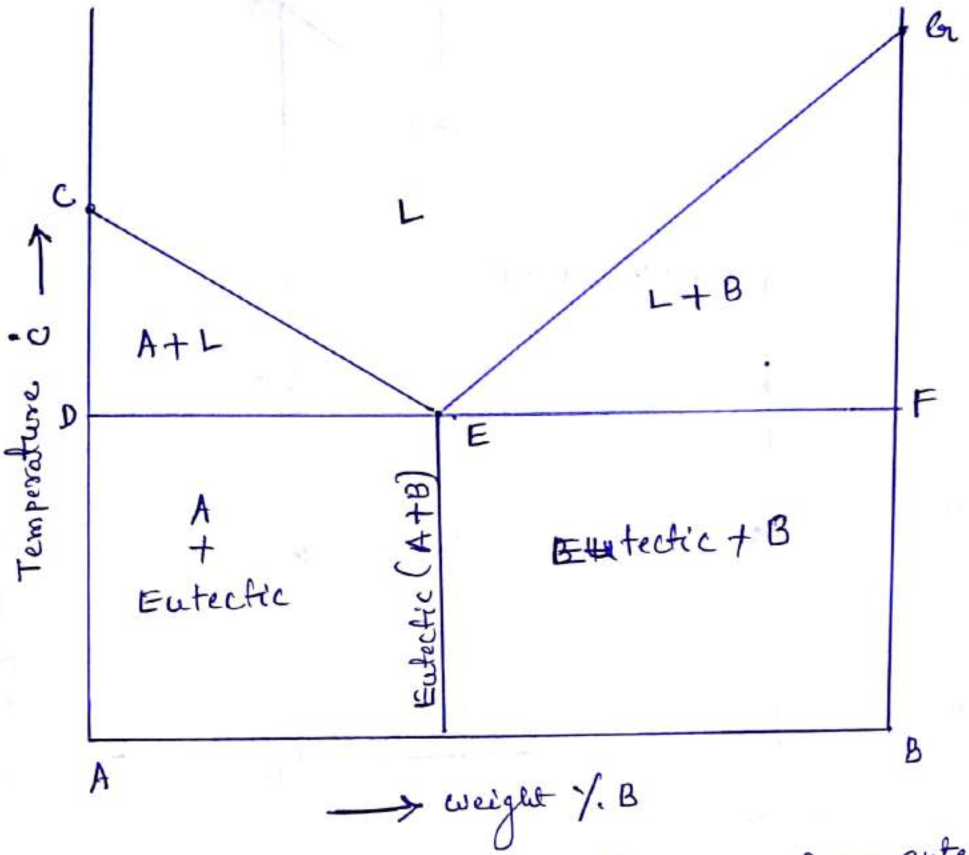


Fig 2.6: Binary phase diagram of an eutectic System showing complete insolubility in the Solid state.

In the above diagram C and G are the melting temperatures of A and B metals respectively. On adding B to A, or A to B, the melting temperature is lowered following the curves CE and GE respectively. These curves intersect at a point E called the eutectic point which represents the lowest temperature at which the mixture of A and B will melt. The liquidus of the diagram is CEG and solidus is CDEFG. During cooling, eutectic transformation occurs at the line DF except at the points D and F. The composition indicated by point E is Eutectic composition and temperature is eutectic temperature. The cooling of various alloys with changes in microstructure is explained below.

