Material Science & Metallurgy

UNIT-1

1.1 Introduction of Materials Science and Engineering

Materials Science – Investigating relationships that exist between the structure and properties of materials.

Materials Engineering – On the basis of these structure-property correlations, designing or engineering thestructure of a material to produce a pre-determined set of properties.

Structure

Structure of a material usually relates to the arrangement of its internal components.

Subatomic - Structure involves electrons within the individual atoms and interactions with their nuclei.

Atomic level- structure encompasses the organization of atoms or molecules relative to one another.

Microscopic - Which contains large groups of atoms that are normally agglomerated together.

Macroscopic – viewable with the naked eye**.**

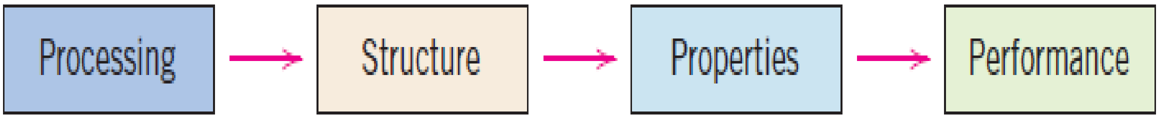
Property

A property is a material trait in terms of the kind and magnitude of response to a specific imposed stimulus.Properties are made independent of material shape and size.

Example-

A specimen subjected to forces will experience deformation,A polished metal surface will reflect light.

Properties of solid materials may be grouped into six different categories: (1) mechanical, (2)electrical, (3) thermal, (4) magnetic, (5) optical and (6) deteriorative.



The four components of the discipline of materials science and engineering and their interrelationship.

Classification of Materials

Solid materials have been conveniently grouped into three basic classifications:

(1) metals, (2) ceramics, and (3) polymers**.**

1. Metals-

- Materials in this group are composed of one or more metallic elements (such as iron, aluminum, copper, titanium, gold, and nickel), and often also nonmetallic elements (for example, carbon, nitrogen, and oxygen) in relatively small amounts.
- Atoms in metals and their alloys are arranged in a very orderly manner.
- In comparison to the ceramics and polymers, are relatively dense.
- Mechanical Property- relatively stiff and strong , ductile (i.e., capable of large amounts of deformationwithout fracture), and are resistant to fracture.
- Metallic materials have large numbers of nonlocalized electrons; that is, these electrons are not bound toparticular atoms.Many properties of metals are directly attributable to these electrons.
- Example, metals are extremely good conductors of electricity,and heat, and are not transparent to visiblelight; a polished metal surface has a lustrous appearance.
- Some of the metals (viz., Fe, Co, and Ni) have desirable magnetic properties.

2. Ceramics

- Ceramics are compounds between metallic and nonmetallic elements; they are most frequently oxides,nitrides, and carbides.
- Examples-aluminum oxide (or alumina, Al_2O_3), silicon dioxide (or *silica*, SiO_2),silicon carbide (SiC),silicon nitride (Si_3N_4).
- Examples of traditional ceramics — clay minerals (i.e., porcelain), cement, and glass.

Properties-

- Relatively stiff and strong—stiffnesses and strengths are comparable to those of the metals , very hard,extremely brittle (lack ductility),.highly susceptible to fracture.
- Thermal and electrical Properties- Insulative to the passage of heat and electricity low electricalconductivities and are more resistant to high temperatures
- Optical characteristics-Ceramics may be transparent, translucent, or opaque.

Polymers

Carbon-based compounds

- Chain of H-C molecules. Each repeat unit of H-C is a monomer e.g. ethylene (C2H4), Polyethylene –(– CH2 –CH2)n.
- Polymers include the familiar plastic and rubber materials.
- Many of them are organic compounds that are chemically based on carbon, hydrogen, and other nonmetallic elements (viz. O, N, and Si).
- They have very large molecular structures, often chain-like in nature that have a backbone of carbon atoms. Some of the common and familiar polymers are polyethylene (PE), nylon, poly (vinyl chloride)(PVC), polycarbonate (PC), polystyrene (PS), and silicone rubber.

Properties

- Low densities, not as stiff nor as strong as ceramics and metals.
- Extremely ductile and pliable (i.e., plastic).
- Relatively inert chemically and unreactive in a large number of environments.

Limitations

- Tendency to soften and/or decompose at modest temperatures, which, in some instances,limits their use.
- Low electrical conductivities and are nonmagnetic.

Composites

- A composite is composed of two (or more) individual materials, which come from the categoriesdiscussed above—viz., metals, ceramics, and polymers.
- Objective-to achieve a combination of properties that is not displayed by any single

materialExamples

- Cemented carbides (WC with Co binder)
- Plastic molding compounds containing fillers
- Rubber mixed with carbon black
- Wood (a natural composite as distinguished from a synthesized composite)

Advance Materials

- Materials that are utilized in high-technology (or high-tech) applications are sometimes termed advancedmaterials.

Examples

- Include electronic equipment (camcorders, CD/DVD players, etc.), computers, fiber-optic systems, spacecraft, aircraft, and military rocketry, liquid crystal displays (LCDs), and fiber optics.
- These advanced materials may be typically traditional materials types (e.g., metals, ceramics, polymers)whose properties have been enhanced, and, also newly developed, high-performance materials.
- Advanced materials include semiconductors, biomaterials, and what we may term“ materials of thefuture.

Biomaterials

- Biomaterials are employed in components implanted into the human body for replacement of diseased ordamaged body parts.
- These materials must not produce toxic substances and must be compatible with body tissues (i.e., mustnot cause adverse biological reactions).
- All of the above materials—metals, ceramics, polymers, composites, and semiconductors—may be usedas biomaterials.

Example-

Titanium and its alloy, Co-Cr alloy, stainless steel, zirconia, HA, TiO_2 etc.

Semiconductors

- Semiconductors have electrical properties that are intermediate between the electrical conductors (viz. metals and metal alloys) and insulators (viz. ceramics and polymers).
- The electrical characteristics of these materials are extremely sensitive to the presence of minute concentrations of impurity atoms, for which the concentrations may be controlled over very small spatialregions.
- Semiconductors have made possible the advent of integrated circuitry that has totally revolutionized the electronics and computer industries (not to mention our lives) over the past three decades.

The Materials Selection Process

- Pick Application and determine required Properties.
- Properties: mechanical, electrical, thermal, magnetic, optical, deteriorative.
- Properties- Identify candidate Material(s)
- Material: structure, composition.
- Material- Identify required Processing
- Processing: changes structure and overall shape

Example: casting, sintering, vapor deposition, doping forming, joining, annealing.

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
    - Primary bonding
    - 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

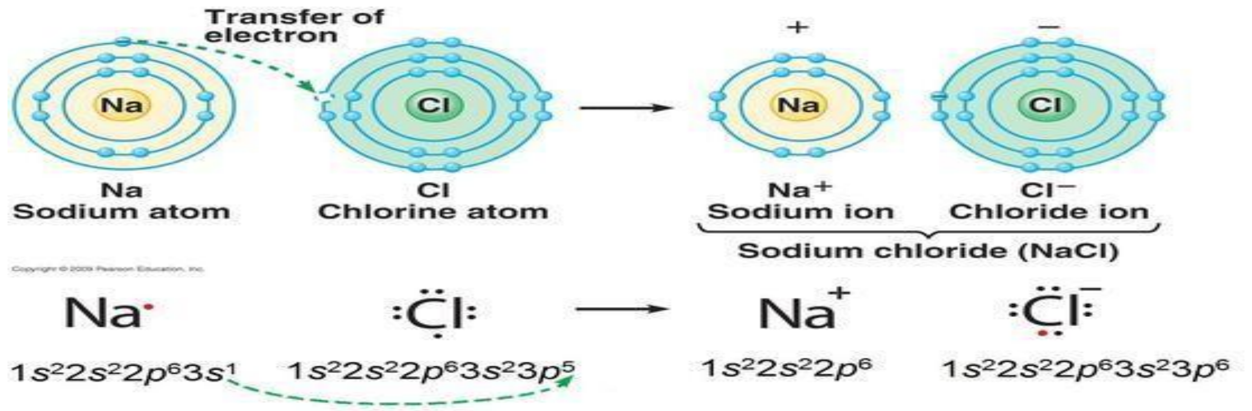
Ionic Bond:

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 Materials

Ionically bonded materials usually have moderate hardness and fairly high melting points. They are generally soluble and are poor conductors of electricity because their constituent ions are fairly stable and neither lose nor gain electrons easily. They are usually highly symmetric and nondirectional (isotropic), because their cations tend to evenly surround themselves with as many anions as space permits.

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

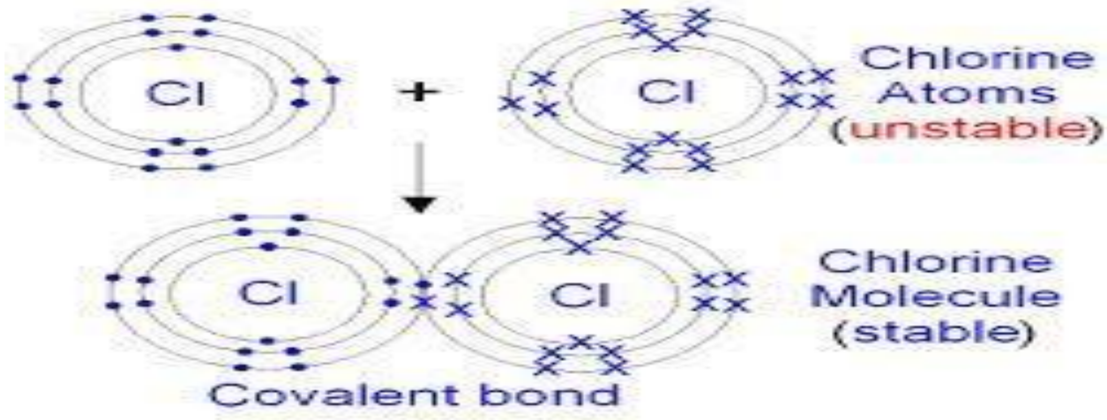


Fig: covalent bond formation of chorine molecule

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

Properties of Covalent Materials

Covalent bonds are the strongest of the chemical bonds. Covalently bonded materials generally have very high melting points and are generally insoluble. They typically do not conduct electricity as solids or in solution. Because covalent bonds are highly directional, covalently bonded materials tend to have less symmetry than ionically bonded materials.

