STRUCTURE OF METALS & ITS ALLOYS:

BONDING IN SOLIDS:

When the atoms of the elements combines to form molecules a force of attraction is developed between the atoms, which holds them together this force is known as "**Bond".**

Atoms are held together in solids by electrostatic forces of attraction.

An electric force of attraction occurs between positively and negatively charged particles, and there are various ways in which such electric forces can be produced between atoms in solids.

Causes of Bonding:

The atoms or molecules forms bonds with another, in order to achieve stable configuration in the following 3 ways

- ➢ By loosing one or more electrons to another atom
- ➢ By gaining one or more electrons from another atom
- ➢ By sharing one or more electrons with another atom

Classification of Bonds :

- According to the nature of forces of attraction bonds are classified as

    - o Primary bonding

    - o Secondary bonding

- **Primary bonds:**

    - Primary bonds are inter atomic bonds in which electro static force holds the atoms together.

    - They are more stable and relatively strong bonds.

    - Examples- metallic, ionic and covalent bonds

- **Secondary bonds:**

    - Secondary bonds are inter molecular bonds in which the weak forces holds the molecules together

    - These weak forces are known as vanderwall's force.

    - They are relatively weak.

    - Examples- dispersion bond, dipole bond and hydrogen bond.

Secondary bond is weak and less stable when compared to primary bond

Types of Primary Bond:

1. Ionic Bond
2. Covalent Bond
3. Metallic bond

1. Ionic Bond:

1. It is also known as electro valent bond
2. It is formed between atoms of metals and nonmetals

3. An ionic bond is formed when one or more electrons, from the outer most shell of one atom, are transformed to the outermost shell of another atom

4. The electro static attraction b/w the oppositely charged ions forms the ionic bond

5. Following are the two conditions are necessary for the bond formation :

   1. The atom which loses the electron should have low ionization energy. It means that a small amount of energy is requires to remove the electron from its outermost energy level

   2. The atom which gains the electron should have high electron affinity. It means that the atom should be able to readily accept an electron from its outermost energy level

Ex: formation of ionic bond in sodium chloride (NaCl)
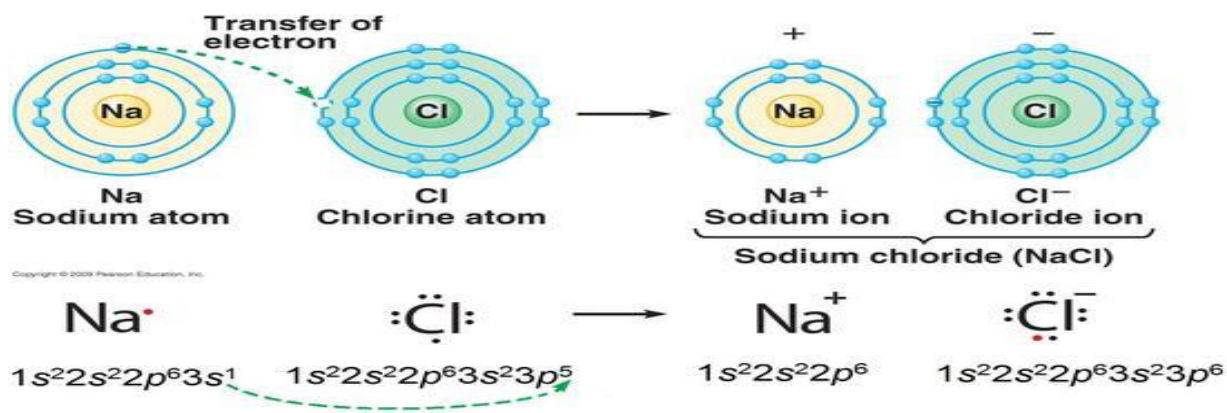
➢   The atomic no of Na is 11 and Cl is 17 .the atomic structure of both Na and Cl atoms are shown in fig. Thus we see that the Na atom has 1electron in its outer most energy level and Cl atom has 7 electrons in its outer most energy level
➢ The Na atom has tendency to lose its electron in its outermost energy level to have a stable configuration. more over the Cl atom has a tendency to accept one electron (lost by Na atom) in its outer most energy level to have a stable electronic configuration of argon

Properties of ionic solids:

1. Ionic solids are rigid, uni directional and crystal in nature
2. The ionic solids have very low electrical and thermal conductivities
3. The ionic solids have high hardness due to their crystalline structure
4. The ionic solids are not malleable and ductile
5. They have high melting and boiling temperature
6. They exist in the form of solids only
7. They are freely soluble in water but slightly soluble in organic solvents

Covalent bond:

➢ It exist due to the electrostatic force of attraction b/w atoms which share the electron pairs to form a covalent bond
➢ It is formed b/w similar or dissimilar atoms

Ex: O_2, CO_2, C_2H_6, H_2O, Sic
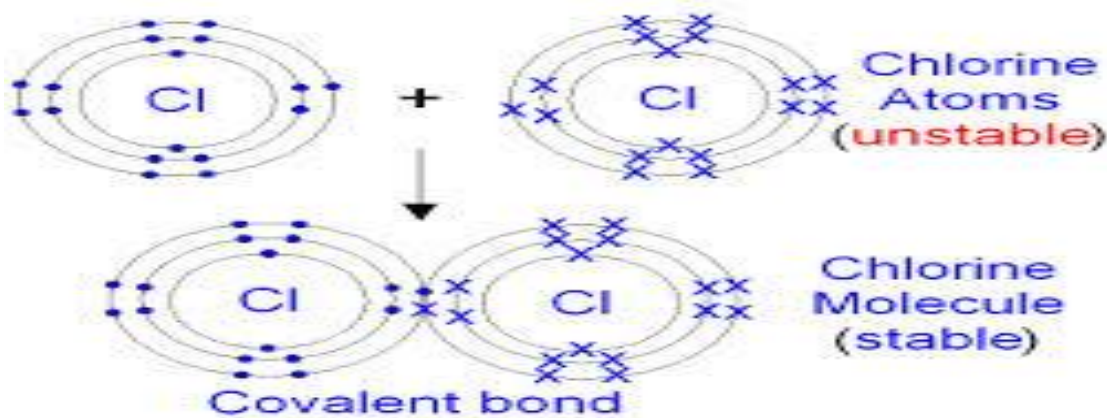
Fig: covalent bond formation of chorine molecule

In Cl molecule it consists of 7 electrons in its outer most shell. it need one more electron to achieve stable configuration Argon it share another chlorine atom as shown in fig

Note :

➢ When the atoms share one pair of electron the bond formed is single bond, two or three pair of electron, the bond formed is single or double or triple covalent bond

They are two types of covalent bands-

• Non Polar

- bonded atoms that share e⁻'s <u>equally</u>

  - same <u>atoms</u> bonded

      ex. Cl – Cl: Cl_2

- Polar

    - bonded atoms that do not share e⁻'s equally

    - <u>different</u> atoms bonded

                    H

        ex. H – N – H: NH_3

Properties of ionic solids:

- ✓ These are bad conductors of electricity

- ✓ These compounds are low melting & boiling temp

- ✓ These are not soluble in water ,but are soluble in organic components such as benzene, toluene etc

3. Metallic bond:

A bond formed by the attraction between electron cloud and positively charged <u>ion</u> (cation) of same or different metals
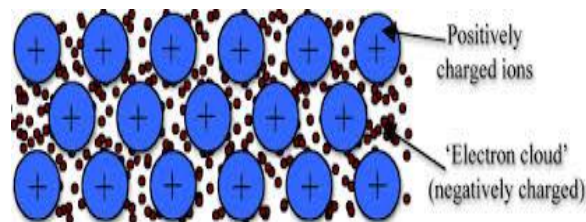
Fig: Metallic bond formation

Properties of metallic solids:

- ✓ These are high electrical and thermal conductivities

- ✓ Metallic solids have crystalline structure but are soft in nature

- ✓ These solids are low melting and boiling temperature than ionic solids

- ✓ These are exist in the form of solids only

- ✓ These are neither soluble in water nor organic solvents

2. Secondary Bond

1. Dispersion bond:

- This bond as shown in a symmetrical molecule.

- The electrons are uniformly distributed around the nucleus.

- But due to mutual repulsion, electrons disperse in asymmetrical manner the displacement of positive and negative charges, and forms a dipole (pair of two opposite and equal charges).

- These dipoles oscillate and influence each other resulting in a weak attraction force which forms the dispersion bond.

- Example- molecules of the inert gas are held by dispersion bond.

2. Dipole bond:

- Unequal sharing of electrons between the atoms results that the center of positive and negative charges does not coincide and the electrical dipole (molecule with one end positive and other end negative).

- These dipoles provide molecular attraction resulting in the formation of dipole bond.

- Dipole bonds are weaker than ionic bonds but stronger than dispersion bond.

Example- formation of hydrogen chloride (HCL).

In HCL, molecule region near the hydrogen nucleus is highly positive and opposite region near the chlorine nucleus is negative.

Attractive between the regions results dipole bond.

3. Hydrogen bond:

- Hydrogen bond results between hydrogen atom and any other elctro-negative atoms such as oxygen and nitrogen.

Example-

In water molecules two H_2 ends of the molecule being slightly positive (i.e. from proton) relative to the oxygen atom (electron).

Each water molecule form a dipole.

Hydrogen bond occurs as a result of electro-static attraction between these molecule from a dipole.

BOND ENERGY OR BINDING ENERGY: It is defined as the energy to break the bond or to separate the atom is known as "**bond energy"**

➤ It is expressed in kj/mole

BOND LENGTH:

➢ The bond length may be defined as equilibrium separation (r) b/w the centre-to-centre of two bonding atoms.
➢ The force of attraction b/w the two bonding atoms, smaller will be the equilibrium separation and hence smaller the bond length.
➢ The primary bond are more stronger than the secondary bond, then the bond length of primary bond are smaller than those of secondary bonds
➢ The bond length of primary bond are in the range of 1-2 A^O,for secondary bonds of 2-5 A^O
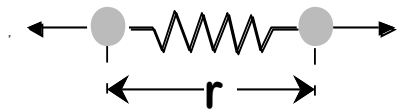
Fig: bond length

Crystallization of solids:

➢ **crystal** or **crystalline solid** is a solid material whose constituent atoms, molecules or ions etc are arranged in an ordered pattern extending in all three dimensions. which are acquired under the action of inter molecular forces.
➢ Crystals are also known as grains
➢ The boundary separating the two adjacent grains is called grain boundary
➢ The scientific study of crystals and crystal formation is known as *"crystallography."*
➢ The process of crystal formation via mechanisms of crystal growth is called *"Crystallization or solidification."*
➢ All materials are crystalline in nature.
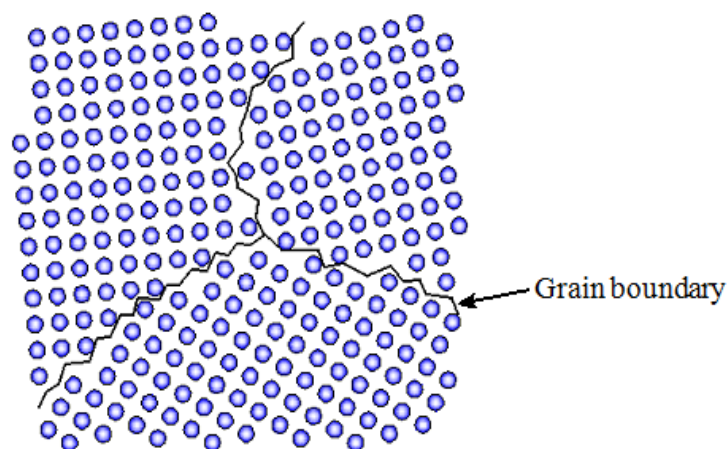
➢ **Single Crystals:** Crystals can be *single crystals* where the whole solid is one crystal. Then it has a regular geometric structure with flat faces.

- ➢ **Polycrystalline Materials:**
    - o A solid can be composed of many crystalline grains, not aligned with each other. It is called *polycrystalline***.**
- ❖ The grains can be more or less aligned with respect to each other. Where they meet is called a *grain boundary***.**

❖ **Crystalline and Non-crystalline materials**

- ➢ **Crystalline Solids:-**
- ❖ In crystalline substances the atoms are arranged in regular pattern then it's called crystalline solids.
- ❖ the distance b/w any two successive toms is equal
  Example: Cu, Al, Fe etc

- ➢ **Non-Crystalline Solids or Amorphous solids :**
    - ❖ The irregular arrangement of the atoms in a crystal is called Non-Crystalline solids
    - ❖ The atomic distance b/w any two successive atoms is not equal
      Example: glass, rubber etc
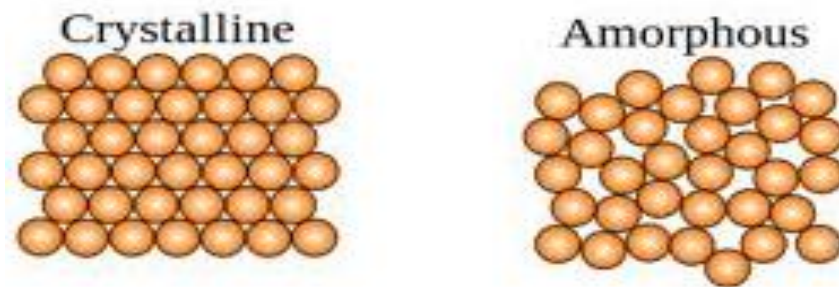
Fig: Crystalline and Non-crystalline materials

Anisotropy & Isotropy:

- ➢ The properties of polycrystalline solids may be differ greatly in different directions and such an unequality of properties in various crystallographic directions is called *Anisotropy***.**
- ➢ Amorphous substances such as glass will display the same properties in any directions or planes are called *isotropic***.**

Lattice: It denotes the position of atoms or molecules in the crystal.