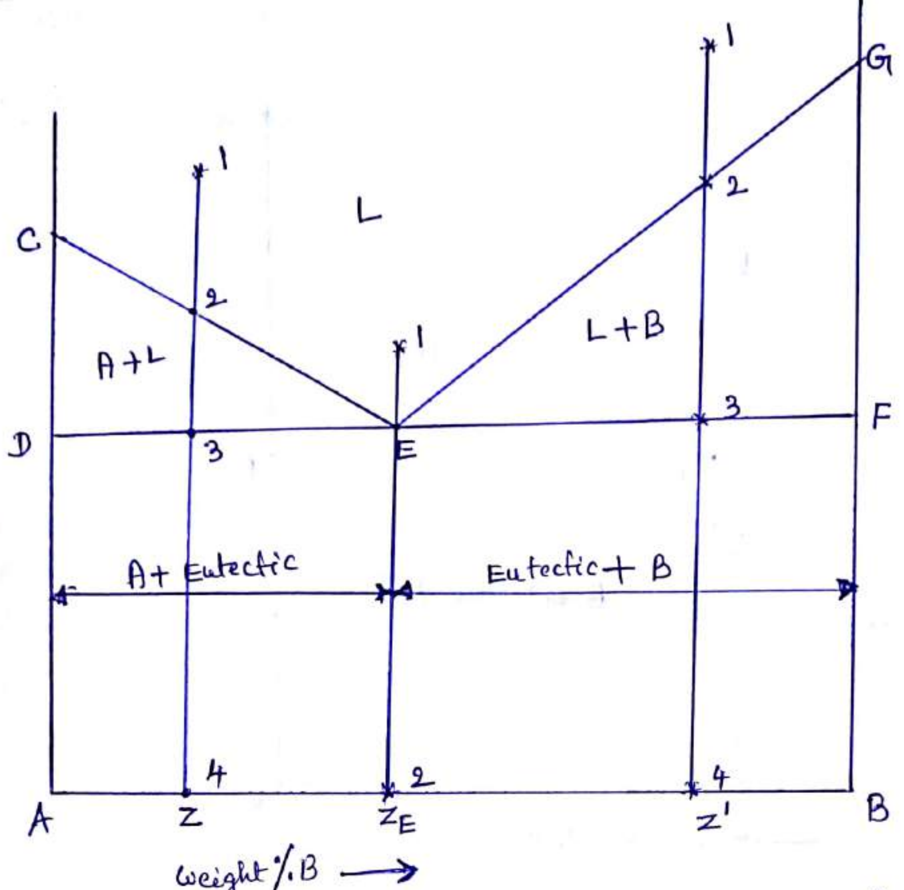


Fig 2.7: Eutectic system same as fig 2.6

(i) cooling of hypoeutectic alloy with Z%B:

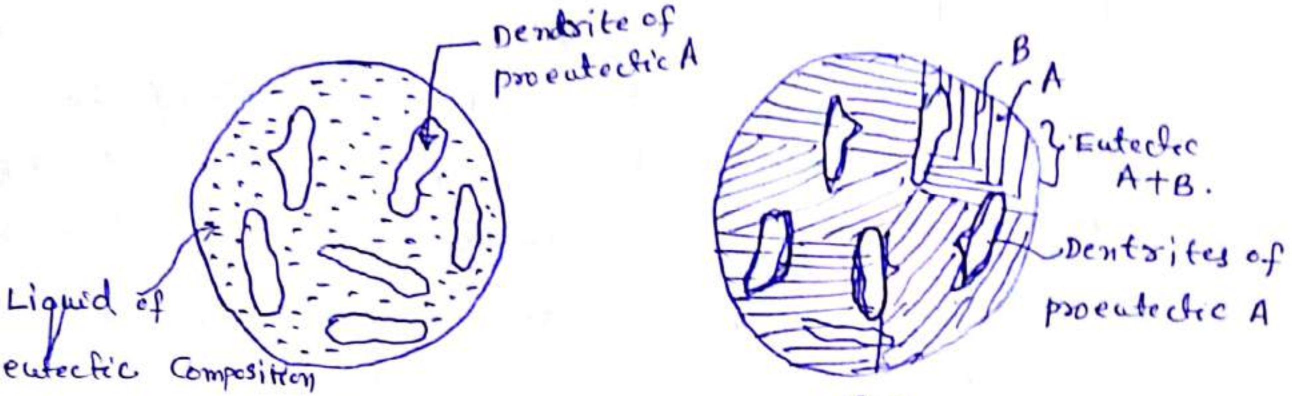
The alloy Z%B is marked by a vertical line on the fig 2.7 and cooling is explained from a temperature point 1 to room temperature i,e point 4.

ⓐ From 1 to 2, there is no change in the liquid state of the alloy. At just below 2, solidification starts and A seperates out from liquid and with further cooling, the amount of A increases. This continues up to 3. The composition of liquid varies along the liquidus line CE and composition of A does not change because of no solubility of B in A. At just above 3, the amount of A and liquid can be found out by the lever rule as below:

$$\text{Amount of } A = \frac{3E}{DE} \times 100$$

$$\text{Amount of liquid} = \frac{D3}{DE} \times 100$$

This phase A which has separated before the eutectic transformation is called proeutectic or free or Primary A (pro means before). The micro structure is shown in fig. 2.8 ⓐ



(a)

(b)

Fig 2.8: Shows changes in structure during solidification of a hypoeutectic alloy

ⓑ At 3, this liquid of eutectic composition and amount $\frac{D3}{DE}$ solidifies at constant temperature and transforms to an eutectic mixture of A and B, usually in a lamellar form as below:

$$\text{Liquid (of Eutectic Composition)} \underset{\text{heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} A + B$$

The alloy completely solidifies at 3.

The amount of eutectic will be the same as the amount of liquid i,e $\frac{D3}{DE}$. The microstructure is shown in fig. 2.8 ⓑ.

ⓒ From 3 to 4, no change occurs in the structure.

(ii) cooling of an eutectic alloy with composition Z_E % B

In Fig 2·7, the alloy is marked by a vertical line at the point E i,e. eutectic composition. The microstructural changes during cooling from point 1 to room temperature are explained below.

From 1 to E, there is no change in the liquid phase of the alloy. At just below E (or at E), the liquid of Eutectic Composition freezes at constant temperature. and gives an uniform lamellar mixture of A and B by an eutectic transformation mechanism indicated as below.

$$\text{Liquid} \longrightarrow A + B$$

The microstructural change is shown in Fig 2·9. The amounts of A and B in the eutectic will be the same as in the original alloy.

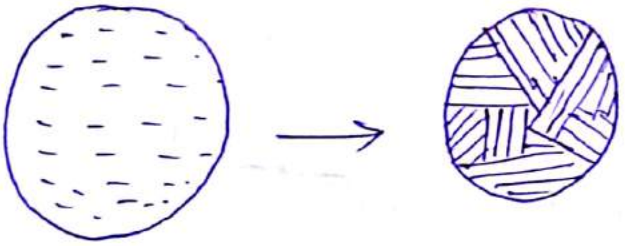


Fig 2·9 : shows change in structure during solidification of an eutectic alloy

The entire liquid solidifies at the eutectic temperature indicated by point E. and there is no change in the structure from E to 2. Same structure will be seen under microscope at room temperature.