Metallic bond:

A bond formed by the attraction between electron cloud and positively charged ion (cation) of same or different metals

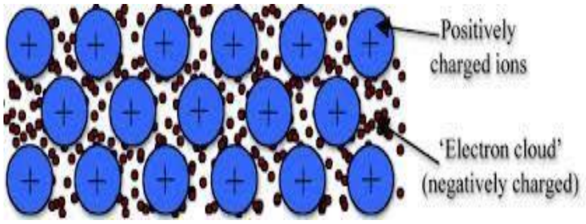


Fig: Metallic bond formation

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 "**<u>bond energy</u>**"

- 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

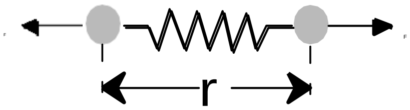
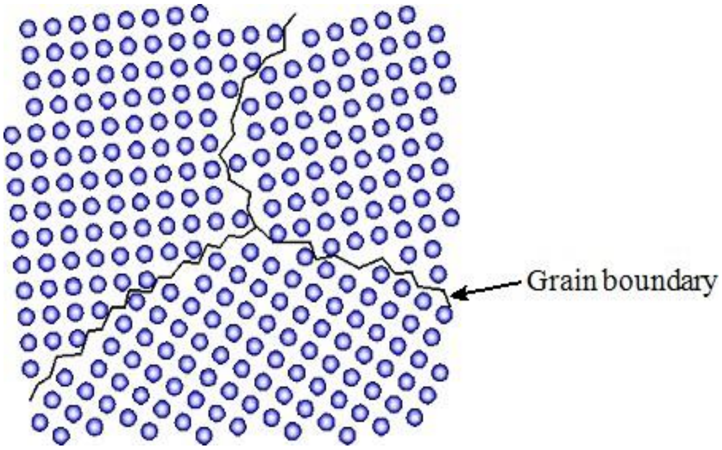


Fig: bond length

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:**
  - 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 atoms 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

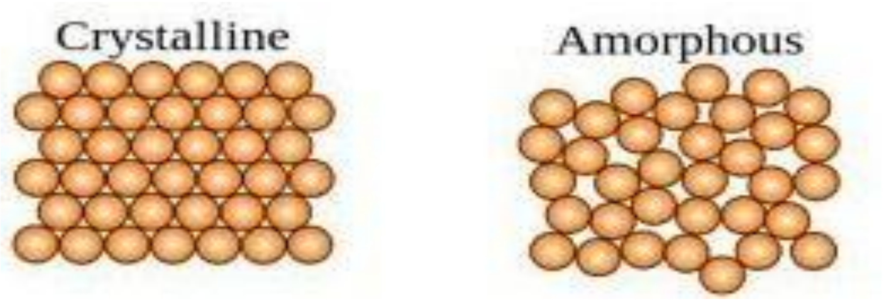


Fig: Crystalline and Non-crystalline materials

Anisotropy & Isotropy:

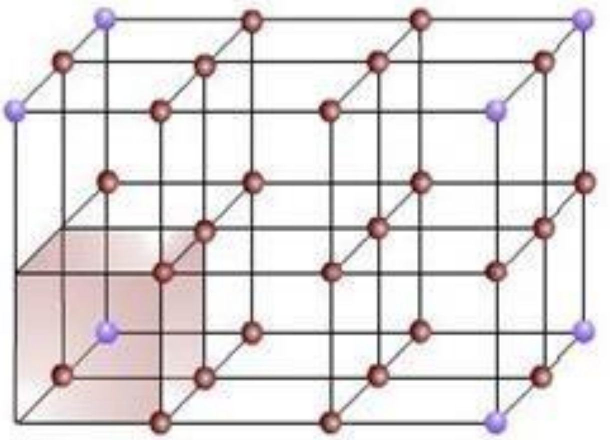
- The properties of polycrystalline solids may be differ greatly in different directions and such an unequality of properties in various crystallographic directions is called ***Anisotropy.***
- Amorphous substances such as glass will display the same properties in any directions or planes are called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

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

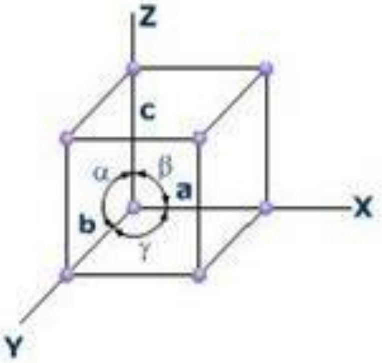
Space lattice: It differs from a crystal structure in that a space lattice is an array of points in three-dimensional space in which every point has surroundings identical to the every other point in the array. Where as a crystal structure is an arrangement of atoms in crystal.

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

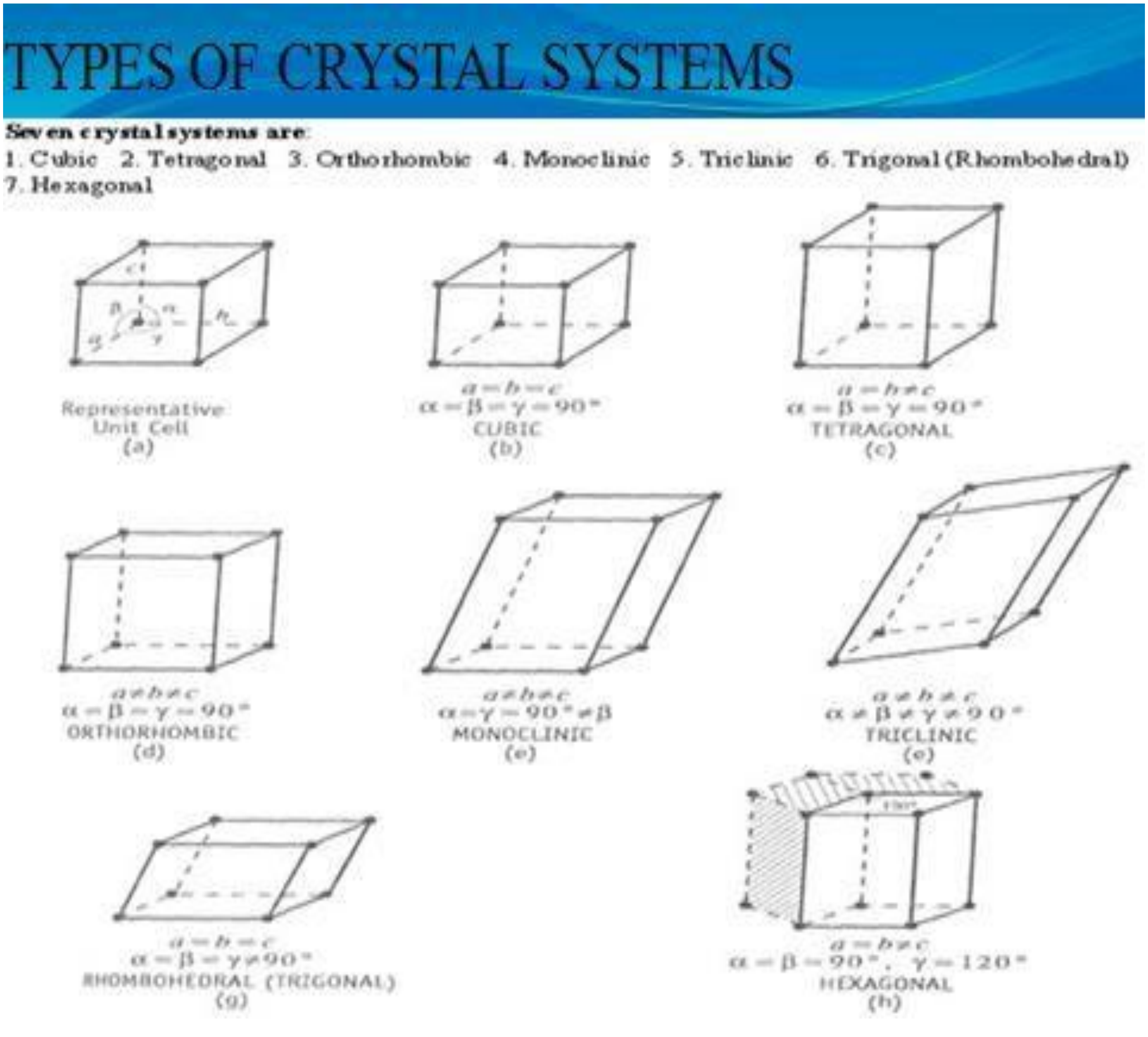
Primitive cell: It is defined as a unit cell which possesses lattice points at its corners only

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)