Space lattice: It differs from a crystal structure in that a space lattice is an array of points in three-dimensional space in which every point has surroundings identical to the every other point in the array. Where as a crystal structure is an arrangement of atoms in crystal.
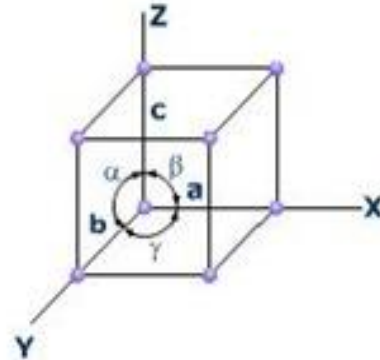
Or

The array of lattice points in three-dimensional space is called space lattice.
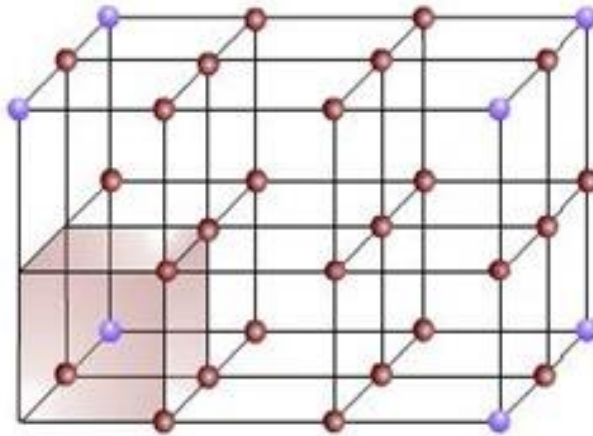
Representation of space lattice and unit cell

Representation of dimensions of a unit cell

<u>Unit cell</u> : It is the smallest portion of the crystal which shows the arrangement and position of atoms in a crystal structure

Where   a, b,c,-intercepts along axes along x,y,z and

                    α, β, γ-interfacial angles

Primitive cell: It is defined as a unit cell which possesses lattice points at its corners only

Example: A simple cubic cell

Non-Primitive cell: The unit cell which contain more than one lattice point, are called Non-primitive cell

Ex: body centered and face centered cubic structures contain more than one lattice point per unit cell

   ❖ If no of lattice points per unit cell are two the unit cell is called doubly primitive cell.
   ❖ If no of lattice points per unit cell are three or four the unit cell is called triply primitive cell or quadruply primitive cell

TYPES OF CRYSTAL SYSTEMS

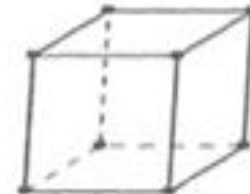**Seven crystal systems are:**

1. Cubic   2. Tetragonal   3. Orthorhombic   4. Monoclinic   5. Triclinic   6. Trigonal (Rhombohedral)
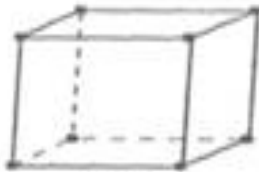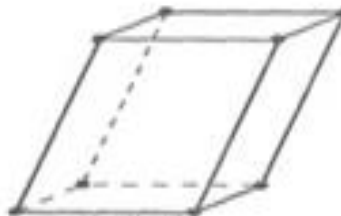7. Hexagonal
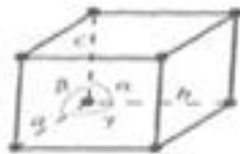
Representative
Unit Cell
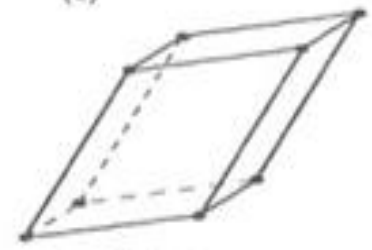(a)
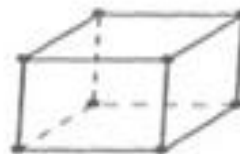
$a = b = c$
$\alpha = \beta = \gamma = 90°$
CUBIC
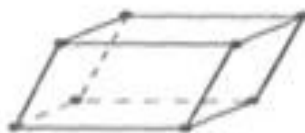(b)

$a = b \neq c$
$\alpha = \beta = \gamma = 90°$
TETRAGONAL
(c)

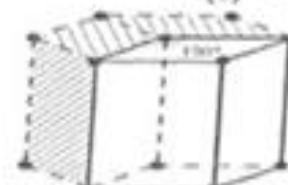$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$
ORTHORHOMBIC
(d)

$a \neq b \neq c$
$\alpha = \gamma = 90° \neq \beta$
MONOCLINIC
(e)

$a \neq b \neq c$
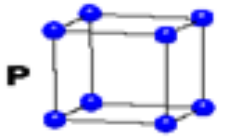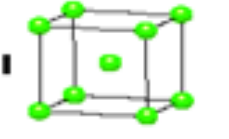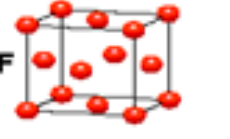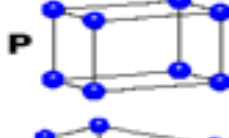$\alpha \neq \beta \neq \gamma \neq 90°$
TRICLINIC
(e)
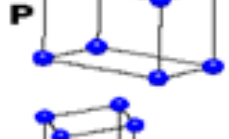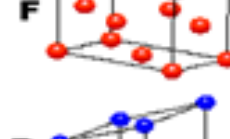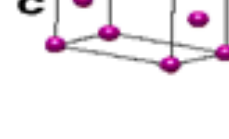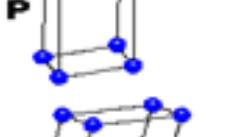
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$
RHOMBOHEDRAL (TRIGONAL)
(g)

$a = b \neq c$
$\alpha = \beta = 90°, \quad \gamma = 120°$
HEXAGONAL
(h)

Bravais Lattice
14 types of lattices, called *Bravais lattices*, make up the crystal system. The lengths of the sides, a, b, and c, and the angles between them can vary for a particular *unit cell*.

CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$

TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

Packing factor (p.f)

- Packing factor or packing density is defined as the volume occupied by the atoms in a unit cell to the volume of unit cell.

- Packing fraction = vol.of atoms in a unit cell / volume of unit cell
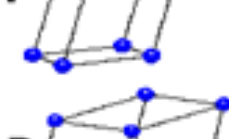
    For a cubic structure, $p.f = n.4/3\ \pi r^3 / a^3$

    Where   r = radius of atoms

              n = effective no.of atoms per unit cell

              a = lattice parameter of the structure

P.Fis less then the atoms are arranged in loosely packed and when the P.F is more then the atoms are arranged in close packed

CRYSTAL STRUCTURE OF METALS

Most metals crystallize into 4 forms of crystal systems:

- ❖ Simple Cubic crystal structure (S.C.C)
- ❖ Face-centered cubic structure (F.C.C)
- ❖ Body-centered cubic structure (B.C.C)
- ❖ Hexagonal close-packed structure (F.C.C)

1. Simple cubic structure:

In this structure 8 corners of the cube are occupied by 8 atoms.

No of atoms in the unit cell of S.C.C:

The unit cell contains 8 atoms one at each corner of the cube, since each corner atom is shared by 8 eight surrounding cubes the unit cell of S.C.C contains

8 atoms at the corners 8X1/8 =1 atom

Atomic packing factor of S.C.C:

P.F = vol.of atoms in a unit cell / volume of unit cell

Consider a s.c.c structure as shown in fig;

Where; a=length of each side of cube

r=atomic radius
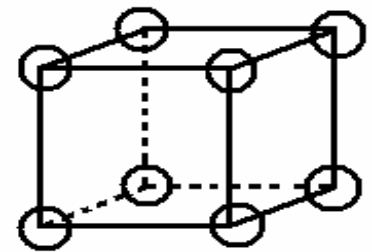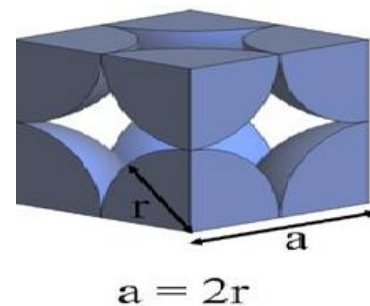
$r = a / 2$

Volume of atoms in the unit cell $= n.4/3\ \pi r^3$

$$= 1X4/3\ \pi\ (a/2)^3 =\ \pi a^3 /6$$

Volume of unit cell $= a^3$

p.f $= (\pi a3 /6) / a\quad =\quad \pi / 6 = 52\ \%$

P.f is the about 52% and hence this structure is loosely packed,

Polonium is the only element which shows this type of structure,

2. Body-centered cubic structure (B.C.C)

In B.C.C structure the unit cell contain 8 atoms and 1 atom in the centre of the cell

No of atoms in the unit cell:

In B.C.C structure the unit cell contains 8 atoms at each corner of the cube and one atom in the centre of the cube

Since each corner is shared by 8 surrounding cubes and the atom in the centre cannot be shared by another cube.
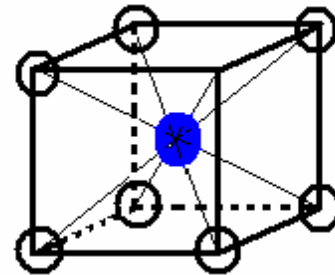
Fig: B.C.C

8 atoms at the corners x 1/8 =1 atom

1 centre atom   =1 atom
_____

2 atoms

$$\sqrt{3}a = 4R$$
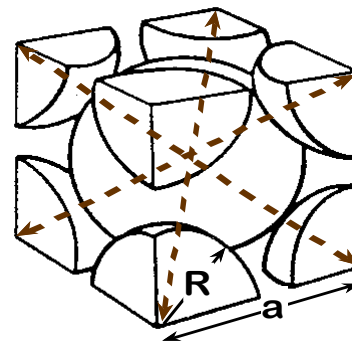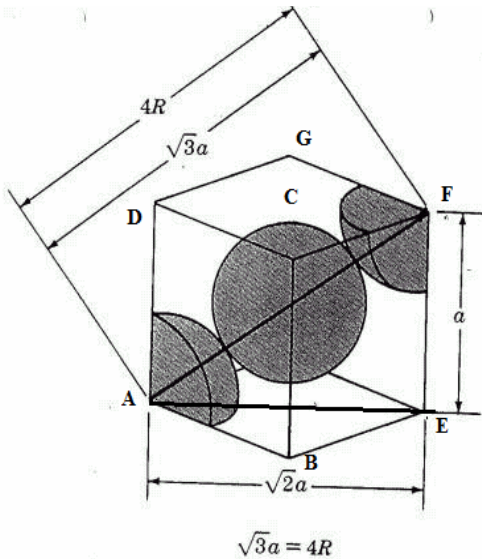
Atomic packing factor of B.C.C:

From $\triangle$ le AEB; AE^2 = $A B^2 + BE^2$

= $a^2 + a^2$

AE^2 = $2a^2$

AE   =   √2a

From △le AEF, AF^2 =AE^2+EF^2

$$(4r)^2 = 2a^2 + a^2$$

$$16r^2 = 3a^2$$

$$a = 4r/\sqrt{3}$$

We know that;

Volume of the unit cell = a^3 = (4r/√3)^3

Volume of the atom in the unit cell =   n.4/3 πr^3

$$= 2 \times 4/3\ \pi r^3$$

Packing factor (p.f):

P.f = 2x4/3 πr^3 /(4r/√3)^3=0.68=68%

Examples- chromium, iron, molybdenum, potassium, sodium, tungsten, vanadium

P.f is 68% and it is not a closely packed structure.

Face-centered cubic structure:

Face-Centered Cubic
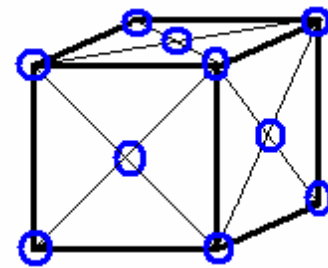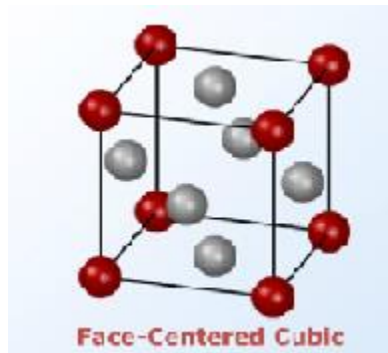
In FCC structure, there are eight corner of the cube occupied by eight atoms, and six atoms occupy the centre of six of the cube atoms

Examples- AL, copper, gold, lead, nickel, platinum, silver.
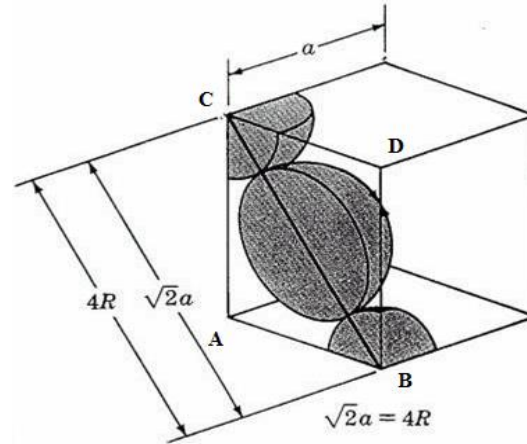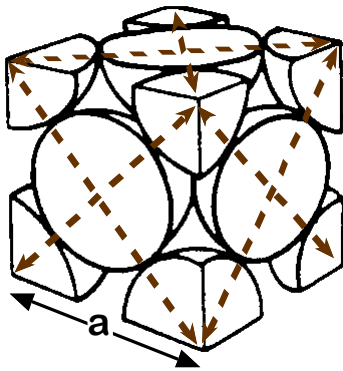
Effective no.of atoms: (n)

In FCC structure effective no.of corner atom is 8x1/8 = 1.

Each face centered atom is shared by two unit cells, there are six faces in a unit cell of cubic structure.