(iii) Cooling of a hyper-eutectic alloy with z'%B :

In Fig 2.7, the alloy z'%B is marked by a vertical line and cooling is explained from point 1 to point 4 i.e room temperature.

ⓐ From 1 to 2, there is no change in the liquid state of the alloy. At just below 2, solidification starts and B separates out from the liquid. As the temperature decreases, amount of B increases. In general, the average composition of liquid changes along the liquidus line and that of solid along the solidus line. In this case, the liquid composition will vary along the line EG and solid (i.e B) will vary along the line GF. Since GF is a vertical line due to complete insolubility of A in B, B composition does not change. This continues till the eutectic temperature is reached i.e Point 3. At Point 3, the amounts of liquid and B by lever rule are as below.

$$\text{Amount of liquid} = \frac{3F}{EF}$$

$$\text{and Amount of B} = \frac{E3}{EF}$$

The microstructure is shown in Fig 2.10 (a).

Fig 2.10 : shows the change in structure during solidification of a hypereutectic alloy.

ⓑ At 3, this liquid of eutectic composition and amount equal to $\frac{3F}{EF}$ solidifies at constant temperature and forms an eutectic mixture of A and B in lamellar morphological form. The microstructure is shown in Fig 2:10 ⓑ.

ⓒ From 3 to 4, no change occurs in the structure and same structure can be observed under the microscope at room temperature.

The solidification characteristics are very much similar to that of a hypoeutectic alloy except the separation of B instead of A as a proeutectic from the liquid state.

Note: Eutectic meaning from Internet

The melting point of a mixture of two or more solids (such as an alloy) depends on the relative proportions of its ingredients. A eutectic or eutectic mixture is a mixture at such proportions that the melting point is as low as possible, and that furthermore all the constituents crystallize simultaneously at this temperature from molten liquid solution. Such a simultaneous crystalization of a eutectic mixture is known as a eutectic reaction, the temperature at which it takes place is the eutectic temperature, and the composition and temperature at which it takes place is called the eutectic point.

The term comes from the Greek eutektos, meaning "easily melted".

PARTIAL EUTECTIC SYSTEMS :

These diagrams are obtained for two metals which have complete solubility in the liquid state and partial solubility in the solid state.

silver Lead Tin

Examples : Ag–Cu, Pb–Sn, Al–Si etc.

A typical phase diagram for such a system is shown in Fig 2.11.