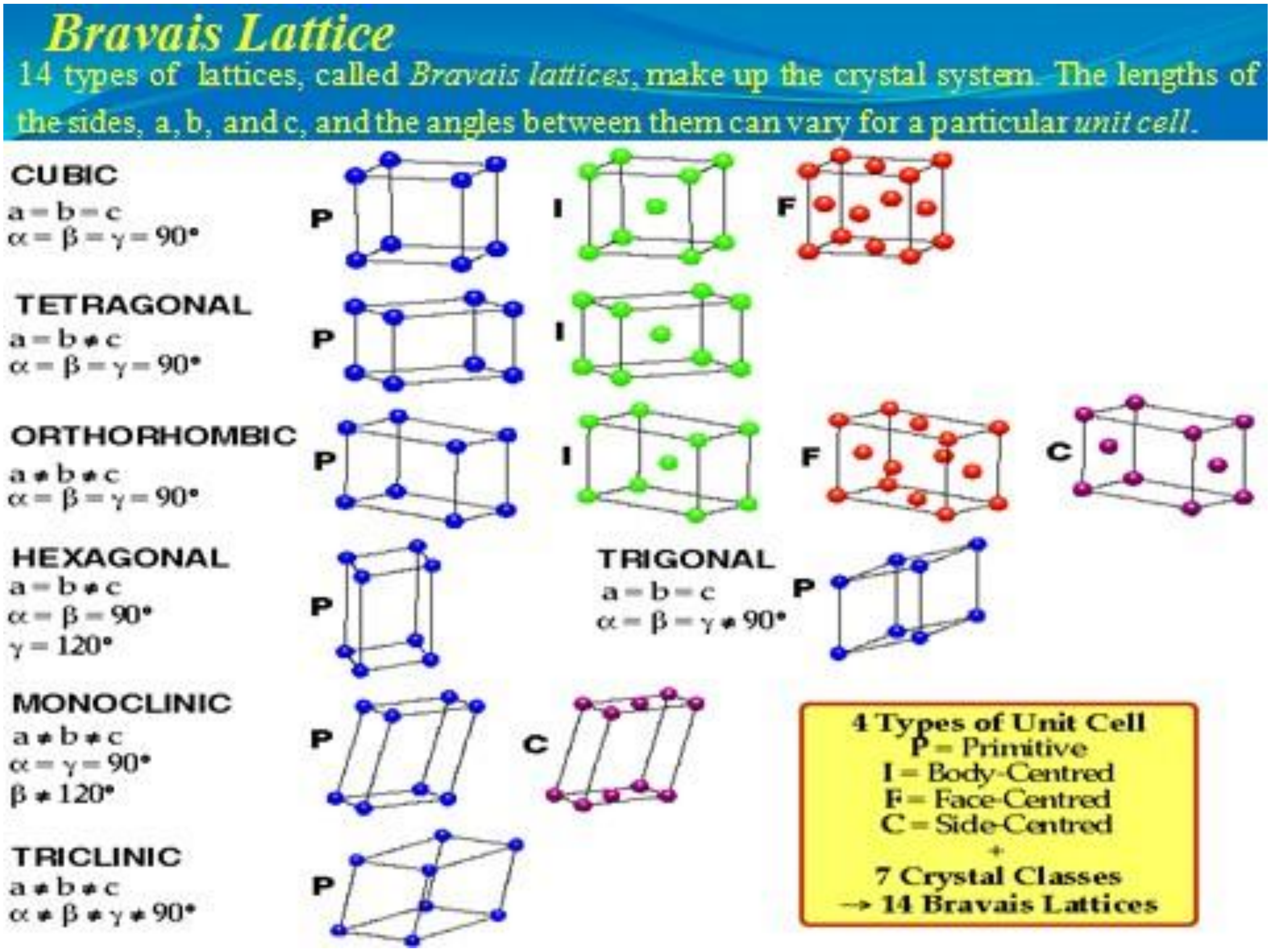
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$
ORTHORHOMBIC
(d)

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

$a = b \neq c$
$\alpha = \beta = 90°,\ \gamma = 120°$
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*.

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

Atomic Packing factor (APF)

- Atomic Packing factor or packing density is defined as the volume occupied by the atoms in aunit 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

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)

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

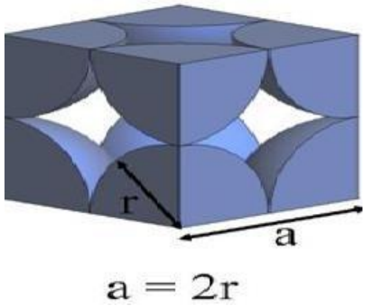
Atomic packing factor of S.C.C:

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,

❖ 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

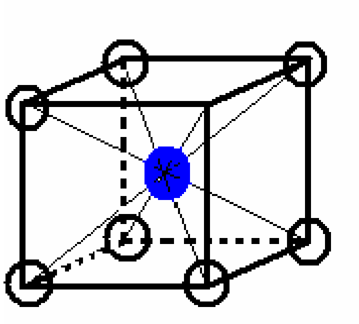


Fig: B.C.C

No of atoms in the unit cell:

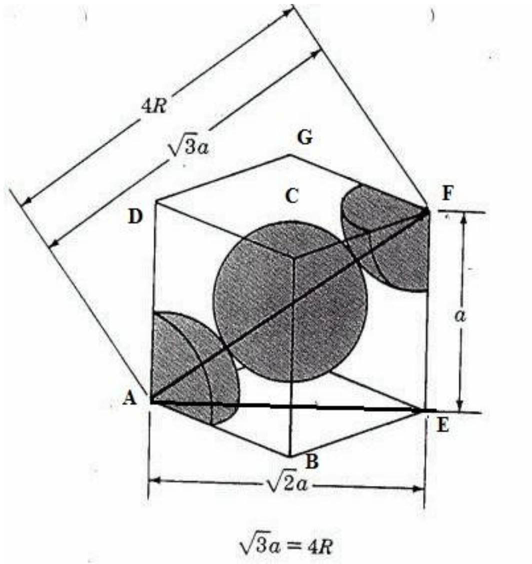
In B.C.C structure the unit cell contains 8 atoms at each corner of the cube and one atom in the centre of the cube

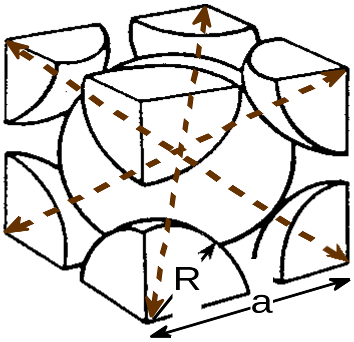
Since each corner is shared by 8 surrounding cubes and the atom in the centre cannot be shared by another cube**.**

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

1 centre atom =1 atom

2 atoms





Atomic packing factor of B.C.C:

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

$= a^2 + a^2$

$AE^2 = 2a^2$

$$AE = \sqrt{2}a$$

From $\triangle$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 = $a^3 = (4r/\sqrt{3})^3$

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

$= 2x4/3\ \pi r^3$

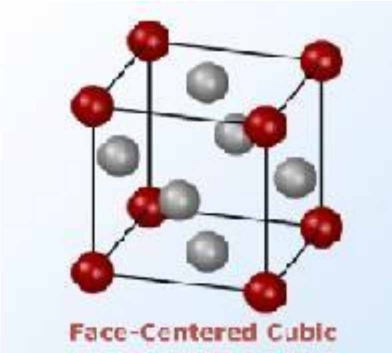
Packing factor (p.f):

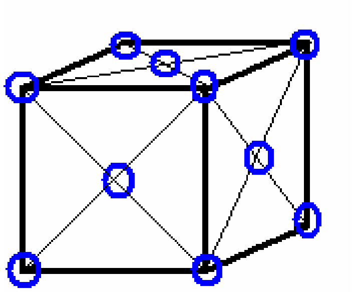
$$P.f = 2x4/3\ \pi r^3 / (4r/\sqrt{3})^3 = 0.68 = 68\%$$

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

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

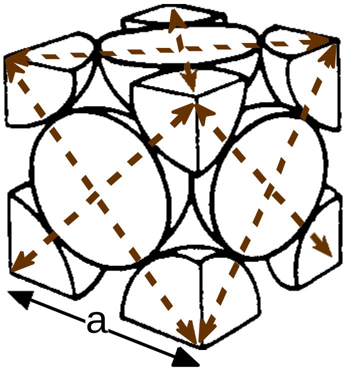
Face-centered cubic structure:

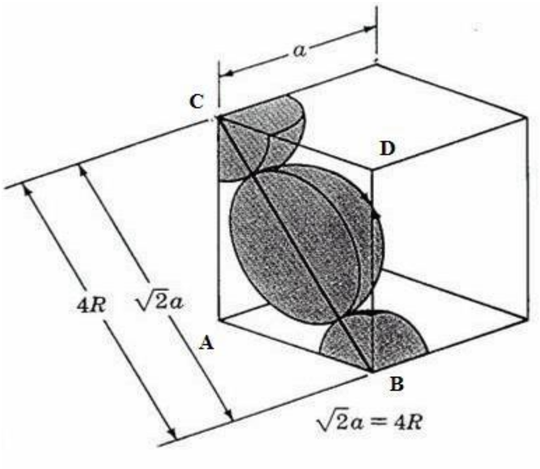




In FCC structure, there are eight corner of the cube occupied by eight atoms, and six atoms occupy the centre of six of the cube atoms

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 △le ABC, $AC^2 = AB^2 + BC^2$

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

$16r^2 = 2a^2$

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

We know that;