Therefore, the effective face-centered atoms = 1/2x6=3

Thus, effective no.of atoms in FCC unit cell,

n = 1/8x8+1/2x6=1+3=4atoms

Packing factor (p.f):

From $\triangle$le ABC, $AC^2 = AB^2 + BC^2$

$$(4r)^2 = a^2 + a^2$$

$$16r^2 = 2 a^2$$

$$8r^2 = a^2 ; \quad a = 2 \times /\sqrt{2}r$$

We know that;

Volume of the unit cell $= a^3 = (2 \times /\sqrt{2}r)^3$

Volume of the atom in the unit cell $=$ n.4/3 πr^3

$$= 4x4/3 \ \pi r^3$$

Packing factor (p.f):   P.f = Volume of the atom in the unit cell/ Volume of the unit cell

$$= 4x4/3 \ \pi r^3 /(2 \times /\sqrt{2}r)^3$$
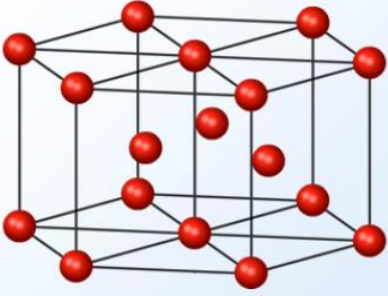
=0.74 or 74%   P.f is high compared to S.C.C and B.C.C

Hexagonal close-packed (HCP) structure:

The atoms in HCP unit cell touch each other.

Since the corner atoms are touching, $a = 2r$

Effective no. of atoms: (n)

There are six corner atoms on both top and bottom layers and each corner atom accounts for 1/6 atom.

Thus contribution from the corner atoms is $2(1/6 \times 6) = 2$.

Also, there are 3 atoms in the middle layer which are not shared by any other unit cell.

The atoms at the center of top and bottom layers one atom $(1/2 \times 2 = 1)$

Thus, effective no. of atoms in HCP unit cell,

$n = 2(1/6 \times 6) + 3 + (1/2 \times 2) = 2 + 3 + 1 = 6$

Packing factor (p.f):

Volume of unit cell can be found by finding out the area of the basal plane and then multiplying this by its height

Area of basal plane is the area ABDEFG.this area is six times the equilateral triangle ABC

Area of $\triangle$ ABC = 1/ 2 x b x h

$\qquad\qquad$ = 1/2 x a x a sin 60^0

$\qquad\qquad$ = 1/2 x a^2 x sin 60^0

Total area of the basal plane = 6 x 1/2 a^2 sin60=3 a^2 sin60^0
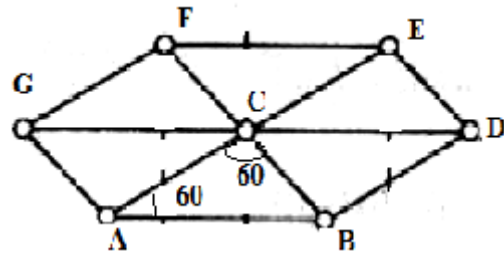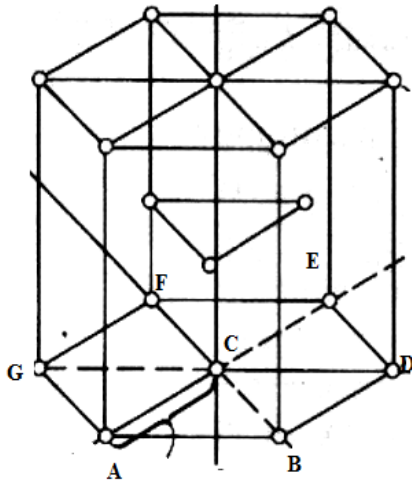
Vol of unit cell   = Area of basal plane x height

$\qquad\qquad$ = 3 a^2 sin60^0 x c

We know;   a = 2r

Vol of atoms in unit cell = n.4/3 πr^3 = 6x4/3 πr^3

Packing factor (p.f):= Volume of the atom in the unit cell/ Volume of the unit cell

$\qquad\qquad$ = 6x4/3 π $(a/2)^3$ /3a^2sin60xc

$\qquad\qquad$ = π a /3xc xsin60^0

The c/a ratio for ideal H.C.P crystal structure is 1.633

$\qquad\qquad$ = π /3x1.633 xsin60^0 =0.74 or 74%

Examples - cadmium, zinc, magnesium, cobalt, zirconium, titanium, beryllium.

P.f is 74% and hence it is closely packed structure.

CRYSTALLIZATION OF METALS

➢ Crystallization or solidification is the process of transition from the liquid state. When the molten metal is cooled, the whole mass does not solidify instantaneously.

It comprises two steps

1. Nucleation (the formation of stable nuclei in the melt)

2. Grain or crystal growth (the growth of nuclei into crystal and the formation of the grain structure.)
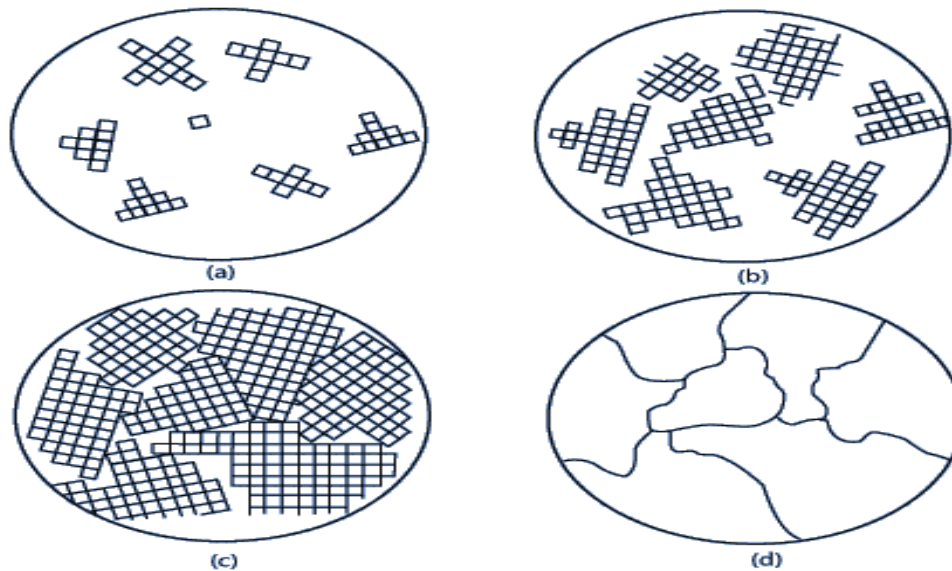
GRAIN

Solidified metal containing many crystals is called polycrystalline metals. The crystals in polycrystalline metals are of irregular shape and are called grains.

GRAIN BOUNDARIES

A **grain boundary** is the interface between two grains, or crystallites, in a polycrystalline material

Or

A grain boundary may be defined as the region b/w two adjacent grains

The grain size expressed in terms of number of grains per unit area or volume

Factors affecting grain size

- Size of grain depends on rate of nucleation and rate of crystal growth
- The combination of high rate of nucleation (N) with a slow rate of crystal growth (G) yields fine grains this combination can be achieved due to rapid cooling
- At faster rate of cooling a large no of grains are nucleated and there is less time for them to grow
- A high value of (G) and low value of (N) coarse grains are formed this combination can be achieves in slow rate of cooling
- Besides the rate of cooling and rate of nucleation the grain size also depends on the temperature of liquid metal, the chemical composition and the impurities present there in
- When the grain size is small the structure of the metal is known as "**fine grained structure**"
- When the grain size is large the structure of the metal is known as "**coarse grained structure**"
-

Effect of grain size on properties:

- The grain size of the metal strongly effects its mechanical properties
- Metals and alloys are stronger if the grain size is reduced there fore every effort is made to produce structure with fine grains
- Metals with fine grain structure possess high strength and hardness also they possesses high fatigue strength and toughness (i.e, resistance to impact).
- Metals with coarse grain structure possesses less tough and less hard but exhibit better creep resistance
- Coarse grain structure gives high ductility good machinability and formability but decrease the hardenability

> The relationship between the yield strength of the metal and the grain size is given by
> Hall-Petch equation, which is

$$\sigma_{yield} = \sigma_{0yield} + \frac{k}{\sqrt{d}}$$
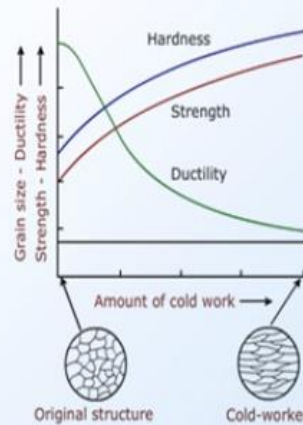
Effect of Grain Boundaries on the
Properties of Metal/Alloys

GRAIN SIZE DETERMINATION

Three basic methods has recomondded by ASTM (AMERICAN STANDARD TESTING AND MATERIALS)

1. Comparison method

2. Heyn method or intercept method

3. Planimetric method or Jeffries method

1. **Comparison method:-**

In this method the grain size is measured by comparison under a magnification of 100X(after etching)with standard grain size AS

> The ASTM grain-size number n is related to N, the number of grains per square inch at a
> magnification of 100x by the relationship $N^* = 2^{n-1}$

Where   N = no of grains per inch square at a magnification of 100 X
            n=ASTM grain size number

2. **Heyn method or intercept method :**

Grain size may be estimated by using an intercept method, described below:

- Straight lines, all of the same length are drawn through several photomicrographs that shoe the grain structure.

- The grains intersected by each line segment are counted.

- The line length is then divided by an average of no.of grains intersected, taken over all the line segments.

- The average grain diameter is found by dividing this result by the linear magnifications of the photomicrographs.

  To each assigned a number, the smaller the grains.

  A specimen must be properly of 100x.

  Grain size is expressed as the grain size no of the chart that most nearly matches the grains in the micrograph.

  Thus, a relatively simple and convenient visual determination of grain size number is possible.

  Grain size number is used extensively in the specification of steels.

IMPERFECTIONS IN CRYSTALS

The perfectly regular crystal structures that have been considered upto now are called ideal crystals in which atoms are arranged in a regular way.

In actual crystals, however, imperfections or defects are always present and their nature and effects are very important in understanding the properties of crystals.

These imperfections affect the properties of crystals such as mechanical strength, chemical reactions, electrical properties etc. to a great extent.

Crystal defects are classified as :

- Point defects or zero dimensional defect

- Line defects or one dimensional defect

- Surface defects or two dimensional defect

- Volume defect

1. Point defects:

Point defects are imperfect point like regions in a crystal. The size of a point defect is one or two atomic diameters.

These defects are completely local in effect, e.g.,a vacant lattice.

Point imperfections are always present in crystals and their presence results in a decrease in the free energy.

The point defects may created as follows:

- By thermal fluctuations

- By quenching (quick cooling) from a higher temperature

- By severe deformation of the crystal lattice; e.g., by hammering or rolling.

The various point defects are discussed as below:

1. **Vacancy**

   A vacancy is the simplest point defect and involves a missing atom within a metal. These defects may come up as result of imperfect packing during the original crystallization.

   They may also arise from the thermal vibrations of the atoms at high temperatures.

2. **Schottky imperfections**

   These are closely related to vacancies but are found in compounds with must maintain a charge balance.

   In schottky defect the removal of positive ion must be counter balanced by the removal of negative ion in order to maintain neutrality.

   The pair of vacancies caused by removal of positive ion and negative ion is called schottky defect.

3. **Interstitialcy**

   It is formed when an extra atom is inserted into the lattice at a normally unoccupied site. This results in atomic distortion.

   The foreign atom may form added alloying agent or simply an impurity.

   The vacancy and interstitialcy are therefore, inverse phenomena.

4. **Frenkel defect**

   If a ion displaced from the normal lattice point to an interstial site, then the defect is known as frankel defect.

The interstitials and frankel defects are less in number than vacancies and schottky defects, because additional energy is required to force the atom into the new position.

Point Defects
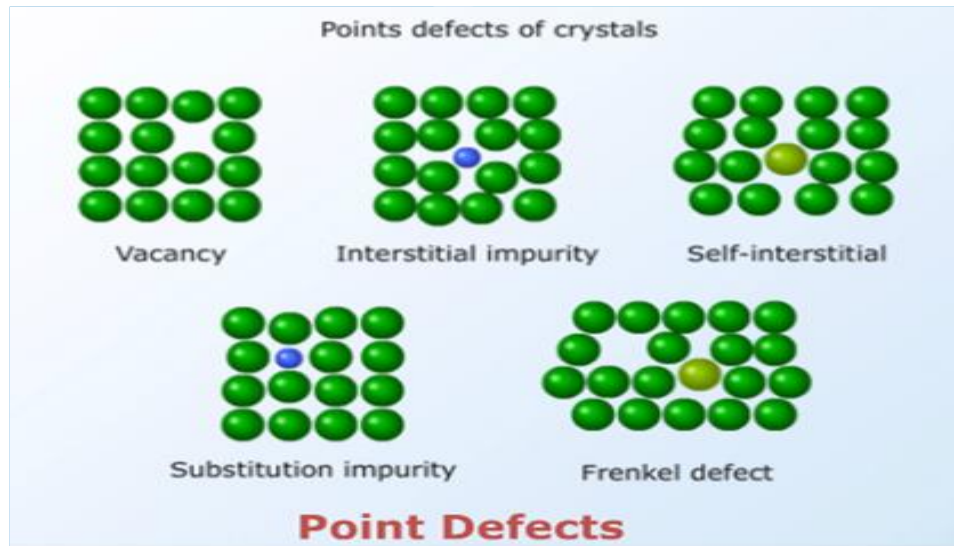
2. Line defects:

- ➤ A linear disturbance of the atomic arrangement, which can move very easily on the slip plane through the crystal is known as dislocation.
- ➤ This dislocation may be caused during growth of crystal form a melt or form a vapour or they may occur during a slip.
- ➤ This defect is created along a line which is also the boundary between the slipped and unslipped regions of the crystal. This defect is common called a "dislocation" and the boundary as the "dislocation line".