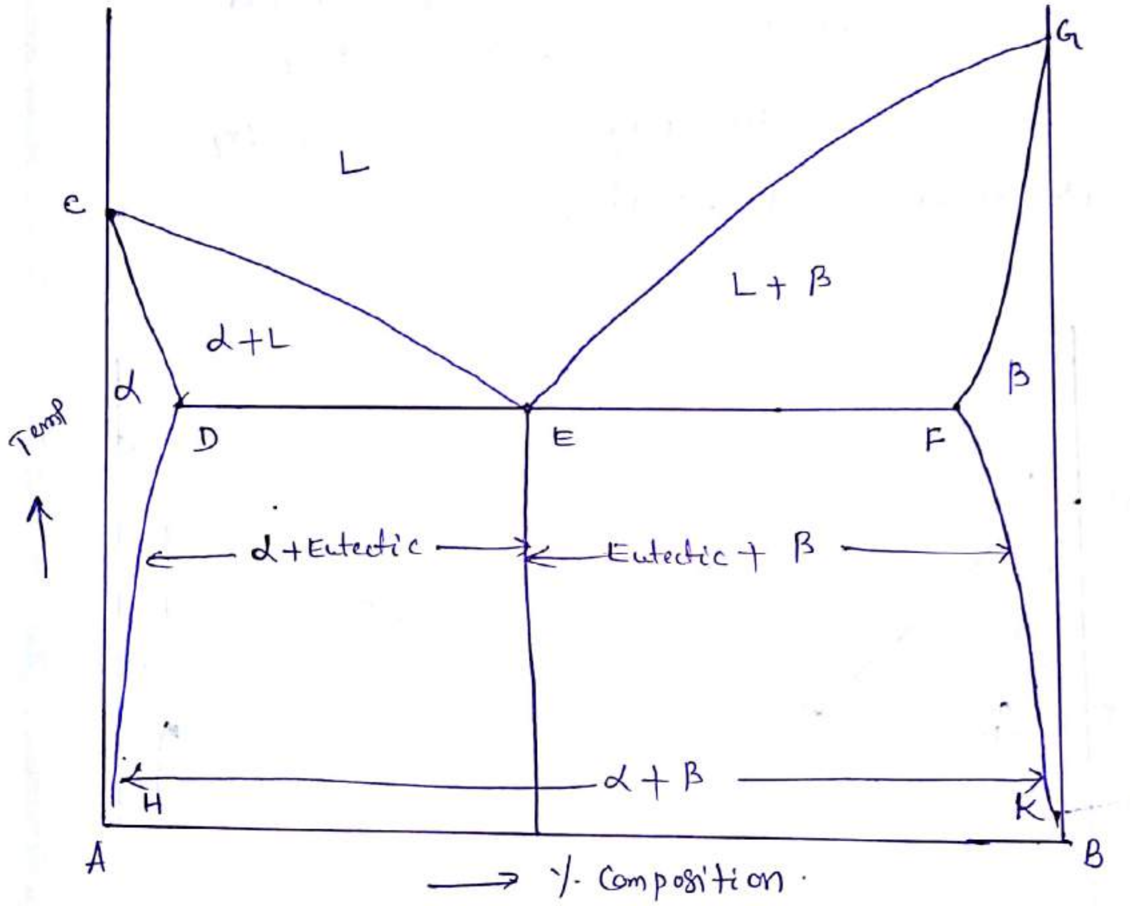


Fig 2·11: Binary eutectic phase diagram showing partial solid solubility.

In Fig 2·11, C and G are the melting points of A and B metals respectively. The liquidus of the diagram is CEG and solidus is CDEFG. α is a solid solution of B in A. and β is of A in B. The points H and K indicate the room temperature solubilities of B in A and A in B respectively. Points D and F indicate the maximum solubility of B in A and A in B respectively at eutectic temperature. The curves HD and HF indicate the solubilities of B in A and A in B respectively as the temperature rises from room temperature to eutectic temperature. These curves are called solvus lines since they indicate the solubilities of one into the other at different temperatures. Point E indicates eutectic composition and eutectic temperature. The eutectic arm is DEF.

The phase diagram of Ag-Cu is shown in Fig 2.12.

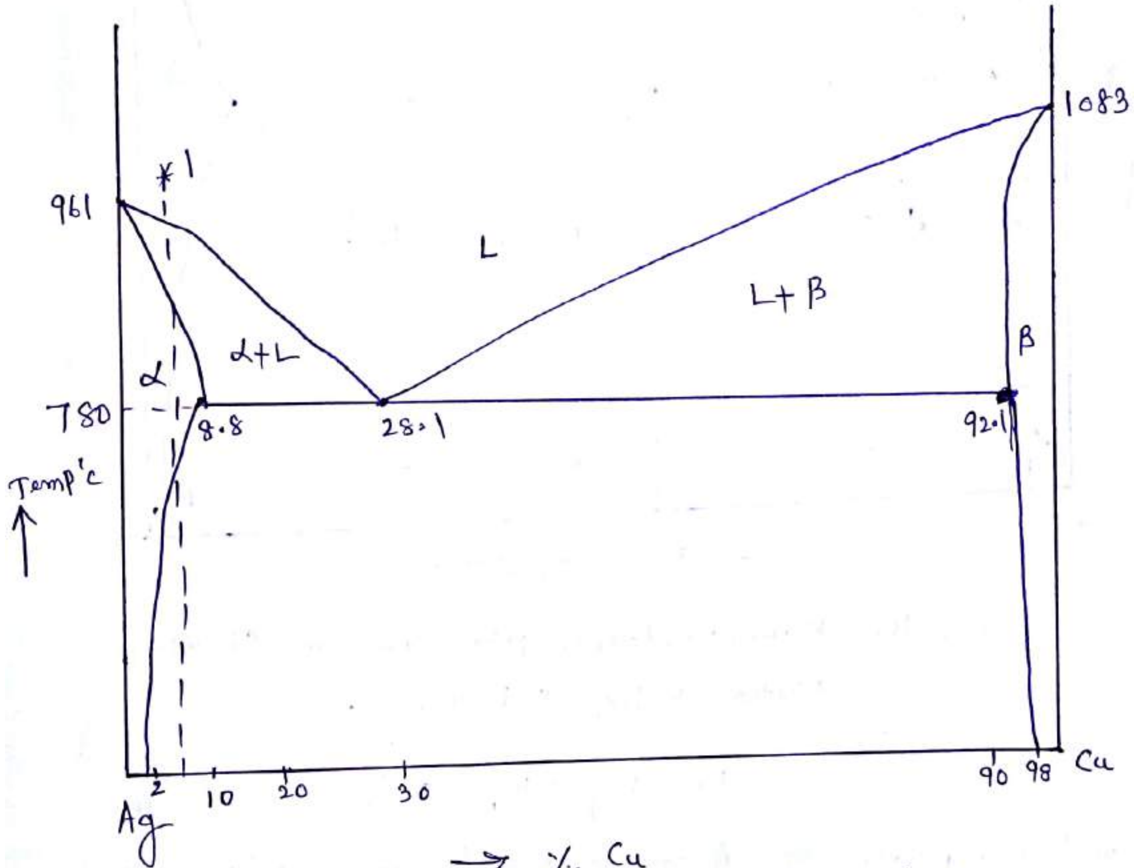


Fig 2.12: phase diagram of Ag and Cu showing partial solid solubility.

The above phase diagram (Fig 2.12) reveals the following details:

ⓐ Melting point of Ag = 961°c,

ⓑ Melting point of Cu = 1083°c

ⓒ Eutectic temperature = 780°c

ⓓ Eutectic Composition = 28.1 % Cu

ⓔ Maximum solubility of Cu in Ag i,e in α - Solid solution (at 780°c i,e eutectic temperature) = 8.8% Cu

ⓕ Max solubility of Ag in Cu i,e in β - solid solution = 7.9% Ag i,e 92.1% Cu

ⓖ · The solubilities of both Cu in Ag and Ag in Cu decrease with decreasing temperature and are around 2% at room temperature.