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

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

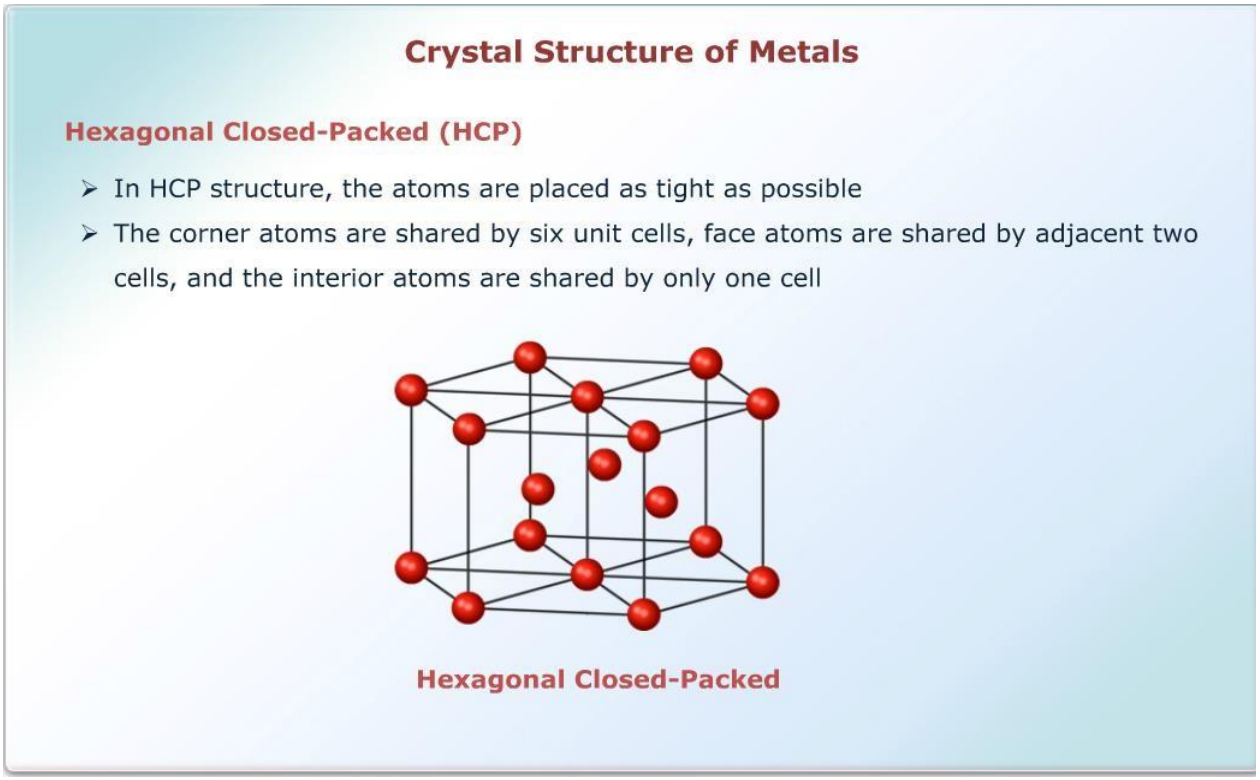
$= 4 \times 4/3\,\pi r^3$

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

$= 4 \times 4/3\,\pi r^3 / (2 \times /\sqrt{2}r)^3$

=0.74 or 74% P.f is high compared to S.C.C and B.C.C

Hexagonal close-packed (HCP) structure:



Crystal Structure of Metals

Hexagonal Closed-Packed (HCP)

- In HCP structure, the atoms are placed as tight as possible
- The corner atoms are shared by six unit cells, face atoms are shared by adjacent two cells, and the interior atoms are shared by only one cell

Hexagonal Closed-Packed

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

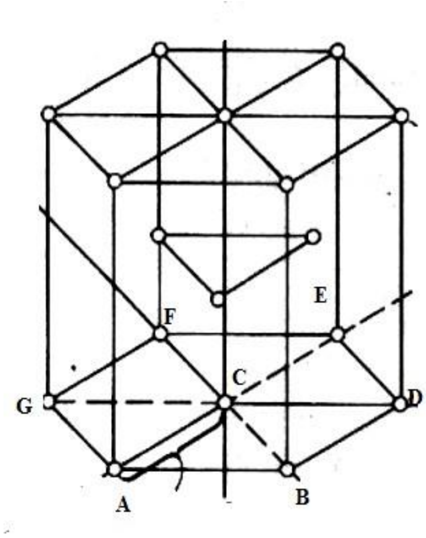
Area of basal plane is the area ABDEFG.this area is six times the equilateral triangle ABC

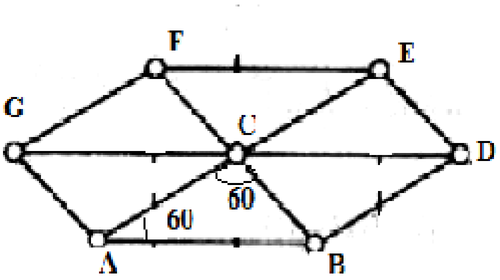
Area of $\triangle$ABC = 1/ 2 x b x h

$= 1/2 \text{ x } a \text{ x } a \sin 60^0$

$= 1/2 \text{ x } a^2 \text{ x } \sin 60^0$

Total area of the basal plane = $6 \text{ x } 1/2\, a^2 \sin 60 = 3\, a^2 \sin 60^0$





Vol of unit cell = Area of basal plane x height

$= 3\, a^2 \sin 60^0 \text{ x } c$

We know; a = 2r

Vol of atoms in unit cell = $n.4/3\, \pi r^3 = 6\text{x}4/3\, \pi r^3$

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

$= 6\text{x}4/3\, \pi\, (a/2)^3 / 3a^2 \sin 60 \text{x} c$

$= \pi\, a / 3\text{x}c\, \text{x}\sin 60^0$

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

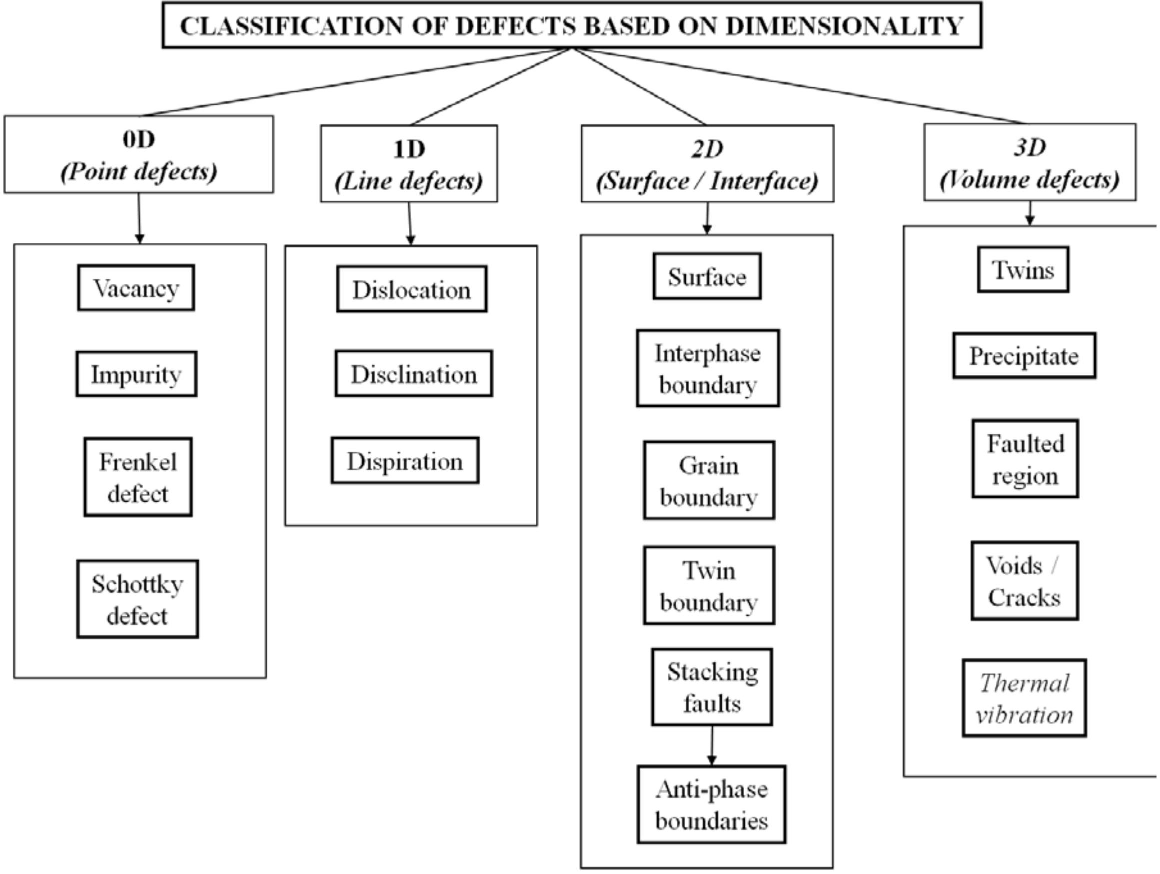
$= \pi / 3\text{x}1.633\, \text{x}\sin 60^0 = 0.74$ or 74%

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

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

Defects in Solids

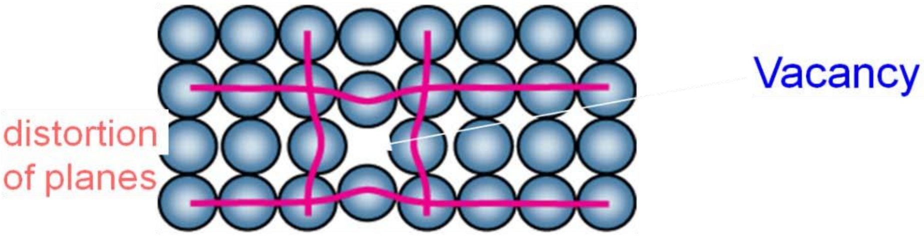
- The term ***“defect”*** or ***“imperfection”*** is generally used to describe any deviation from the perfect periodic array of atoms in the crystal.
- The properties of some materials are extremely influenced by the presence of imperfections such as mechanical strength, ductility, crystal growth, magnetic hysteresis, dielectric strength, condition in semiconductors, which are termed structure sensitive are greatly affected by the-relatively minor changes in crystal structure caused by defects or imperfections.
- There are some properties of materials such as stiffness, density and electrical conductivity which are termed structure-insensitive, are not affected by the presence of defects in crystals.
- It is important to have knowledge about the types of imperfections that exist and the roles they play in affecting the behavior of materials.
- Crystal imperfections can be classified on the basis of their geometry as



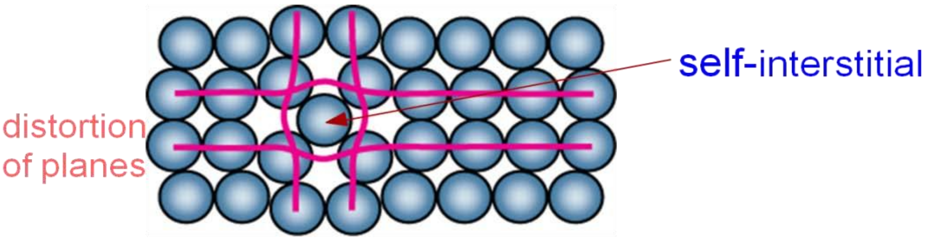
Point Defects in Metals

It is a zero dimension defect, associated with one or two atomic positions.