Types of dislocations are:

- • Edge dislocation (or taylor-orowan dislocation)
- • Screw dislocation

1. Edge dislocation

- • An edge dislocation may be described as an extra plane of atoms within a crystal structure. It is accompanied by zones of compression and tension so that there is a net increase in energy along a dislocation.
- • The displacement distance for atoms around the dislocation is called the "BURGER VECTOR"(b). This vector is at right angle to the edge dislocation.
- • In case of edge dislocation this vector is perpendicular to the dislocation line

2. Screw dislocation

➤ In screw dislocation the atoms are displaced in two separate planes perpendicular to each other.

➤ The lattice points trace a helical path around the dislocation, therefore it is called "screw dislocation".

➤ A screw dislocation has its displacements of burger's vector parallel to the linear defect but there is a distortion of the plane.

➤ The displacements of the atoms from their original position in the crystal is described by the equation:

➤ $r = b\theta/2\pi$ (spiral ramp)

   ▪ where, r= the displacement along the dislocation line,

➤ θ = the angle measured from some axis perpendicular to the dislocation line.

➤ The following dislocation of a screw dislocation are of great importance:

➤ Plastic deformation is possible under low stress, without breaking the continuity of the lattice.

➤ The force required to form and move a screw dislocation is probably somewhat greater than that required to initiate an edge dislocation.

➤ Screw dislocation causes distortion of a considerable distance from the centre of the line and takes the form of spiral distortion of the planes.

➤ Dislocation of both types (combinations of edge and screw) are closely associated with crystallization as well as deformation

(a)   (b)
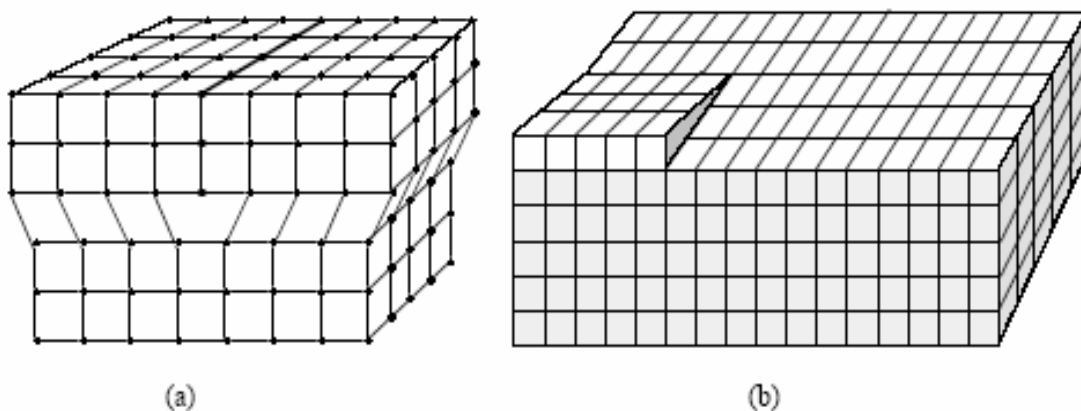
Line defects. (a) Edge dislocation. (b) Screw dislocation.

3. Surface defects:

Surface defects are the two dimensional regions in a crystal. They arise from a change in the stacking of atomic planes on across a boundary.

They are the following two types:

- External defects
- Internal defects

1. **External defects**

   - The external type is just what its name implies, the defects or imperfections represented by a boundary.

   - The external surface of the material is an imperfection itself, because the atomic bonds do not extend beyond it.

   - The surface atoms have neighbours on one side only, while the atoms inside the crystal have neighbours on either side of them.

   - Since these surface atoms are not entirely surrounded by others, they possess higher energy than those of internal atoms.

2. **Internal defects**

   a) Grain boundaries:

   - Grain boundary is a narrow region between two grains of about two to few atomic diameters in width, and is the region of atomic mismatch between adjacent grains.

   - Atoms are arranged less regularly at the grain boundary. This produce less efficient packing of the atoms at the boundary.

   - Thus the atoms along the grain boundary have a higher energy than those within the grains.

   - If the orientation between two neighbouring grains is less than 10^0, then it is called low angle boundary or tilt boundary. In general low angle boundary may be regarded as an array of dislocations.

   - If the mismatch is more than $10\text{-}15^0$, the grain boundary is known as high angle grain boundary.
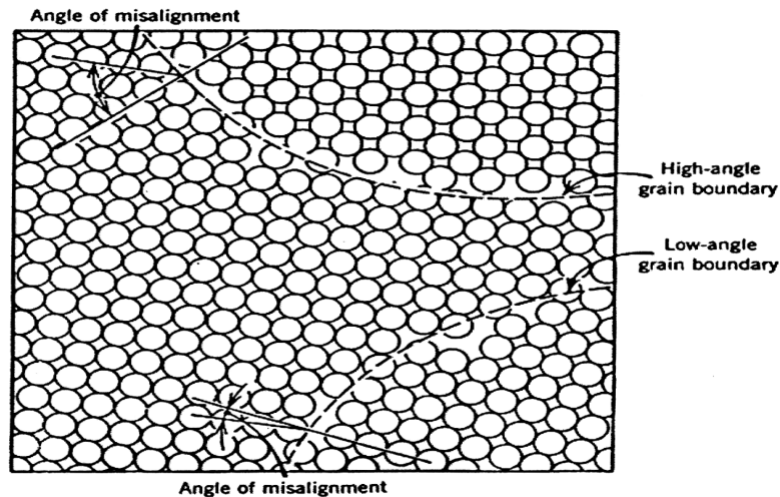
At the grain boundary, there is a disturbance in the atomic packing.

b) Tilt boundary:

- The simplest grain boundary consists of a configuration of edge dislocations between two grains.

- The misfit in the orientation of the two grains (one on each side of the boundary) is accommodated by a perturbation of the regular arrangement of crystals in the boundary region.

- Fig shows some vertical atomic planes termination in the boundary and each termination is represented by an edge dislocation.
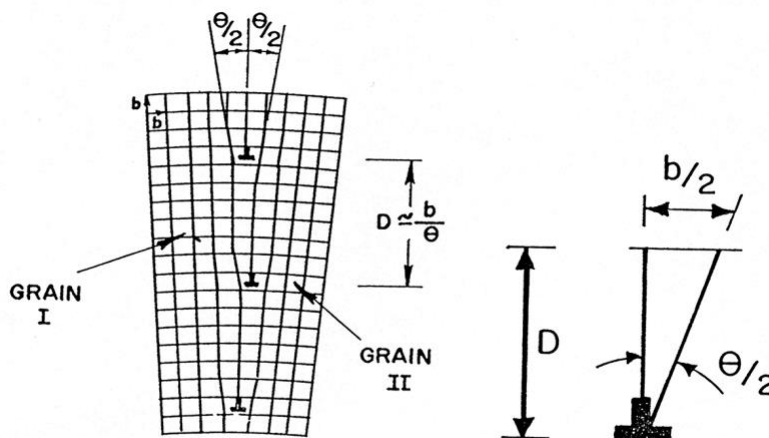
Low-angle tilt boundary

- The mis-orientation at the boundary is related to spacing between dislocations, D, by the following relation:

$$D = \frac{b}{2\sin\left(\dfrac{\theta}{2}\right)} \approx \frac{b}{\theta}$$

for q very small)

where b is the Burgers vector.

- As the mis-orientation q increases, the spacing between dislocations is reduced, until, at large angles, the description of the boundary in terms of simple dislocation arrangements does not make sense.

- For such a case, θ becomes so large that the dislocations are separated by one or two atomic spacing;

  - the dislocation core energy becomes important and the linear elasticity does not hold.

  - Therefore, the grain boundary becomes a region of severe localized disorder.

- Boundaries consisting entirely of edge dislocations are called tilt boundaries, because the misorientation

c) Twist (twin boundary)

- A boundary consisting entirely of **screw dislocations** is called **twist boundary**, because the misorientation can be described by a relative rotation of two grains about an axis.

- It is possible to produce misorientations between grains by combined tilt and twist boundaries. In such a case, the grain boundary structure will consist of a network of edge and screw dislocations.
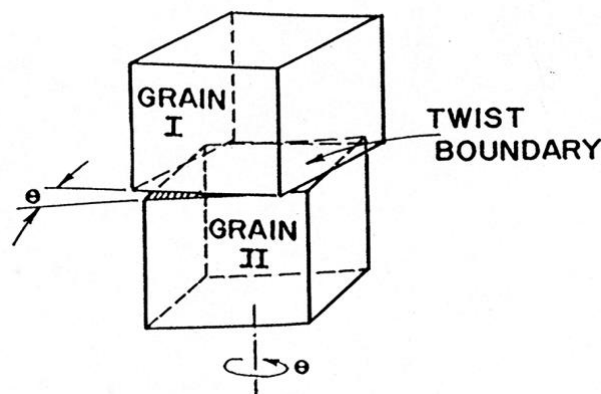
Low angle twist boundary

Twin Boundary: when the boundaries in which the atomic arrangement on one side of the boundary is some what mirror image of the arrangement of atoms of other side, the defect is known twin boundary
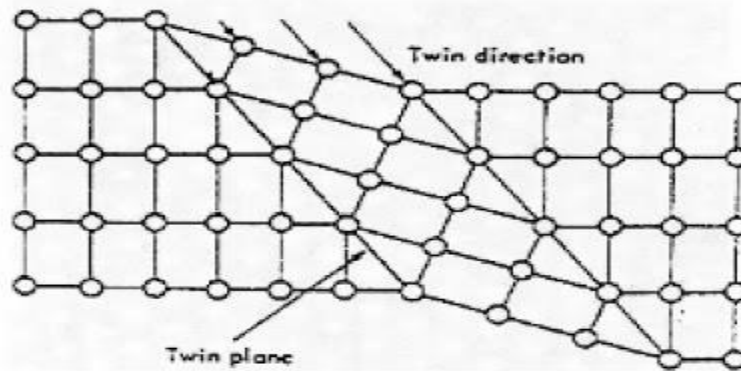
4. volume defects:

- the volume defects are caused due to coglomarations of vacancies in a small region within crystal or the presence of foreign atoms large sizes compared on atomic scale.

- The accumulation of vacancies produces voids, while the foreign atoms produce dissymmetry within crystals.

- These defects effects properties of metal.

- Bulk or volume defects are normally introduced during processing processing and fabrication steps.

THEORY OF DISLOCATION

- Dislocations are defined as the irregularities in the structure of metals.

- These arise from misplacement of bonds the atoms in a part of the plane of a crystal and are considered to be weak centres.

- They are instrumental in affecting the breaking stress and plastic and chemical properties of crystals.

- It is believed that dislocations originate mainly when a crystal is stressed, but some may be produced during the solidification of the metal, due to impurity atoms and thermal vibrations.

- In good crystals the normal density of dislocation lines is around $10^8/cm^2$ where as in deformed crystals it may be as high as $10^2/cm^2$.

IMPORTANT TERMS

System: A part of the universe under study is called system.

Phase: Phase is a homogeneous, physically distinct and mechanically separable part of the system under study.

Component: Pure metal of which the alloy is composed.

Solubiity limit:Maximum concentration of solute that can dissolve in solvent

Variable: A particular phase exists under various conditions of temperature, pressure and concentration. These parameters are called as the variables of the phase.

Component: The elements present in the system are called as components.

Example- Cu-Al system contains compounds CuAl and CuAl$_2$ and therefore, all compositions can be expressed by the molecular species of Cu and Al and hence it is two component system i.e. binary system.

Alloy:

Alloy is mixture of two or more elements having metallic properties. The element present in the largest proportions is a metal and others can be metals or non-metals.

The element which is present in the largest amount is called as the base metal or parent metal or solvent and other elements are called as alloying elements or solute.

Constitution:
- The constitution of an alloy is described by
  - the phases present
  - the weight fraction of each phase
  - the composition of each phase
- The equilibrium constitution is when the alloy has no further tendency to change at a given temperature and pressure

ALLOYING ELEMENTS

The elements deliberately added to the steel in order to modify its properties are called alloying elements.

Classification of alloying elements:

1. Based on their relation with carbon, alloying elements may classified as:

   o Graphitizing elements – silicon, nickel, copper and aluminium.

      These elements may cause the breakdown of cementile and lead to the presence of graphite in the alloy. This result is a decrease in the strength and hardness.

   o Carbide forming elements – manganese, chromium, molybdenum, tungsten, etc.

      These elements may form stable, hard carbides, and if they are in appropriate form (fine carbide particles) increases the strength and hardness

   o Neutral elements – cobalt

      These elements neither form carbides nor causes graphitization.

2. Based on their effect on critical points, alloying elements may be classified as:

   o Austenite stabilizers – nickel, copper, manganese, cobalt

      They arise A_4 point and lower A_3 point. Thus they increase the range of stability of austenite.

   o Ferrite stabilizers – chromium, molybdenum, vanadium

      They lowers A_4 point and rise A_3 point. Thus they increase the range of stability of ferrite.

Necessity of alloying:

Alloying elements are added to achieve the properties suitable for service conditions. The reasons for alloying may be one or more of the following.

- To improve the hardness and wear resistance.

- To improve corrosion resistance.

- To improve magnetic and electrical properties.

- To improve strength and toughness.

- To improve machinability, weldability, hardenability.

- To retain properties at elevated temperature.

-

SOLID SOLUTION

A solid solution is formed when two metals are completely soluble in solid state and also completely soluble in liquid state.