ⓘ Cooling of an alloy with 6% Cu :

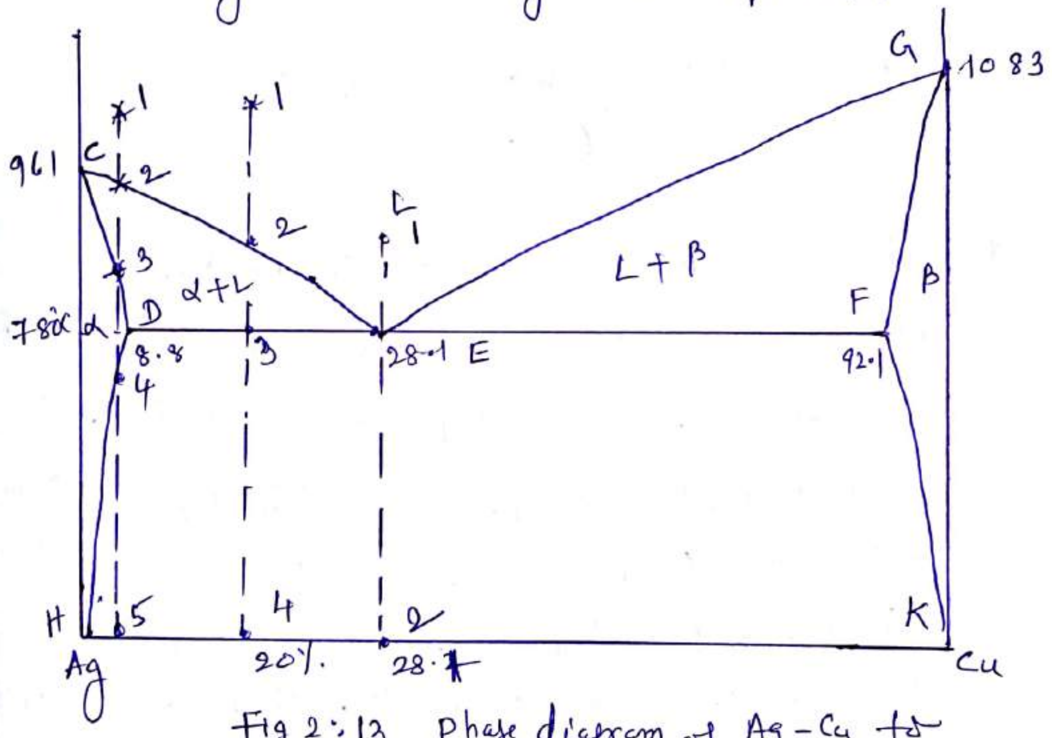


Fig 2:13, Phase diagram of Ag-Cu to explaining cooling at various alloys.

The alloy (6% Cu) is marked vertical line at 6% Cu.

ⓐ From 1 to 2, no change occurs in the liquid state of the alloy.

ⓑ At just below 2, α starts seperating out from the liquid. As the temperature decreases, amount of α increases. The composition of α varies along the solidus line CD and composition of liquid varies along the liquidus line CE. The last liquid solidifies at 3 and gives 100% α solid solution (Fig 2:14 ⓐ)

ⓒ From 3 to 4, no change occurs in the structure.

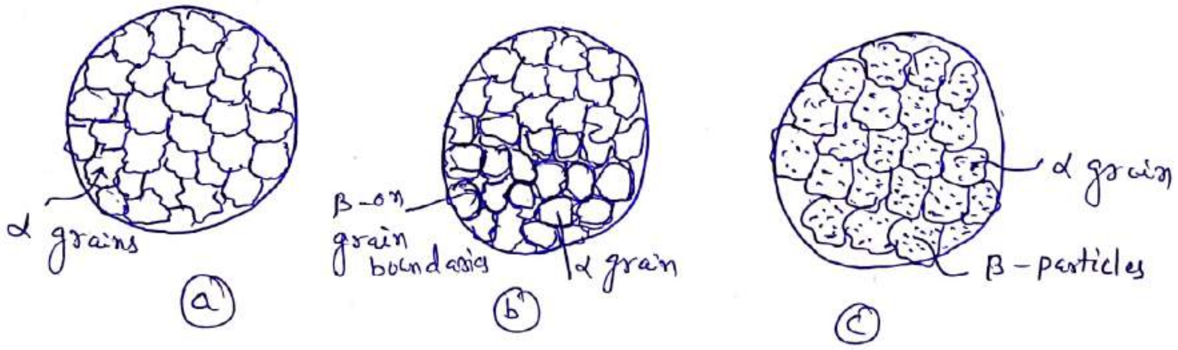


Fig 2:14 : Microstructures during cooling of Ag-6 Cu alloy

ⓓ Below 4, the solubility of Cu in Ag which is indicated by α-solvus line i,e. line DH is less than 6%.. The alloy contains 6% Cu and therefore during cooling below 4, Cu seperates out from α in the form of β solid solution. Cu can not separate out as a pure Cu because of some solubility of Ag in Cu in the solid state. As temperature decreases, amount of β increases and this continues up to room temperature (i,e up to point 5).