Vacancies -The simplest of the point defects is a **vacancy,** or vacant lattice site, one normally occupied from which an atom is missing. All crystalline solids contain vacancies and, in fact, it is not possibleto create such a material that is free of these defects, vacant atomic sites in a structure.



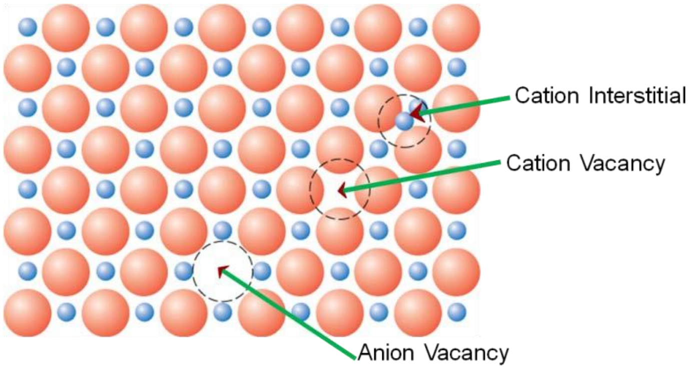
Self-Interstitials- when an atom occupies an interstitial site where no atom would ordinarily appear, causing aninterstitialcy.



Point Defects in Ceramics

Vacancies- vacancies exist in ceramics for both cations and anions.

Interstitials - interstitials exist for cations**,** interstitials are not normally observed for anions because anions are large relative to the interstitial sites.

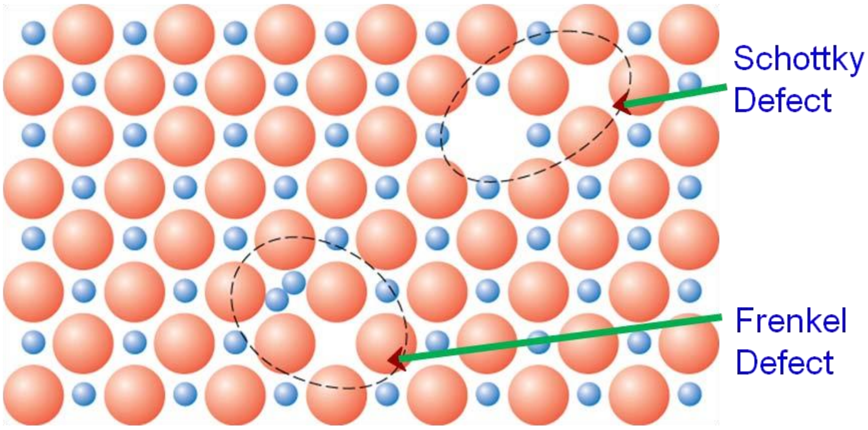


Frenkel Defect

To maintain the charge neutrality, a cation vacancy-cation interstitial pair occur together. This is called a **Frenkel defect**. The cation leaves its normal position and moves to the interstitial site. There is no change in charge because the cation maintains the same positive charge as an interstitial.

Schottky Defect

A cation vacancy–anion vacancy pair known as a **Schottky defect.** To maintain the charge neutrality, removeone cation and one anion; this creates two vacancies.



EFFECT OF POINT IMPERFECTIONS

- The presence of a point imperfection introduces distortions in the crystal.
- In the case of impurity atom, because of its difference in size, elastic strains are created in theregions surrounding the impurity atom.
- All these factors tend to increase the potential energy of the crystal called ***'enthalpy'***. The work donefor the creation of such a point defect is called the '***enthalpy of formation***' of the point imperfection

LINE IMPERFECTIONS

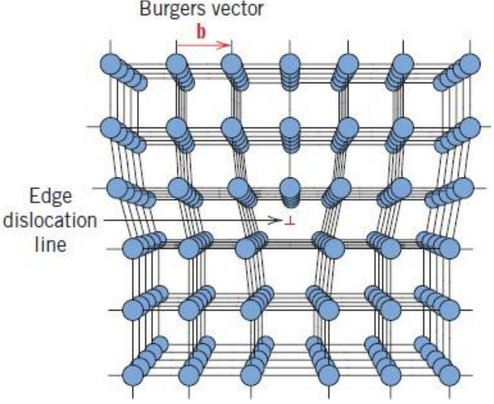
- A *dislocation* is a linear or one-dimensional defect around which some of the atoms are misaligned. The defects, which take place due to distortion of atoms along a line, in some direction are called as '***line defects***'.Line defects are also called dislocations.

- It is responsible for the phenomenon of slip by which most metals deform

plastically.The two types of dislocations are,

Edge dislocation

- It is a linear defect that centers around the line that is defined along the end of the extra half-plane ofatoms.
- The distorted configuration extends all along the edge into the crystal.
- Thus as the region of maximum distortion is centered around the edge of the incomplete plane, thisdistortion represents a line imperfection and is called an edge dislocation.
- Edge dislocations are represented by '⊥' or 'T' depending on whether the incomplete plane starts fromthe top or from the bottom of the crystal.
- These two configurations are referred to as positive and negative edge dislocations respectively.



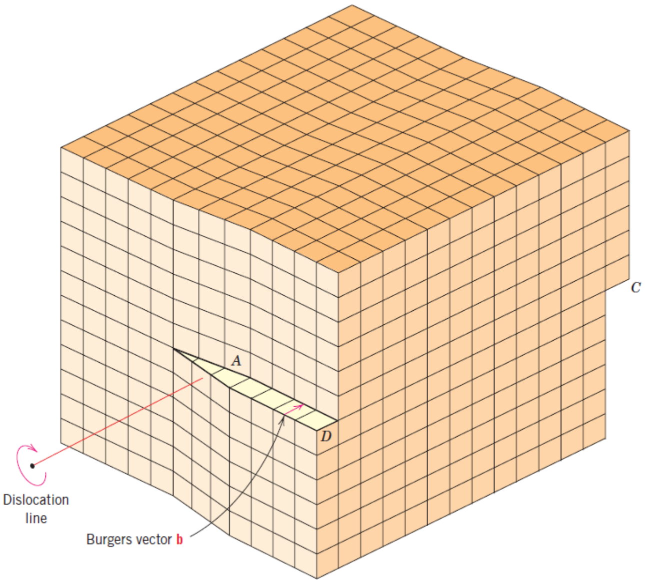
Screw dislocation:-

- In this dislocation, the atoms are displaced in two separate planes perpendicular to each other.

- It forms a spiral ramp around the dislocation.

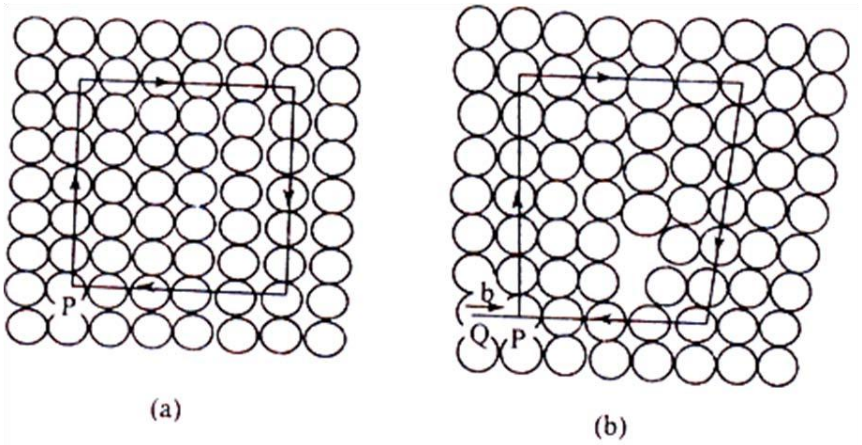
- The Burgers Vector is parallel to the screw dislocation line.

- Speed of movement of a screw dislocation is lesser compared to edge dislocation.



Burgers vector - The magnitude and direction of the lattice distortion associated with a dislocation is expressedin terms of a **Burgers vector,** denoted by a **b**.

The Burger vector can be found by the gap in the Burger circuit which is obtained by moving equal distances ineach direction around the dislocation.



(a)

(b)

Mixed dislocations - Most dislocations found in crystalline materials are probably neither pure edge nor purescrew, but exhibit components of both types; these are termed mixed dislocations.