In other words, when homogeneous mixture of two or more kinds of atoms (metals) occur in the solid state, they are known as a solid solutions.
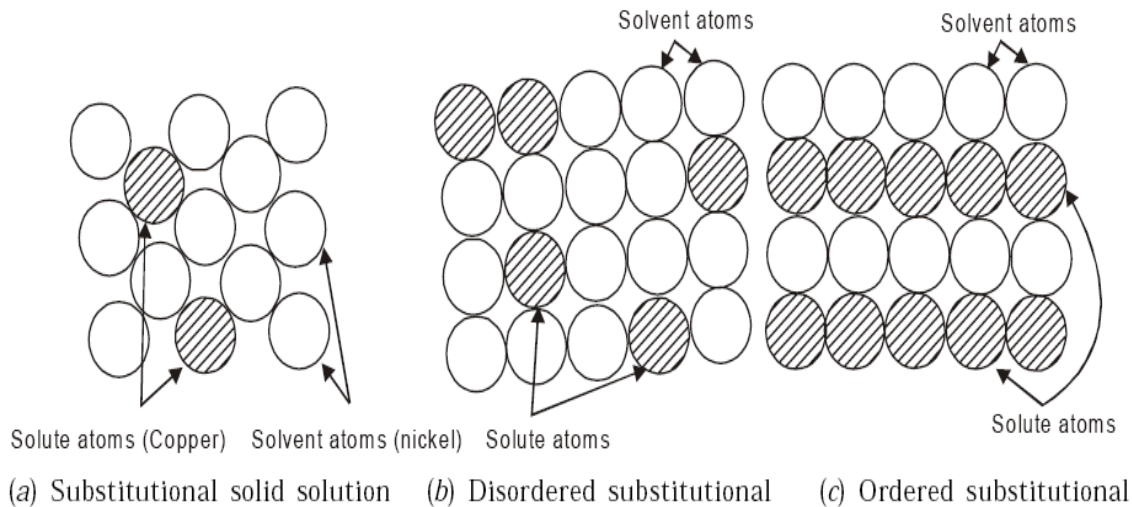
Types of solid solution:

- o Substitutional solid solution

- o Interstitial solid solution

- **Substitutional solid solution:**

  - o it means the atoms of B element i.e solute are substituted at the atomic sizes of A element i.e solvent.

  - o Depending up on the distribution of B atoms in A, Substitutional solid solutions are classified into two types

    - Regular or ordered

    - Random or disordered

    In regular solid solution, the substitution of B atoms in A by a definite order.

    While there is no definite order or regularity in random solid solution.

  - o Au-Cu solid solution shows ordered structure upto 400^0C and disordered structure at high temperature.

  - o Complete regularity through the structure is possible only when two metals are mixed in some proportion like 1:1, 3:1 etc.

  - o Substitutional solid solution formation is favored if the atomic sizes of two metals are nearly equal.

  - o Ordered substitutional solid solution alloys in general are hard and require more energy for plastic deformation than disordered substitutional solid solution alloys.

Solvent atoms   Solvent atoms

Solute atoms (Copper)   Solvent atoms (nickel)   Solute atoms

Solute atoms

(a) Substitutional solid solution   (b) Disordered substitutional   (c) Ordered substitutional

- **Interstitutional solid solution:**

  o In inter solid solutions; the atoms of B occupy the interstitial sites of A.

  o This type of solid solution formation is favored when the atomic size of B is very much small as compared to the atomic size of A.

  o The elements which can form interstitial solid solution with iron are carbon, boron, oxygen, hydrogen, nitrogen.

Solvent atoms (iron)   Solute atoms
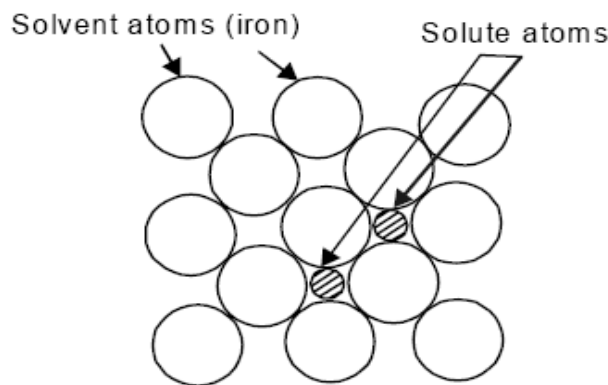
- **Properties of solid solution**

  o Soft

  o Ductile

  o Malleable

- **Advantages of solid solution**

- o Easily cold rolled

- o Pressed or worked

HUME-ROTHERY'S RULES OF SOLID SOLUBILITY

In formation of solid solutions, the solubility limit of solute in the solvent is governed by certain factors. These factors are known as hume-rothery rules of solid solubility. They are as below:

- **Atomic size factor:**

  - o If the atomic sizes of solute and solvent differ by less than 15%, it is said to have a favorable size factor for solid solution formation.

  - o If the atomic size difference exceeds 15%, solid solubility is limited.

- **Chemical affinity factor:**

  - o The greater the chemical affinity of two metals, the more restricted is their solid solubility and greater is the tendency of formation of a compound.

- **Relative valency factor:**

  - o A metal of higher valency can dissolve only a small amount of a lower valency metal.

  - o While the lower valency metal may have good solubility for the higher valency metal.

- **Crystal structure factor:**

  - o Metals having same crystal structure will have greater solubility.

  - o Differences in crystal structure limit the solid solubility.

For continuous solid solubility, atomic size difference should preferably be less than 8% with other factors favorable.

INTERMEDIATE ALLOY PHASES AND ELECTRON COMPOUNDS

- When an alloying element (solute) is added to a given metal (solvent) in such an amount that the limit of solid solubility exceed, a second phase appears with the solid solution.

- This second phase may be another solid solution or an intermediate phase.

- These intermediate phases differ in composition as well as crystal structure from the parent metals and hence their properties also different.

- These phases may have narrow or wide ranges of homogeneity and may or may not have simple chemical formula.

- Some intermediate phases have a fixed composition and they are called intermetallic compounds

- In general intermetallic compounds are hard, brittle and have high melting points.

- The intermediate phases in which the ratio of number of free electrons to the number of atoms is constant are called **electron compounds** and they exhibit similar characteristics.

- Intermediate phases exhibit order-disorder transformation.

    Example- β brass in Cu-Zn alloy system is disorder between 453 and 470^0C and order at a lower temperature.

Equilibrium of Diagrams

Introduction

➤ Equilibrium is the state achieved in an allotted sufficient time

➤ Sometimes, the time in which this equilibrium is achieved might get to be so long (the kinetics can be slow) that a state along the path to the equilibrium may seem to be stable. This is called a metastable state

Importance and Objectives:

➤ It provides the knowledge of phase composition and phase stability as a function of temperature, pressure and composition

➤ It presents the phase existed at a glance of equilibrium conditions of temperature and composition of the alloy

Classification of Equilibrium Diagrams

Unary Phase Diagram

➢ It is a one component phase diagram

➢ Pressure is plotted on the vertical axis and temperature on the horizontal axis as shown in image
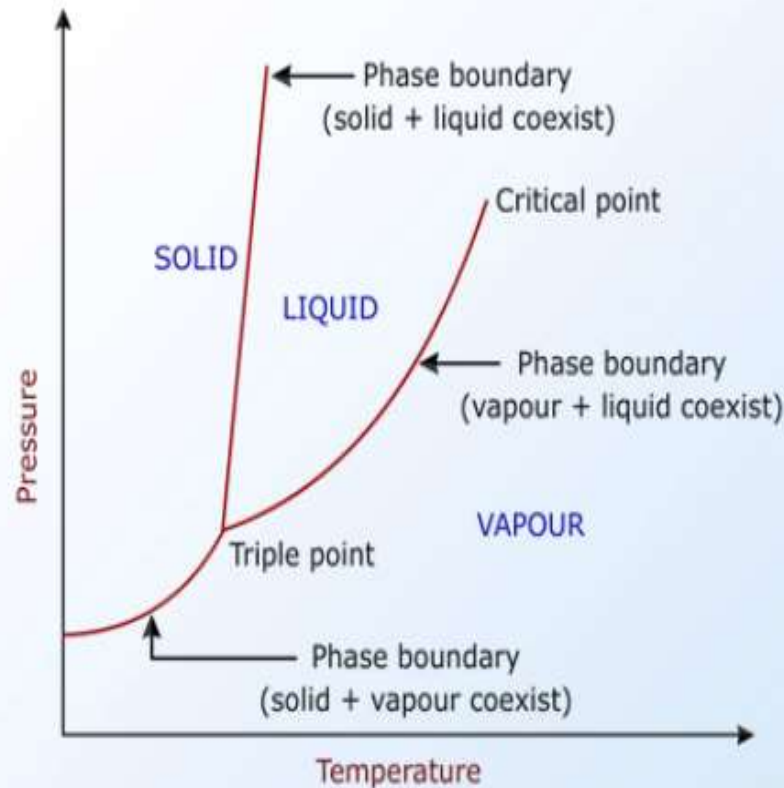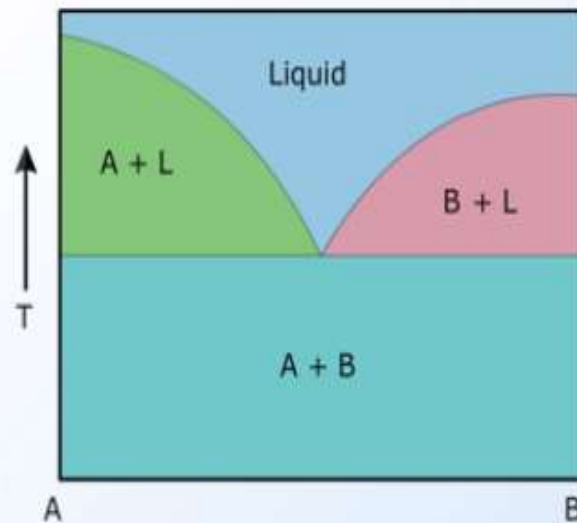

Pressure-Temperature Diagram for Water

Classification of Equilibrium Diagrams

Binary Phase Diagram

➤ It is a two component phase diagram

- Pressure (P)

- Temperature (T)

- Compositional changes (X) on a 2d diagram


Example:

Diopside - Anorthite

Albite - Quartz

Simple Eutectic, No SS

Classification of Equilibrium Diagrams

Ternary Phase Diagram

➢ In most cases, real materials are combination of different elements instead of pure substances. Besides temperature and pressure, composition is also a variable

➢ Phase diagrams for materials with more than two components are complex and difficult to represent
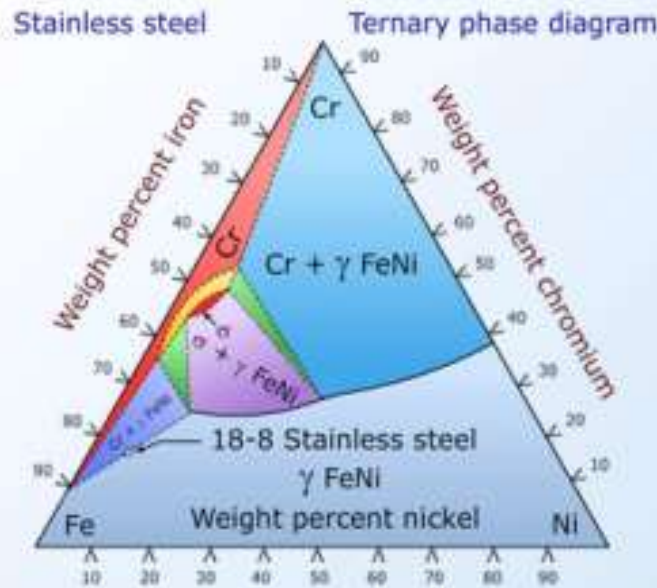
Ternary Phase Diagram

Construction of Equilibrium Diagrams

Metallographic Methods

> This method is practiced by heating samples of an alloy to different temperatures, awaiting the establishment of equilibrium, and then rapidly cooling to restore their structure (structure during high-temperature)

> The samples are then examined microscopically

> The rapidly cooled metals do not always retain their high-temperature structure

Gibbs' Phase Rule

Statement:

➤ The interconnection of the number of degrees of freedom, the number of components and the number of phases is given by the phase rule

➤ The following relation must be satisfied for all the metals under equilibrium conditions,
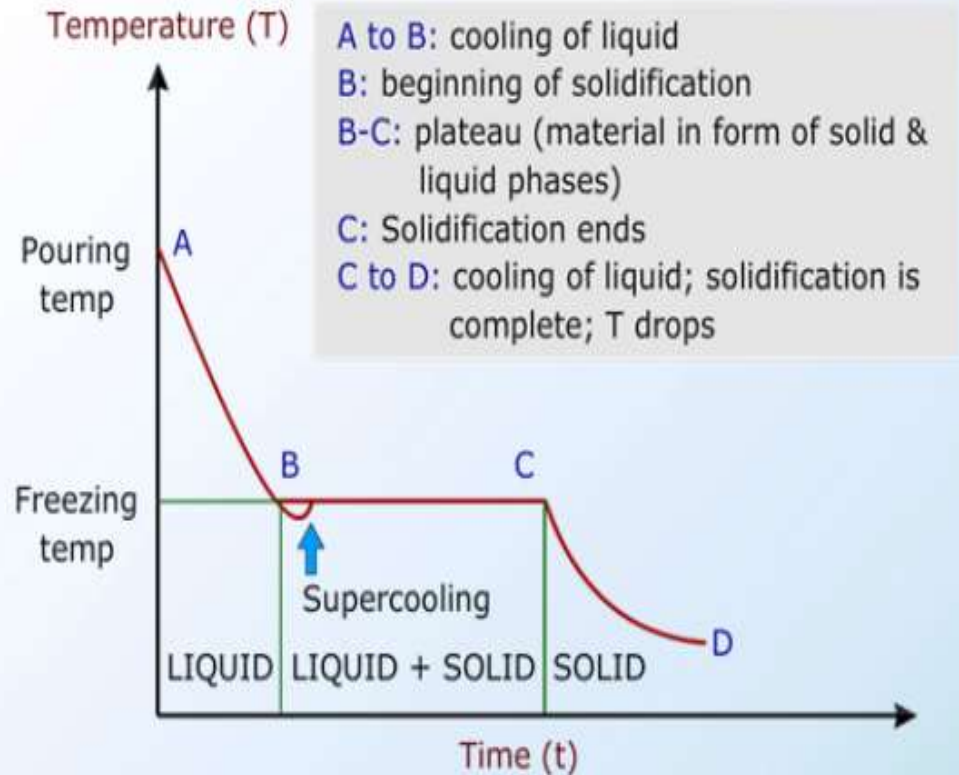
$$P + F = C + n$$