At room temp:

$$\text{Amount of } \alpha = \frac{\text{length } 5K}{\text{length } HK}$$

and

$$\text{Amount of } \beta = \frac{\text{length } H5}{\text{length } HK}.$$

The total amount of Cu in α plus β remains the same as the original composition of the alloy i,e. 6% Cu

This β may appear at the grain boundaries of α or may get entrapped in the grains, depending on the cooling rate. Slower the cooling, chances of β to appear at the grain boundaries is higher. The microstructure under slow cooled condition is shown in Fig 2.14 ⓑ.

Rapid cooling suppresses the separation of β and the structure at room temperature becomes similar to that of Fig 2.14 ⓐ. but super saturated. This super-saturated structure decomposes at room temperature, or elevated temperature and give β precipitate in α grains as shown in Fig 2.14 ⓒ.

(ii) Cooling of hypoeutectic alloy with 20% Cu:

The above alloy is marked on Fig 2.13 by a vertical line at 20% Cu.

(a) From 1 to 2, no change occurs in the liquid state of the alloy.

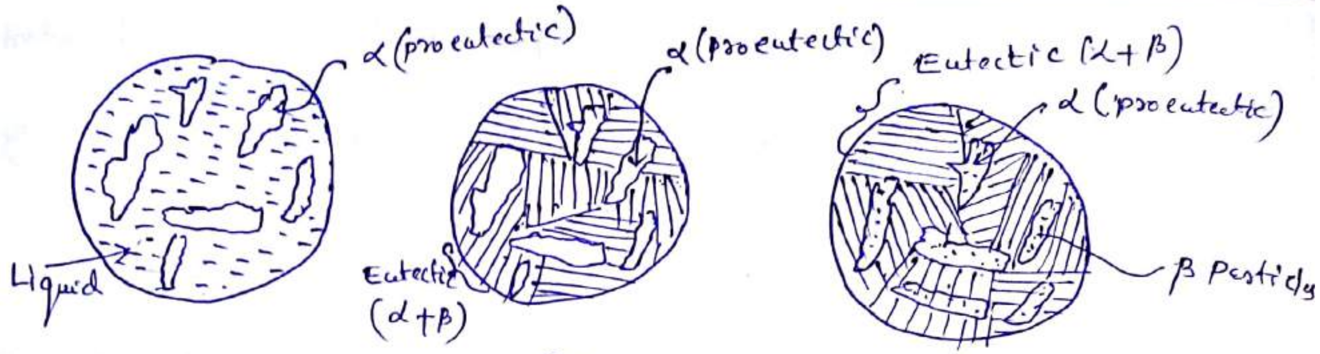
(b) At just below 2, α starts separating out from the liquid. As the temperature decreases, the amount of α increases and this continues up to 3. The composition of α changes along its solidus line CD and composition of liquid changes along the liquidus line CE.

Applying lever rule at 3:

$$\text{Amount of } \alpha = \frac{\text{length } 3E}{\text{length } DE}$$

$$\text{Amount of liquid} = \frac{\text{length } D3}{\text{length } DE}$$

The microstructure is shown in Fig 2.15(a) 3



(a) (b) (c)

Fig 2.15: Shows the changes in structure of Ag-20 Cu alloy during cooling

ⓒ At 3, this liquid of eutectic composition solidifies at constant temperature and transforms to an eutectic mixture of α and β by eutectic transformation mechanism.

$$\underset{(\text{of } 28.1\%\ Cu)}{\text{Liquid}} \longrightarrow \underset{(\text{of } 8.8\%\ Cu)}{\alpha} + \underset{(\text{of } 92.1\%\ Cu)}{\beta}$$

This eutectic mixture appears in lamellar morphological form as shown in fig 2.15 ⓑ.

ⓓ Below 3, the solubility of α is decreasing along the line DH and that of β along the line FK. Due to this, β separates out from α and α separates out from β. This continues upto 4. i.e. room temperature. For better understanding, we will see the changes in proeutectic α and eutectic mixture separately.

From proeutectic α, β separates out and this β may appear at grain boundaries or inside the grains depending on the cooling rate. It usually appears inside the grains unless the cooling is extremely slow.

Eutectic is a lamellar mixture of α and β. From α-lamella, β separates out and

and from β lamella, α separates out. Due to this, only the proportions of α and β, (or widths of α and β lamellae) will change and the appearance as such does not change. Therefore, at room temperature, microstructure may show particles of β in the proeutectic α along with the lamellar eutectic mixture of α and β as shown in Fig 2.15 ⓒ. However, the amount of β separating in the proeutectic α being small, it may not be revealed by the optical microscopes at the magnifications employed for general study of microstructures and hence the alloy may appear similar to Fig 2.15 ⓑ at room temperature.