Surface imperfections

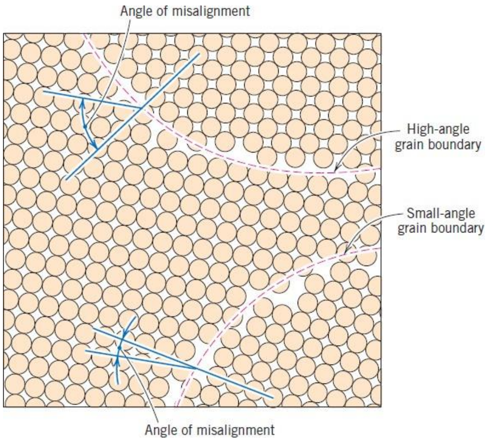
- Surface imperfections arise from a change in the stacking of atomic planes on or across a boundary.
- The change may be one of the orientations or of the stacking sequence of atomic planes.
- In geometric concept, surface imperfections are two- dimensional. They are of two types external andinternal surface imperfections.

External Surfaces

- They are the imperfections represented by a boundary. At the boundary the atomic bonds are terminated.
- Surface atoms are not bonded to the maximum number of nearest neighbors, and are therefore in a higher energy state than the atoms at interior positions. The bonds of these surface atoms that are not satisfied give rise to a surface energy, expressed in units of energy per unit area (J/m2 or erg/cm2).

Grain Boundaries

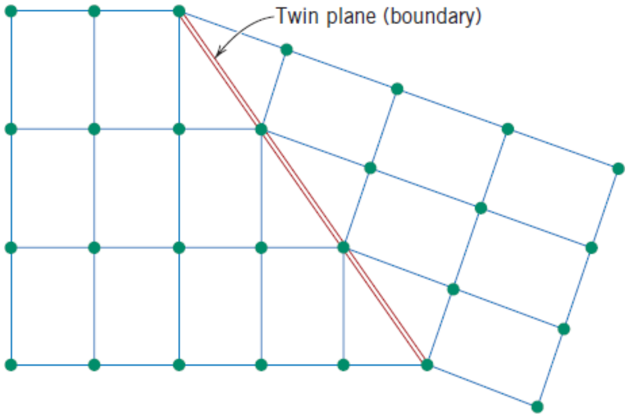
- The boundary separating two small grains or crystals having different crystallographic orientations inpolycrystalline materials.



Twin Boundaries

- A *twin boundary* is a special type of grain boundary across which there is a specific mirror lattice symmetry; that is, atoms on one side of the boundary are located in mirror-image positions of the atoms on the other side.

- The region of material between these boundaries is appropriately termed a *twin.*
- Twins result from atomic displacements that are produced from applied mechanical shear forces (mechanical twins), and also during annealing heat treatments following deformation (annealing twins).



Volume Defects-

These include pores, cracks, foreign inclusions, and other phases. They are normally introduced during processing and fabrication steps.

Effect on property

- There are some properties of materials such as stiffness, density and electrical conductivity which are termed structure-insensitive, are not affected by the presence of defects in crystals while there are many properties of greatest technical importance such as mechanical strength, ductility, crystal growth, magnetic.

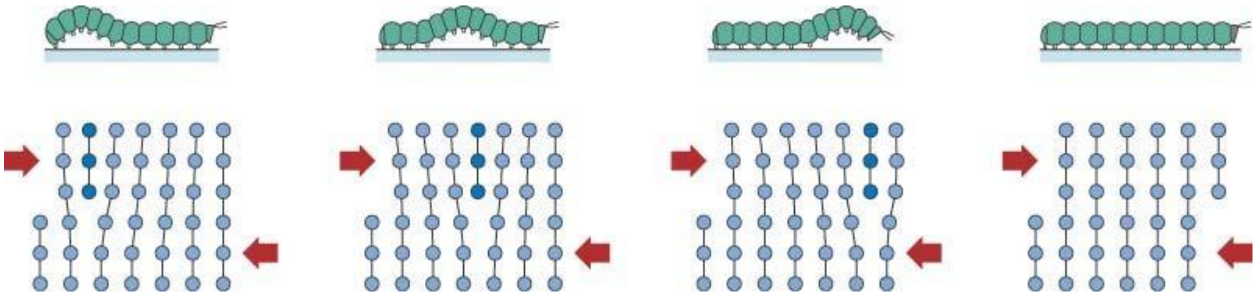
- Hysteresis, dielectric strength, condition in semiconductors, which are termed structure sensitive are greatly affected by the-relatively minor changes in crystal structure caused by defects or imperfections.

Mechanisms/modes of plastic deformation

Plastic deformation in crystalline solid is accomplished by means of various processes mentioned below; amongwhich slip is the most important mechanism.
Plastic deformation of crystalline materials takes place by mechanisms which are very different from that for amorphous materials (glasses). Plastic deformation in amorphous materials occur by other mechanisms including flow (~viscous fluid) and shear banding.

Plastic deformation by dislocation Motion (SLIP)

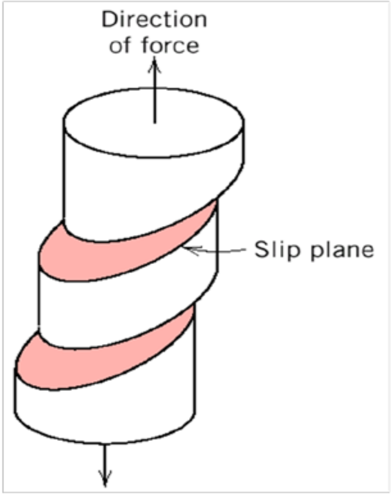
- SLIP is the most important mechanism of plastic deformation. At low temperatures (especially in BCCmetals) twinning may also become important.
- At the fundamental level plastic deformation (in crystalline materials) by slip involves the motion of dislocations on the slip plane *(creating a step of Burgers vector).*
- Slip is caused by shear stresses (at the level of the slip plane). Hence, a purely hydrostatic state of stresscannot cause slip.
- A slip system consists of a slip direction lying on a slip plane.
- Slip is analogous to the mode of locomotion employed by a caterpillar



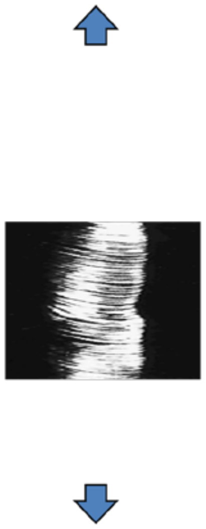
- Dislocations move more easily on specific planes and in specific directions.
- Ordinarily, there is a preferred plane (slip plane), and specific directions (slip direction) along whichdislocations move. The combination of slip plane and slip direction is called the slip system.
- The slip system depends on the crystal structure of the metal.
- The slip plane is the plane that has the most dense atomic packing (the greatest planar density). The slip direction is most closely packed with atoms (highest linear density).
- In CCP, HCP materials the slip system consists of a close packed direction on a close packed plane.
- Just the existence of a slip system does not guarantee slip → slip is competing against other processes like twinning and fracture. If the stress to cause slip is very high (i.e. CRSS is very high), then fracture may occur before slip (like in brittle ceramics).
- For slip to occur in polycrystalline materials, 5 independent slip systems are required. Hence, materials which are ductile in single crystalline form may not be ductile in polycrystalline form. CCP crystals (Cu,Al, and Au) have excellent ductility.
- At higher temperatures more slip systems may become active and hence polycrystalline materials which are brittle at low temperature may become ductile at high temperature.

Slip in Single Crystal

- If a single crystal of a metal is stressed in tension beyond its elastic limit, it elongates slightly and a step appears on the surface due to the relative displacement of one part of the crystal with respect to the others and the elongation stops.
- Further increase in the load causes movement of another parallel plane, resulting in another step. Similarly numbers of small steps are formed on the surface of the single crystal that are parallel to one another and loop around the circumference of the specimen.
- Each step (shear band) results from the movement of a large number of dislocations and their propagation in the slip system.



Macroscopic slip in single crystal

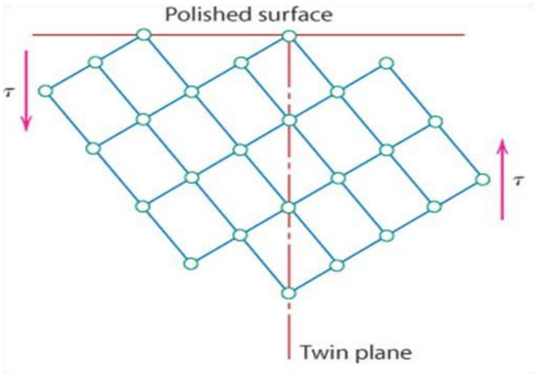


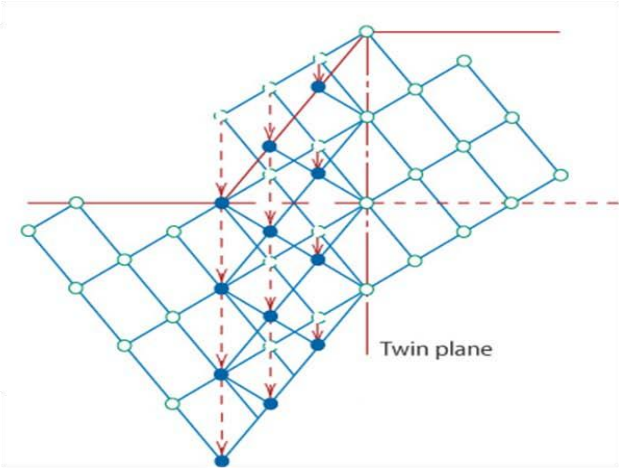
Slip in a zinc single crystal

- Extent of slip in a single crystal depends on the magnitude of shearing stress produced by external loads,geometry of the crystal structure and the orientation of he active slip planes with respect to the shearing stress.
- Slip begins when the shearing stress on slip plane in the slip direction/Resolved Shear Stress (RSS) reaches a critical value called the Critical Resolved Shear Stress (CRSS) and plastic deformation starts *(The actual Schmid's law)*
- Even if we apply an tensile force on the specimen → the shear stress resolved onto the slip plane is responsible for slip.