Solidification of a Pure Metal

➤ Solidification occurs by the nucleation and growth of crystals in the melt

➤ Nucleus is the small cluster of atoms having the right crystalline arrangement

➤ At any temperature below the melting point, a nucleus has to be of a certain minimum size, called the critical size

➤ When the temperature is lowered, the vibrations of the atoms gradually decreases, increasing the chances of survival of small clusters. Therefore, the critical size of the nucleus decreases with decreasing temperature

Cooling Curve of a Pure Metal

➤ Plotting a cooling curve for a pure metal will exhibit a horizontal line at its melting or freezing temperatures

➤ Between A and B, the metal exists in a "liquid" state

➤ Freezing starts at B and completes at C. Between B and C the metal is in the "liquid + solid" state

➤ Below the point C the metal is in "Solid" state

A to B: cooling of liquid
B: beginning of solidification
B-C: plateau (material in form of solid & liquid phases)
C: Solidification ends
C to D: cooling of liquid; solidification is complete; T drops

Cooling Curve of a Pure Metal

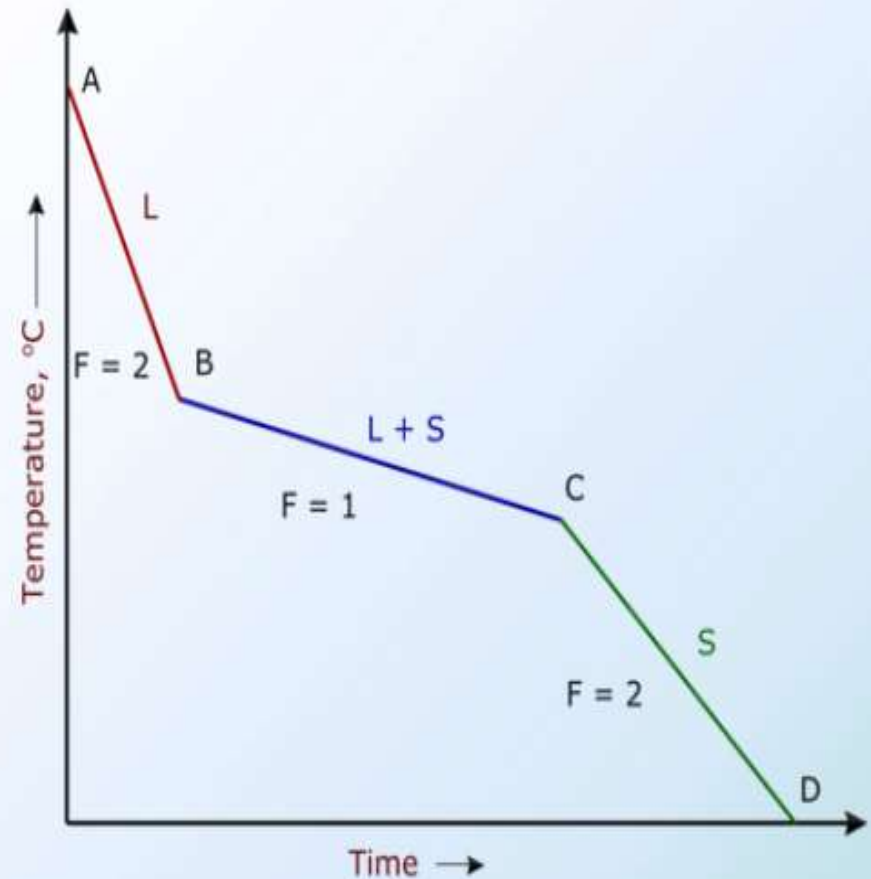# Construction of Equilibrium Diagrams

X-ray Diffraction Technique

➤ This method is practiced by measuring the lattice dimensions and representing the appearance of a new phase, either by change observed in lattice dimension or by the advent of a latest crystal structure

Thermal Analysis

➤ By constructing a cooling diagram for each amalgam, the temperature change in the initial and final phase is determined

➤ Phase diagrams are constructed by using these measured temperatures

Cooling Curve of a Solid Solution

- A solution in solid state consisting of the combination of two types of atoms in one space lattice form is called a solid solution

- A solute is the minimal part of the solution or the metal that is dissolved

- During the solidification of the solution, the temperature may not be equal to freezing point of the pure solvent

Cooling Curve of a Solid Solution

Thermal Analysis Method

> Most common method used for construction of equilibrium or phase diagrams is the 'Thermal Analysis Method'

Step 1: Prepare large number of alloys of varying compositions.

Step 2: Plot curves of the above materials as shown in image.

Step 3: Transfer these temperatures to a 'Temperature Vs. Composition' graph as shown in the image.

Step 4: Draw smooth curves through the points L_1, L_2, L_3, L_4, ..., L_{10}, L_{11}, and S_1, S_2, S_3, S_4, ..., S_{10}, S_{11} respectively which represents the liquid us and solidus temperature diagrams as shown in image

.

Thermal Analysis Method

➤ At any temperature T, the average composition of the existing liquid is given by the point X and average composition of the existing solid is given by the point Y as shown in image
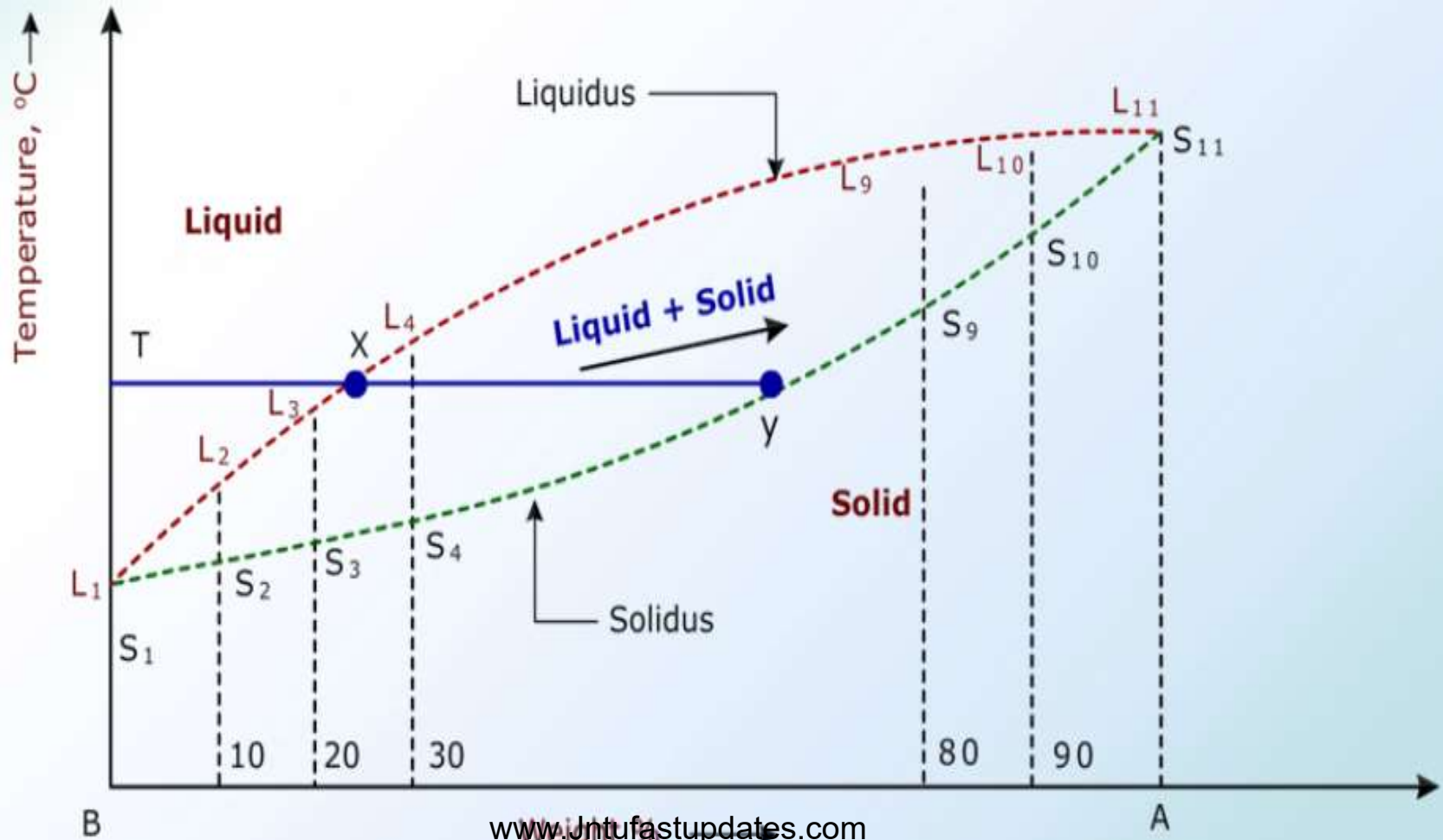
Lever Rule

> Lever rule is used for finding the amounts of phases existing in a binary system for a given alloy at any temperature under consideration
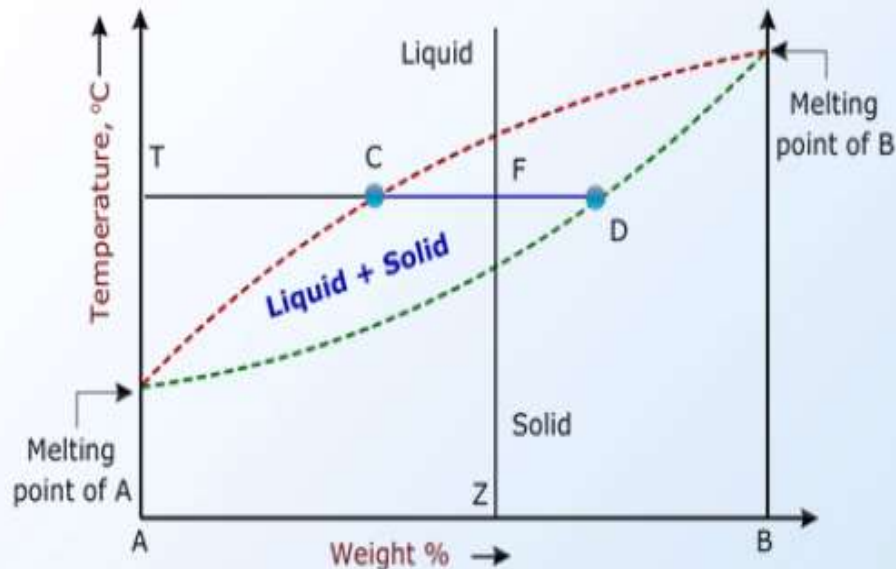
| The amount of B in the alloy | = | The amount of B in the solid | + | The amount of B in the liquid |

(Amount of solid) x (Its lever Arm) = (Amount of liquid) x (Its lever Arm)

Common Types of Phase Diagrams

➤ The most common types of phase diagrams are:

- Isomorphous Systems

- Eutectic Systems

- Partial Eutectic Systems

- Layer Type Systems

Properties of Alloys

Specific Heat and Coefficient of Thermal Expansion:

➤ These properties of alloys are governed by the law of mixtures.

Melting point:

➤ Greater the difference in valencies between the metals of alloys, the wider is the melting range.

Boiling point:

➤ Boiling point (like melting point) is transformed into a boiling range by the adding alloying element.

Isomorphous Systems

➢ The main conditions for complete solubility in the solid state are:

- Two components should have the same crystal structure
- Size of the atoms should be very similar

➢ Let us consider the solidification of the alloy containing 60% of metal B
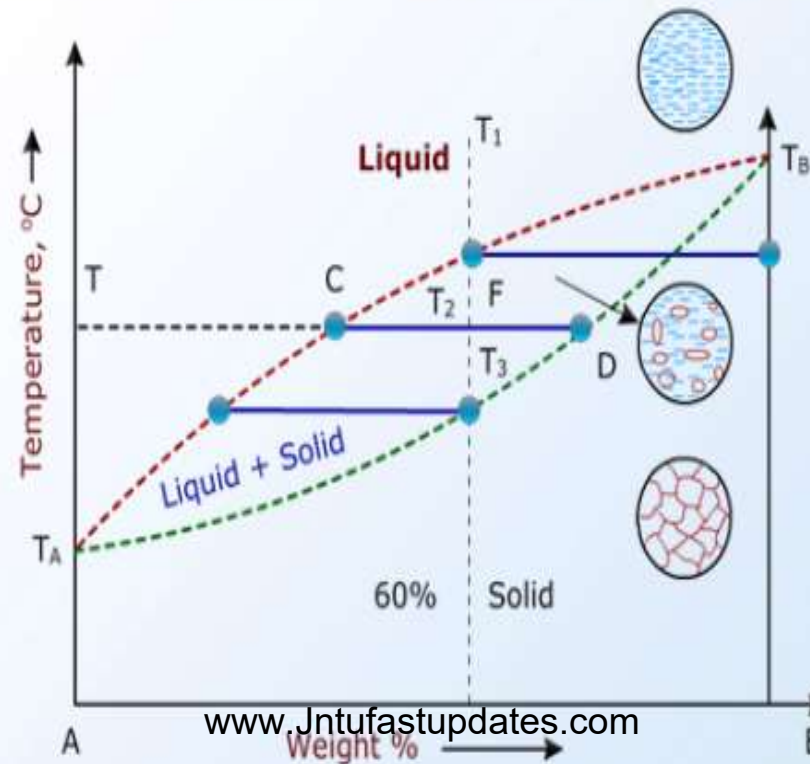
Isomorphous Systems

➢ Freezing starts at the temperature T_1. Here, the first crystal of the solid solution of metals A and B separate from the liquid alloy

➢ In liquid phase at equilibrium, the concentration of the solid solution is determined by the point of crossing of a horizontal line which passes through the specified temperature with the solidus