(iii) Cooling of eutectic alloy with 28.1% Cu:

The alloy is marked by a vertical line in Fig 2.13 at 28.1% Cu

ⓐ From temperature 1 to eutectic temperature E, there is no change in the liquid state of the alloy. At just below E (or at E), the liquid solidifies at constant temperature and gives an eutectic mixture of α and β, in the lamellar morphological form.

$$\underset{(\text{of } 28.1\%\ \text{Cu})}{\text{Liquid}} \longrightarrow \underset{(\text{of } 8.8\%\ \text{Cu})}{\alpha} + \underset{(\text{of } 92.1\%\ \text{Cu})}{\beta}$$

The amounts of α and β in the eutectic are:

$$\underset{(\text{of } 8.8\%\ \text{Cu})}{\text{Amount of } \alpha} = \frac{\text{length of EF}}{\text{length DF}}$$

$$\underset{(\text{of } 92.1\%\ \text{Cu})}{\text{Amount of } \beta} = \frac{\text{length DE}}{\text{length DF}}$$

The microstructure is shown in Fig. 2.16

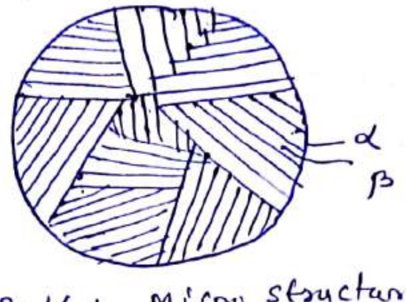


Fig 2.16 : Micro structure of an eutectic alloy.

(b) From E to 2, there is almost no change in the structure except slight changes in the amounts of α and β in the eutectic mixture due to changes in solubilities of α and β with decreasing temperature. Due to this, the widths of the lamellae will change, but the structure appearance remains similar to that of Fig 2.16.

Amount of α and β in the eutectic at room temperature are:

$$\text{Amount of } \alpha = \frac{\text{length } 2K}{\text{length } HK}$$

$$\text{Amount of } \beta = \frac{\text{length } H2}{\text{length } HK}$$

(IV) Cooling of hypereutectic alloys :

The microstructural changes during cooling of hypereutectic alloys are very much similar to that of hypoeutectic alloys except that the proeutectic phase will be β instead of α. Structure morphology is also similar to those of hypoeutectic alloys.

Invariant reactions (Transformations in alloys).

Eutectic : Liquid $\underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}}$ Solid 1 + Solid 2

Eutectoid : solid 1 $\underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}}$ solid 2 + solid 3

Peritectic : Liquid + solid 1 $\underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}}$ Solid 2.

Peritectoid : Solid 1 + Solid 2 $\underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}}$ Solid 3

Monotectic : Liquid 1 $\rightleftharpoons$ Liquid 2 + Solid.

Some Important phase diagrams.

* Cu – Ni System : It is Isomorphous system. and is shown in Fig 2:18.

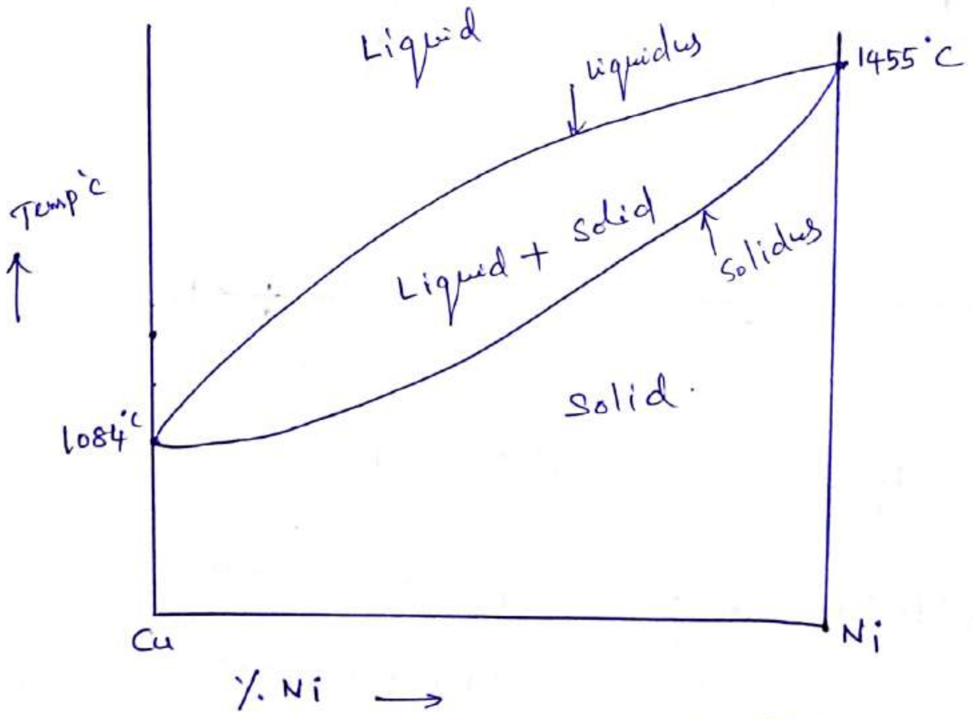


Fig 2 : 18 : Cu – Ni System.

Problems on phase diagrams

metal A melts at 650°c and metal B melts at 450°c, when alloyed together A and B donot form any compound or intermediate phase. The solid solubility of metal A in B and of B in A are negligible. The metal pair forms an eutectic at 40% A and 60% B which solidifies at 300°c. Assume the liquidus line to be straight. Draw the phase diagram for the alloy series and find:

ⓐ The temperature at which the alloy 70% A and 30% B starts and completes solidification.