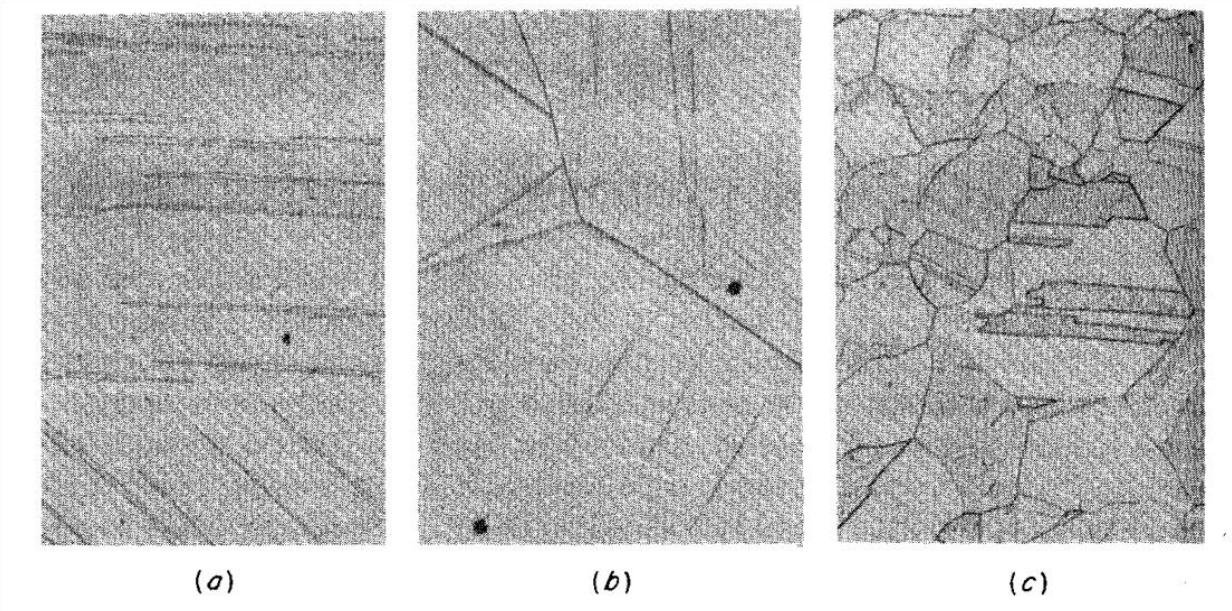
Plastic deformation by Twin

- In addition to slip (dislocation movement), plastic deformation can also occur by twinning.
- Twinning results when a portion of the crystal takes up an orientation that is related to the orientation ofthe rest of the un twinned lattice in a definite, symmetrical way.
- Twinned portion of the crystal is a mirror image of the parent crystal and the plane of symmetry betweenthe two portions is called twinning plane.
- Twinning may favorably reorient slip systems to promote dislocation movement.





- Twins are generally of two types: Mechanical Twins and Annealing twins
- Mechanical twins are generally seen in bcc or hcp metals and produced under conditions of rapidrate of loading and decreased temperature.
- Annealing twins are produced as the result of annealing. These twins are generally seen in fccmetals.
- Annealing twins are usually broader and with straighter sides than mechanical twins.



(a) Mechanical Twins (Neumann bands in iron), (b) Mechanical Twins in zinc produced by polishing (c)Annealing Twins in gold-silver alloy

- Twinning generally occurs when the slip systems are restricted or when the slip systems are restricted or when something increases the critical resolved shear stress so that the twinning stress is lower than the stress for slip.

- So, twinning generally occurs at low temperatures or high strain rates in bcc or fcc metals or in hcp metals.

- Twinning occurs on specific twinning planes andtwinning directions.

Recovery, Recrystallization & Grain Growth

Recovery

- Recovery takes place at low temperatures of annealing.
- Apparently no change in microstructure.
- During recovery, some of the stored internal strain energy is relieved through dislocation motion due toenhanced atomic diffusion at the elevated temperatures.
- Leads to reduction in the number of dislocations.
- This process also removes the residual stresses formed due to cold working significant.
- The recovering of physical and mechanical properties varies with the temperature and time.
- Recovery is a relaxation process with the following characteristics:

- There is no incubation period
- Recovery rate is large at the beginning, and then it slows down till it is near zero
- Recovery has a limit value varying with temperature; the higher the temperature, the greater is the limitvalue and the shorter is the time needed to reach the limit value
- The greater the deformation, the greater is the initial recovery rate, and decrease in grain size helps toaccelerate the recovery process

The characteristic of recovery can be expressed as the following equation:

$$\frac{dx}{dt} = -cx$$

Where
t is the time of heating under constant temperature
x is the fraction of property increase caused by cold work after
heatingc is a constant related with material and temperature
The value of constant parameter c can be described with the Arrhenius equation:

$$c = c_0 exp\left(\frac{-Q}{RT}\right)$$

Recrystallization

- After recovery is complete, the grains are still in a relatively high strain energy state.

- Recrystallization is the formation of a new set of strain-free and uniaxial grains that have low dislocationdensities.

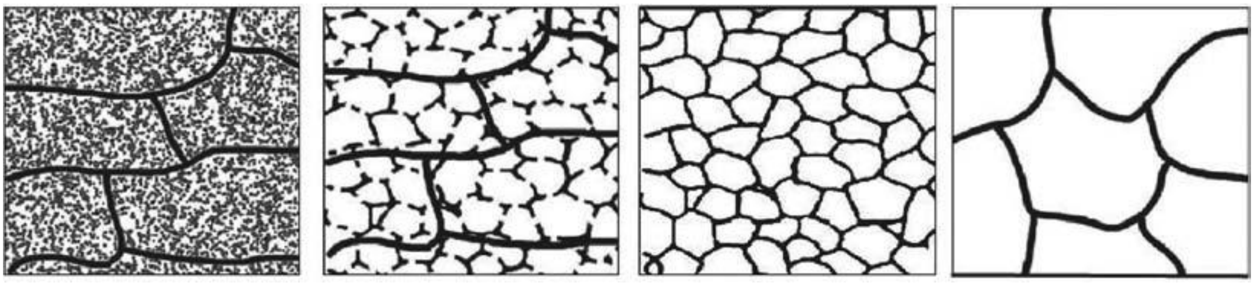
- The temperature at which materials are recrystallized is known as the recrystallization temperature,$T_{recrystallization} \in (0.3 - 0.5)\ T_m$

- The driving force to produce the new grain structure is the internal energy difference between strainedand unstrained material.
- •The new grains form as very small nuclei and grow until they consume the parent material.
- Recrystallization is a heterogeneous process and dependent on the deformation state of steels.
- The kinetics of recrystallization depends on nucleation rate, N, and growth rate, G.

Grain Growth

- After recrystallization, the strain-free grains will continue to grow if the metal specimen is left at elevated temperatures. Grains begin to grow via grain boundary immigration; this phenomenon is called grain growth.

- Grain growth is driven by the tendency to decrease the total boundary surface energy by decreasing thegrain boundary area.
- Large grains grow at the expense of smaller grains.



(b) (c) (d)

a)

Fig.1.1. (a) Work hardening, (b) recovery, (c) recrystallization, and (d) grain growth during annealing.

Grain Size Measurement

The 3 measuring methods:

1. Comparison charts.
2. Jeffries Planimetric Grain Size.
3. Heyn / Hilliard / Abrams Intercept method.

Comparison Method

The most simple and easy way to measure the average grain size is using the comparison charts. You only have to look on the eyepiece and compare the image you see there with the standard charts, that´s it. You can also use the grain size reticle on the eyepiece to have a more accurate comparison, because the grain size standard charts are printed in the reticle, and you can compare it while observing on the eyepiece. Is fast and easy, but is only for the average grain size, not for individual grains.

Jeffries Planimetric Grain Size

With this method you will know the Grain Size number from calculating the average of the grain area.

The measurement is done in 2 steps.

Step #1 is to calculate the average grain area in mm^2 you can do that counting the intercepted grains for the reference circle and counting the entire grains inside the reference circle.

Step #2 Calculate the ASTM Grain Size Number, using the value of the average area.

Calculate the average grain area in mm at 100x magnification. (N A = Number of grains per mm^2)

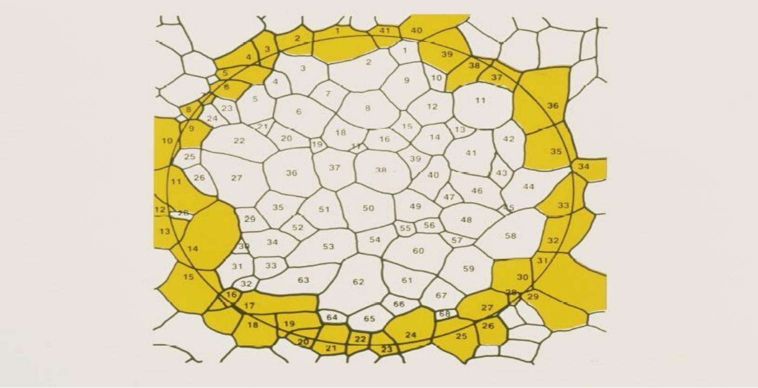
$N A = f (N_1 + (N_2 / 2))$

f= Jeffries multiplier

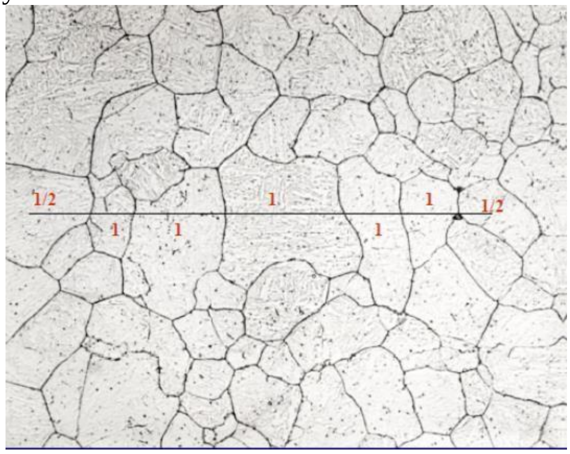
; f = Mag ^{2}/ circle area

N1= Number of grains completely inside the circle.