Copper-Nickel Phase Diagram

➤ Lever rule is employed for finding out the amounts of phases existing in a binary system for a given Cu-Ni alloy at any temperature
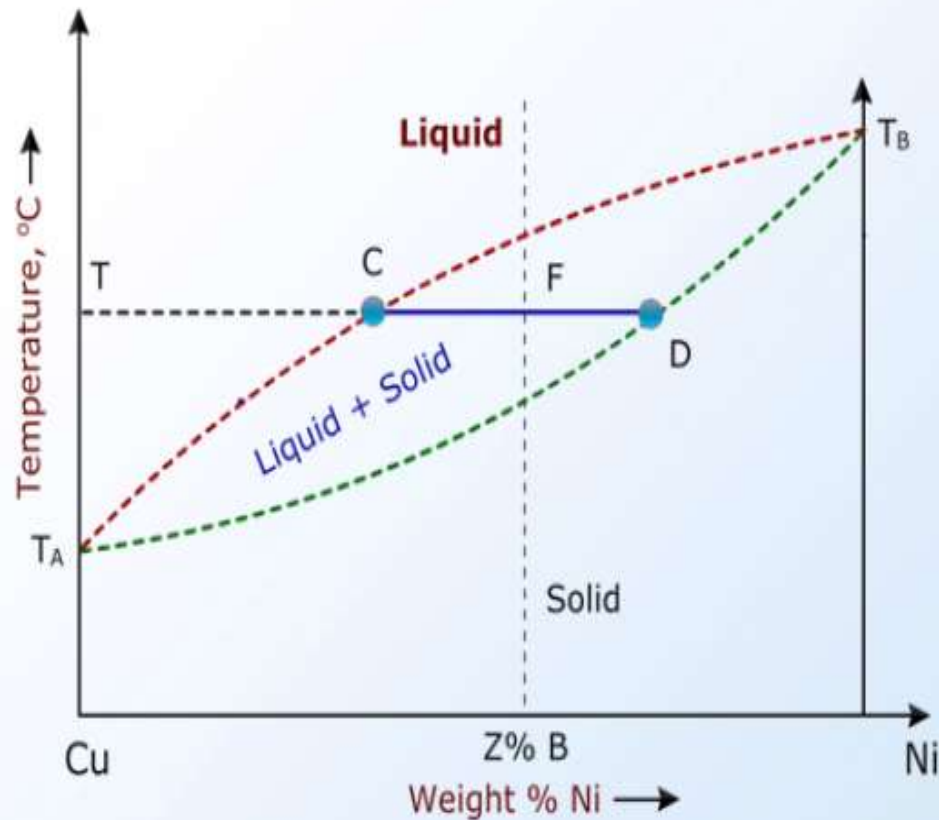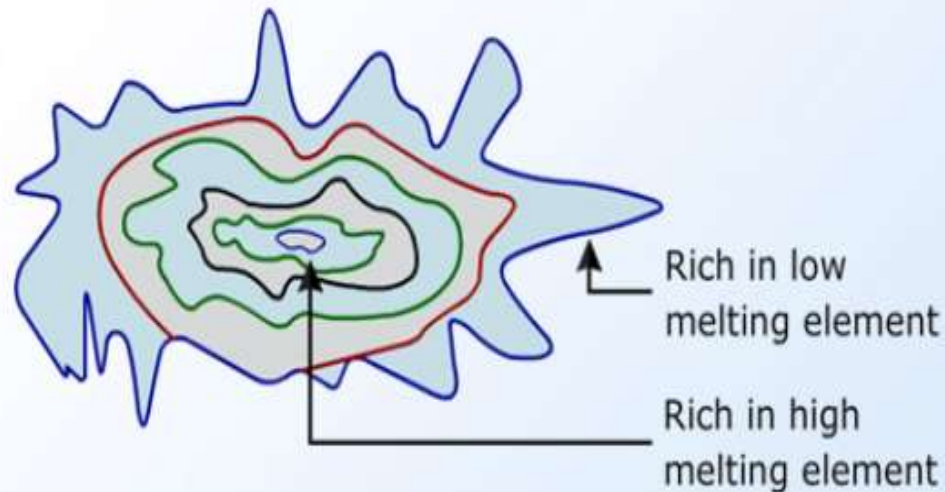

Cu-Ni Phase Diagram

Coring

> Variation in composition observed from point to point or centre to surface of a grain or dendrite (micro-segregation) in a solidified alloy at room temperature is called coring.

Rich in low melting element

Rich in high melting element

**Cored dendrite**

Transformation in Solid State Allotropy

Transformations in the Solid State

➤ There are several equilibrium changes and reactions which take place entirely in the solid state. They are known as Transformations in the Solid State.

Allotropy Change

➤ Allotropy is defined as the property of chemical elements to exist in two or more different forms. Allotropy change exists in dual or polycrystalline structures (based upon their temperature)
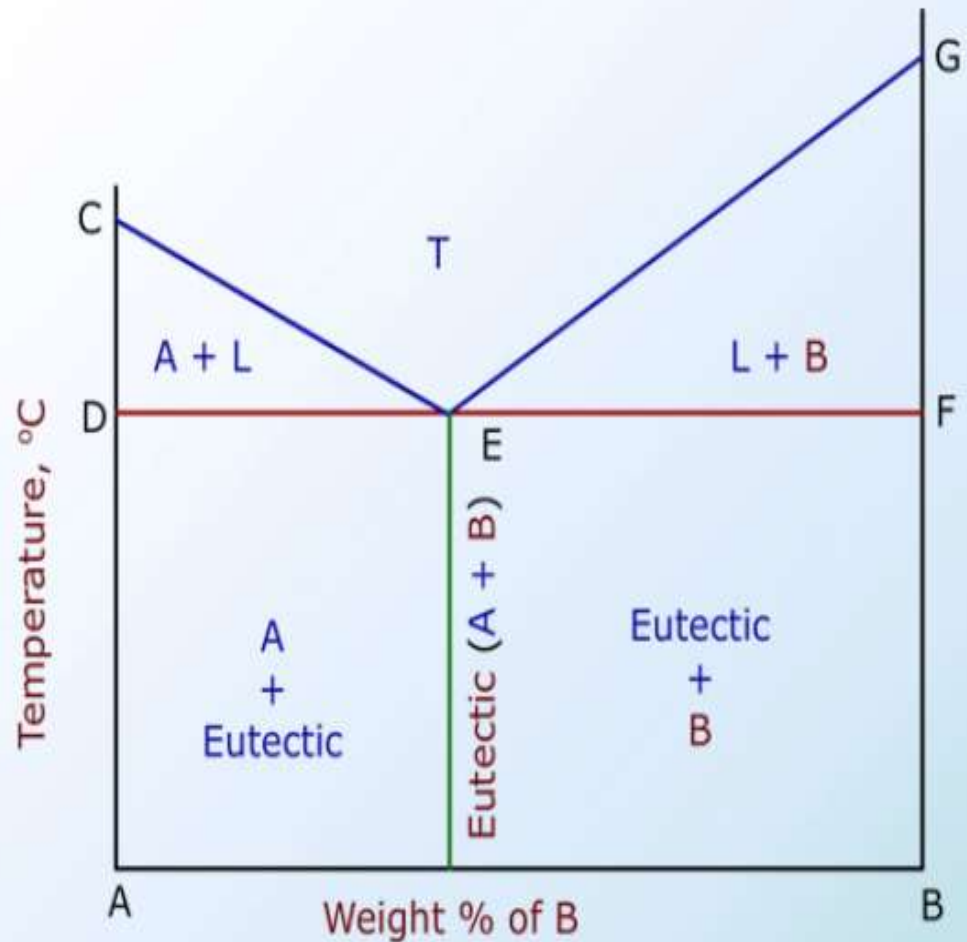
Examples are Iron, manganese, cobalt and tin
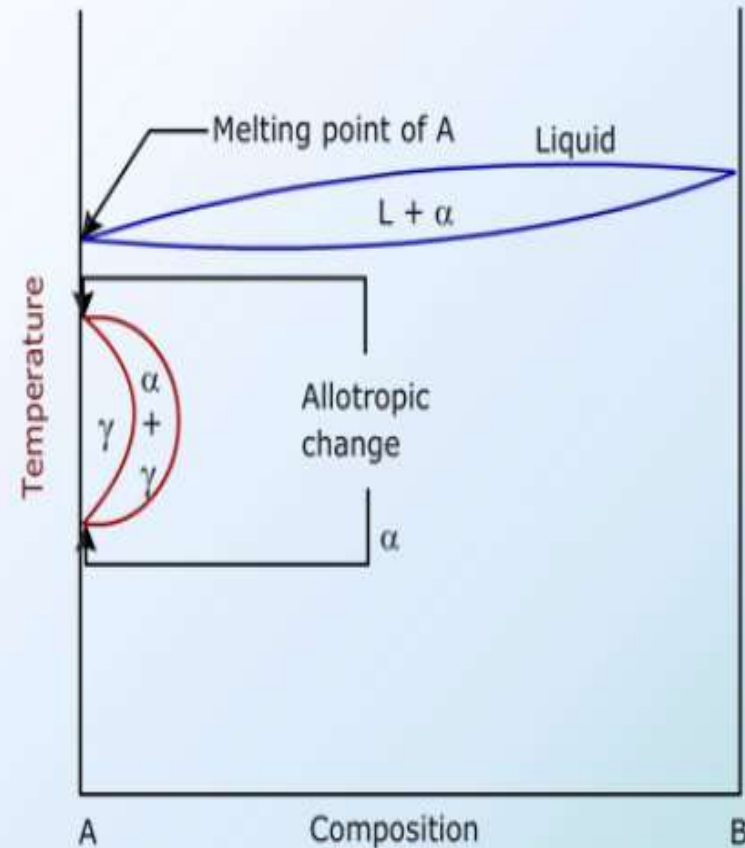
Allotropic Changes

Eutectic System

➤ Binary alloy eutectic system can be grouped as

- Two metals completely dissolve in the liquid state but does not dissolve at all in the solid state
- Two metals completely dissolve in the liquid state but partly dissolve in the solid state
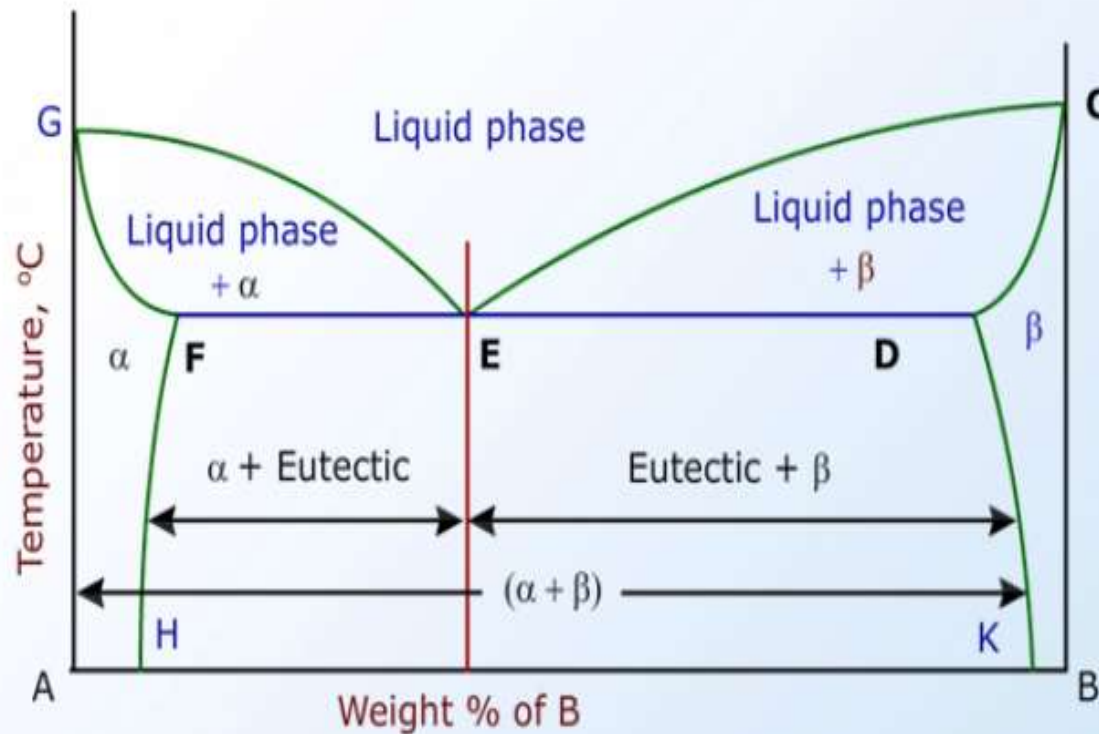

Partial Eutectic Systems

Eutectic System

➤ The alloy whose composition is represented by the eutectic is called eutectic alloy

➤ The quantitative relation between the weights of the α and β phases

$$\frac{Weight\ of\ \alpha - phase}{Weight\ of\ \beta - phase} = \frac{T'\gamma}{T'\delta}$$