ⓑ For the same alloy, the amount of solid phase and liquid phase at 400°c.

olution: From the graph (PB①).

ⓐ For given alloy i,e 70% A & 30% B.

solidification starts at X = 475°C

solidification ends at Y = 300°C.

ⓑ For given alloy i,e 70% A & 30% B.

At 400°C

$$\% \text{ solid phase (A)} = \frac{NO}{MO} \times 100$$

$$= \frac{43-30}{43-0} \times 100$$

$$= \frac{13}{43} \times 100$$

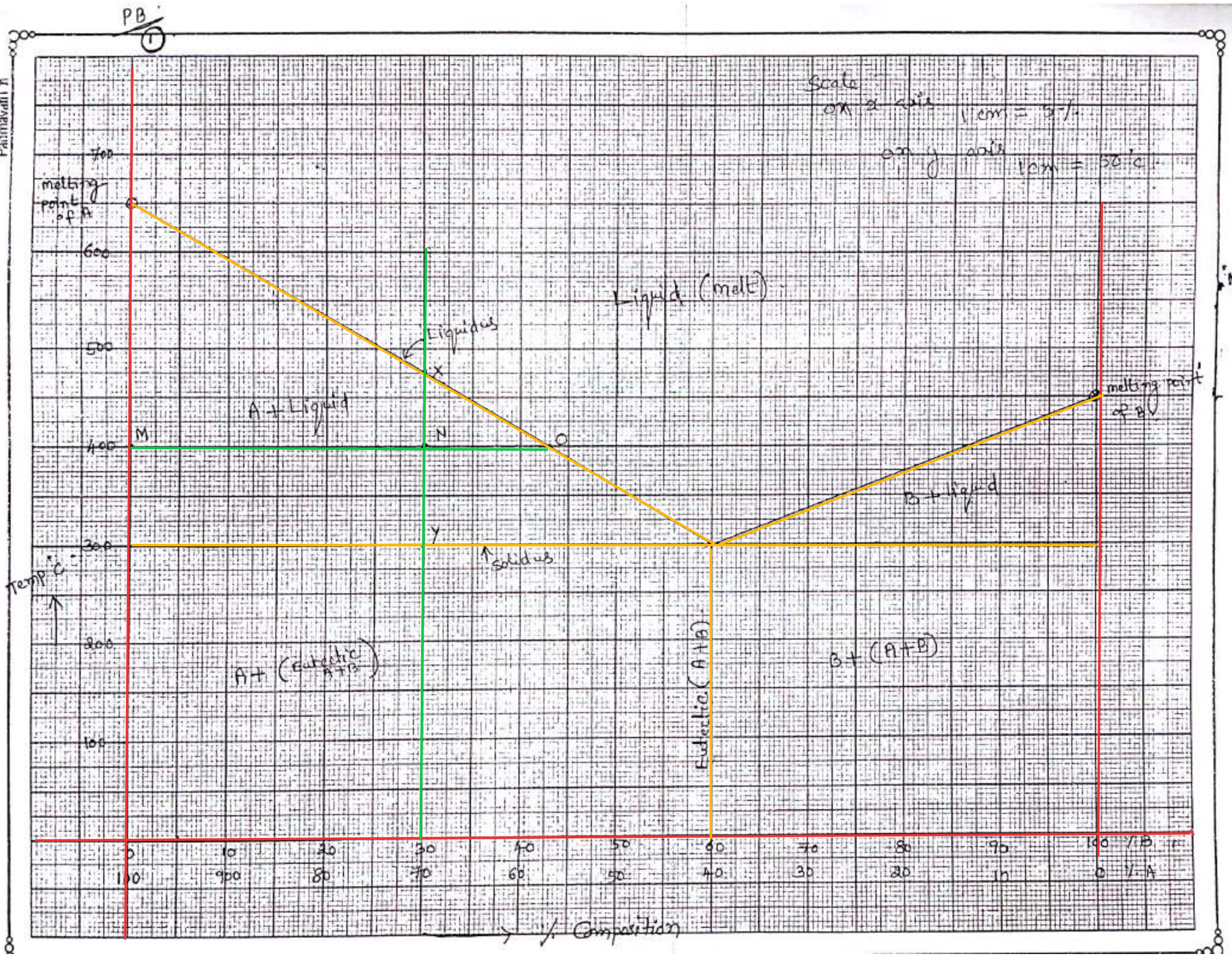
$$= 30.2\%$$

$$\% \text{ liquid phase} = \frac{MN}{MO} \times 100$$

$$= \frac{30-0}{43-0} \times 100$$

$$= \frac{30}{43} \times 100$$

$$= 69.8\%$$


PB
①
Scale
on x axis 1 cm = 5 %
on y axis 1 cm = 50 °C
700
melting point of A
600
500
400
300
200
100
Temp °C
Liquid (melt)
Liquidus
X
A + Liquid
M
N
O
Y
Solidus
B + liquid
melting point of B
A + (Eutectic A+B)
Eutectic (A+B)
B + (A+B)
0 10 20 30 40 50 60 70 80 90 100 % B
100 90 80 70 60 50 40 30 20 10 0 % A
% Composition