Partial Eutectic Systems

> These diagrams are obtained for two metals which have complete miscibility (the property of liquids to mix in all proportions, forming a homogeneous solution) in the liquid state and partial solubility in the solid state
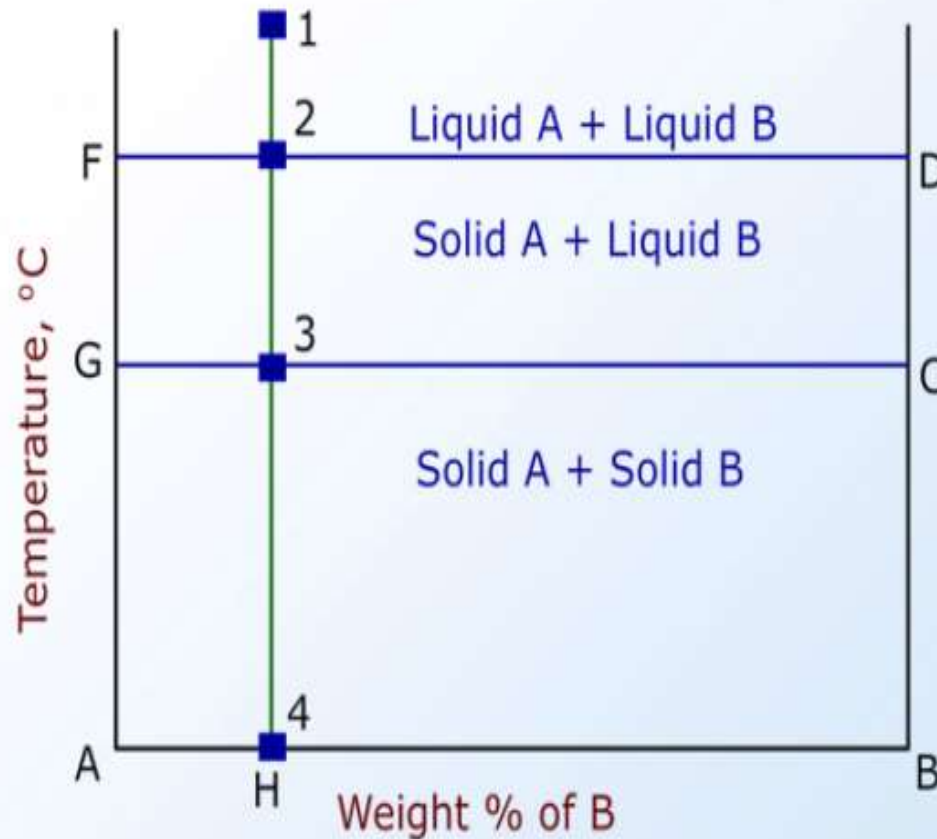

Partial Eutectic Systems

Layer Type Systems

> The binary phase diagram of a layer type system is obtained for two metals which have complete insolubility in the liquid as well as solid state


Layer Type Systems

Peritectic Transformation

> The diagram shows that the crystals of beta solid solution, precipitated at the beginning of solidification, and then they react with the liquid alloy of a definite composition to form new crystals of alpha solid solution at a constant temperature. This process is called Peritectic Transformation

Peritectic Transformation
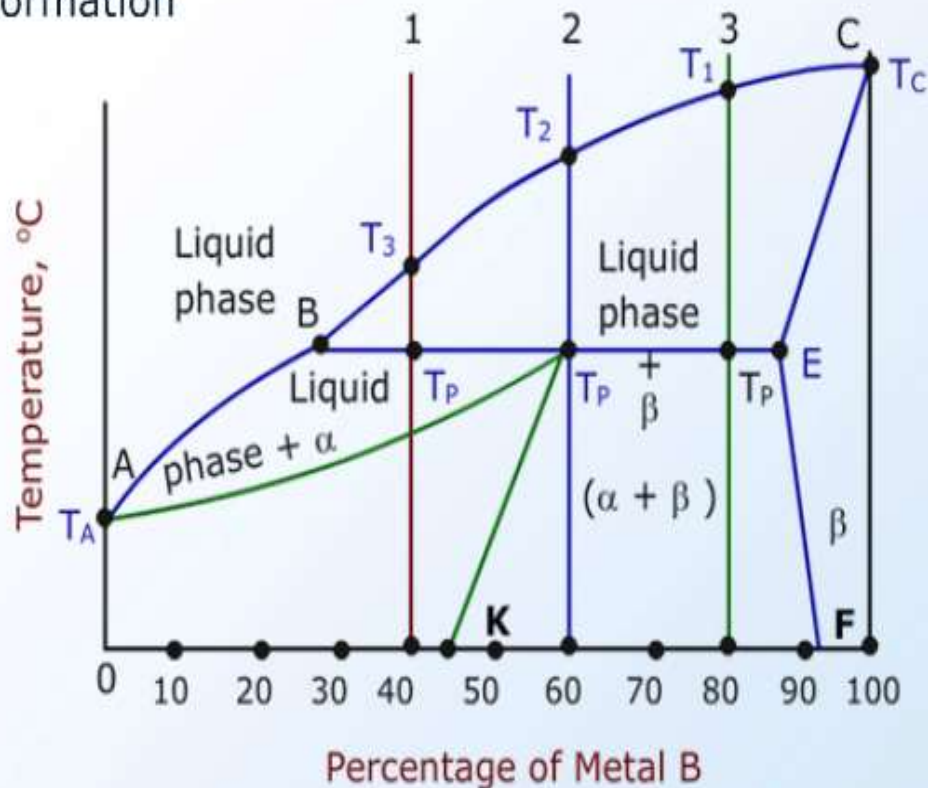
Phase Diagram of Aluminum and Copper

➤ The Cu alloy cools under equilibrium conditions

➤ Now, compare the composition of a solid solution in the Al−4% Cu alloy at room temperature with its composition when the alloy is quenched

➤ The composition of the α, determined from the tie line is about 0.02 percent copper

Phase Diagram of Aluminum and Copper

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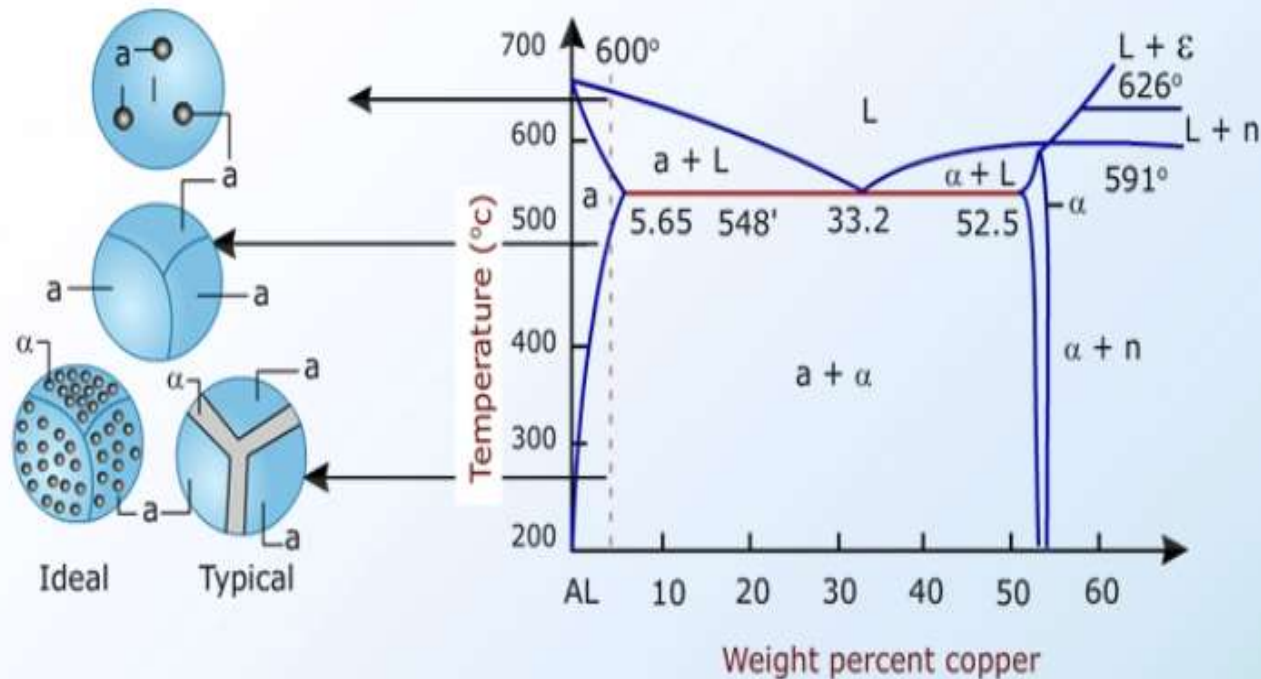
Copper-Zinc Binary Phase Diagram

➤ Cu$_3$Sn has been found to occur at temperatures in excess of 60° C and is generally of minor importance in the study of tin whiskers, as at these temperatures, rate effects dominated the formation of hillocks in lieu of whiskers

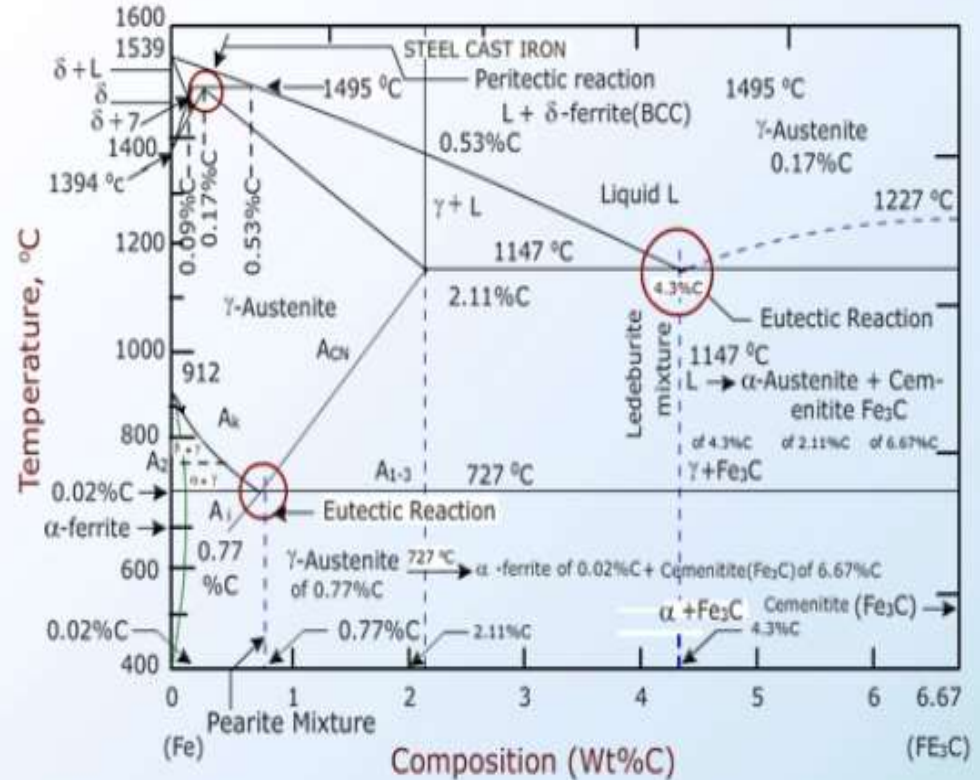➤ The stress relaxation results in eruptions of the surface called Hillocks
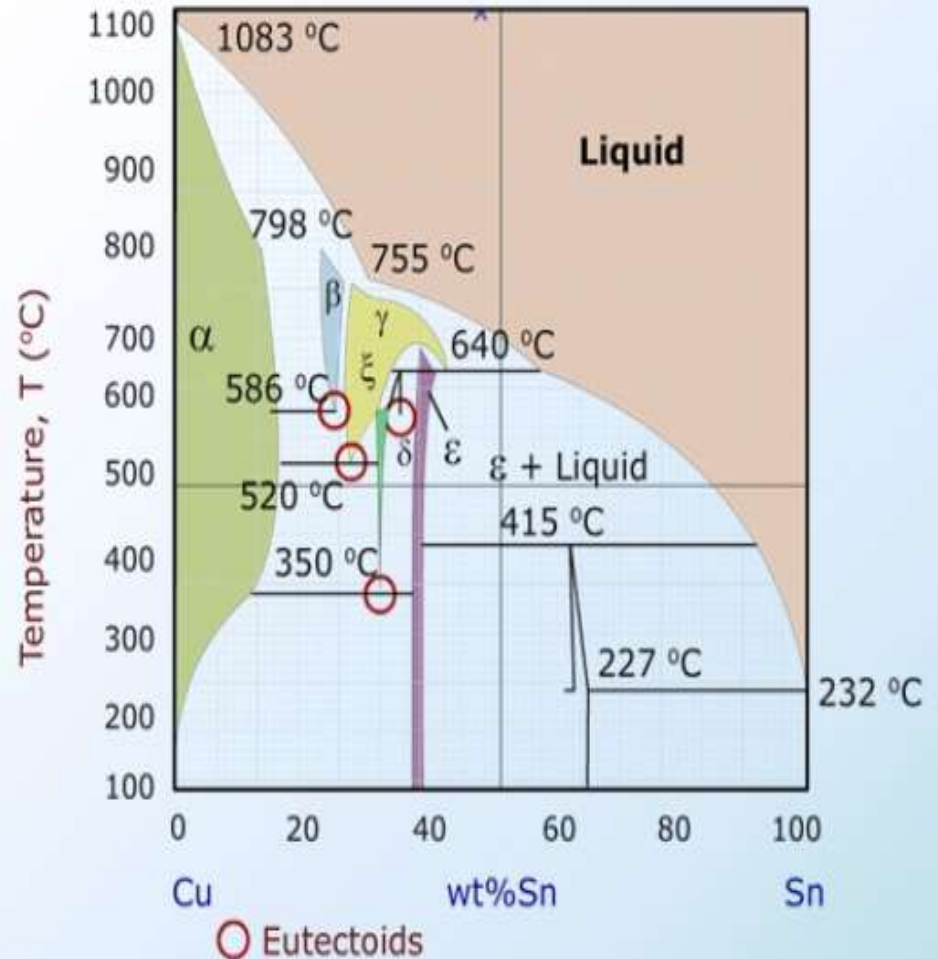
Copper-T$_{in}$ Binary Phase Diagram

Iron-Iron Carbide (Fe-Fe$_3$c) Phase Diagram

Importance of Fe-Fe$_3$c System

➤ The primary structural
materials in any
technologically advanced
culture, i.e., steels and cast
irons are iron-carbon alloys

➤ The phase diagram of the
system is the basic thing on
which the relationships
between heat treatment,
mechanical properties, and
microstructure depends

Iron-Iron Carbide (Fe-Fe$_3$c) Phase Diagram