N2= Number of grains intercepting the circle.



Heyn / Hilliard / Abrams Intercept method
With these method, you have 2 ways to measure. Using a straight line you can calculate the grain size :
#1.- Counting the grains intercepted by the line.



#2-. Counting the grain boundary intersections

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:

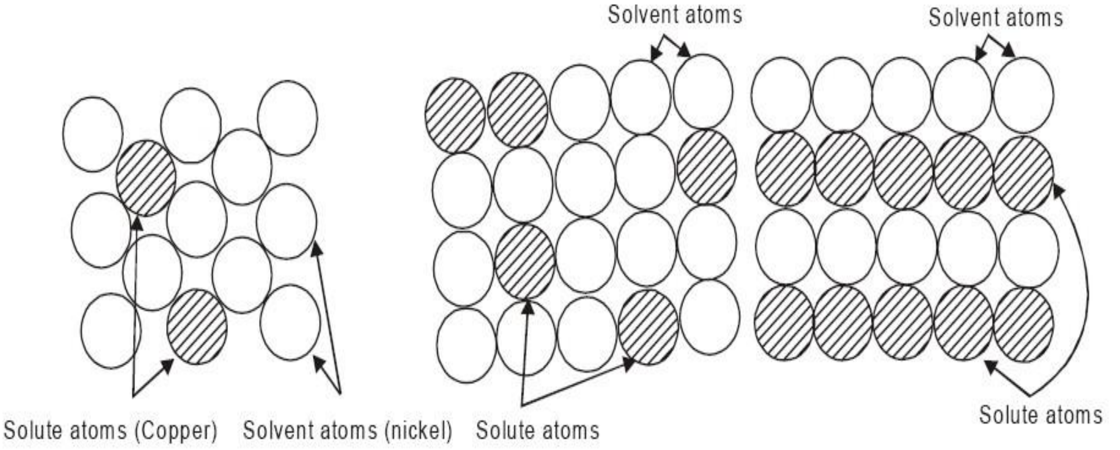
- Substitutional solid solution
- Interstitial solid solution

- **Substitutional solid solution:**
  - it means the atoms of B element i.e solute are substituted at the atomic sizes of A element i.e solvent.
  - Depending up on the distribution of B atoms in A, Substitutional solid solutionsare 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.

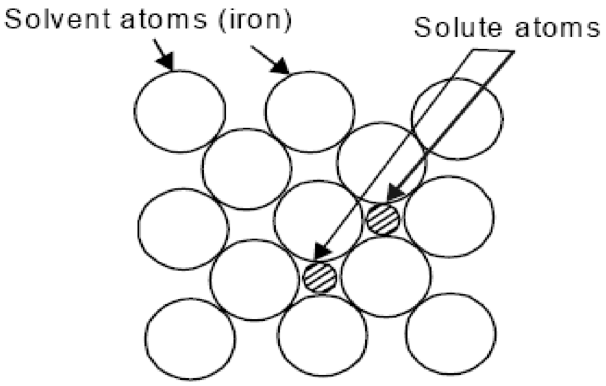
While there is no definite order or regularity in random solid solution.

- Au-Cu solid solution shows ordered structure upto 400^0C and disordered structureat high temperature.
- Complete regularity through the structure is possible only when two metals are mixed in some proportion like 1:1, 3:1 etc.
- Substitutional solid solution formation is favored if the atomic sizes of two metalsare nearly equal.
- Ordered substitutional solid solution alloys in general are hard and require more energy for plastic deformation than disordered substitutional solid solution alloys.



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

- **Interstitutional solid solution:**
  - In inter solid solutions; the atoms of B occupy the interstitial sites of A.
  - 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.
  - The elements which can form interstitial solid solution with iron are carbon, boron, oxygen, hydrogen, nitrogen.



- **Properties of solid solution**
  - Soft
  - Ductile

  - Malleable

- **Advantages of solid solution**
  - Easily cold rolled
  - 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:**
  - If the atomic sizes of solute and solvent differ by less than 15%, it is said to havea favorable size factor for solid solution formation.
  - If the atomic size difference exceeds 15%, solid solubility is limited.
- **Chemical affinity factor:**
  - 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:**
  - A metal of higher valency can dissolve only a small amount of a lower valency metal.
  - While the lower valency metal may have good solubility for the higher valency metal.
- **Crystal structure factor:**
  - Metals having same crystal structure will have greater solubility.
  - 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 ata lower temperature.

Phase Diagram

Introduction

- Phase diagrams are an important tool in the armory of an materials scientist
- In the simplest sense a phase diagram demarcates regions of existence of various phases. (*Phase diagrams are maps)*
- Phase diagrams are also referred to as “equilibrium diagrams” or “constitutional diagrams”. This usage requires special attention: through the term used is “equilibrium”, in practical terms the equilibrium is *not global equilibrium but Microstructural level equilibrium.*
- Broadly two kinds of phase diagrams can be differentiated*→ those involving time and those which do not involve time.
- In this chapter we shall deal with the phase diagrams not involving time.
  - This type can be further sub classified into:
  - Those with composition as a variable (e.g. T vs. %Composition)
  - Those without composition as a variable (e.g. P vs. T)
- Time-Temperature-Transformation (TTT) diagrams and Continuous-Cooling-Transformation (CCT) diagrams involve time.

Components of a system

- Independent chemical species which comprise the system. These could be Elements, Ions,

CompoundsExample: Au-Cu system : Components →Au, Cu (elements)

Ice-water system : Component→H_2O

(compound)Al_2O_3-Cr_2O_3 system :

Components→Al_2O_3, Cr_2O_3

Phase

- A physically homogeneous and distinct portion of a material system (e.g. gas, crystal, amorphous…)
- Gases : Gaseous state always a single phase→ mixed at atomic or molecule level.
- Liquids: Liquid solution is a single phase→ e.g. Nacl in H_2O and Liquid mixtures consists of two or more phases → e.g. Oil in water (*no mixing at the atomic level)*
- Solids: In general due to several compositions and crystals structures many phases are possible.

  - For the same composition different crystal structures represent different phases. E.g. *Fe (BCC)and Fe (FCC)* are different phases

What kinds of phases exist?

- Based on state → Gas, Liquid, Solid
- Based on atomic order → Amorphous, Quasi-crystalline, Crystalline
- Based on band structure → Insulating, Semi-conducting, Semi-metallic, Metallic
- Based on Property → Para-electric, Ferromagnetic, Superconducting
- Based on stability→ Stable, Metastable, Unstable
- Also sometimes- Based on size/geometry of an entity→ Nanocrystalline, mesoporous, layered.

Phase transformation

- Phase transformation is the change of one phase into another. For example
  - ✓ Water → Ice and α-Fe (BCC) → γ-Fe (FCC)

Grain

- The single crystalline part of polycrystalline metal separated by similar entities by a grain boundary

Solute

- The component of either a liquid or solid solution that is present to a lesser or minor extent; the component that is dissolved in the solvent.

Solvent

- The component of either a liquid or solid solution that is present to a greater or major extent; the component that dissolves the solute.

System

- System has two meanings. First, ‘‘system’’ may refer to a specific body of material or object. Or, it may relate to the series of possible alloys consisting of the same components, but without regard to alloy composition.

Solubility Limit

- For many alloy systems and at some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution; this is called a Solubility Limit.

Microstructure

- (Phases + defects + residual stress) & their distributions

- Structures requiring magnifications in the region of 100 to 1000 times. (or) The distribution of phasesand defects in a material.

Phase diagram

- Map that gives relationship between phases in equilibrium in a system as a function of T, P andcomposition. *Map demarcating regions of stability of various phases*

Variables/Axis of phase diagrams

- The axes can be:
    - Thermodynamic (T, P, V)
    - Kinetic (t) or Composition variables (C, %X)
- In single component systems (unary systems) the usual variables are T & P
- In phase diagrams used in materials science the usual variable are T & %X
- In the study of phase transformation kinetics TTT diagrams or CCT diagrams are also used where theaxis are T & t

System Components

Phase diagrams and the systems they describe are often classified and named for the number (in Latin) of components in the system:

Number of components	**Name of system or diagram**
One	Unary
Two	Binary
Three	Ternary
Four	Quaternary
Five	Quinary
Six	Sexinary
Seven	Septenary
Eight	Octanary
Nine	Nonary
Ten	Decinary

Experimental Methods

Thermal Analysis: A plot is made of temperature vs. time, at constant composition, the resulting cooling curve will show a change in slope when a phase change occurs because of the evolution of heat by the phase change. This method seems to be best for determining the initial and final temperature of solidification. Phase changes occurring solely in the solid state generally involve only small heat changes, and other methods give more accurate results.

Metallographic Methods: This method consists in heating samples of an alloy to different temperatures, waiting for equilibrium to be established, and then quickly cooling to retain their high temperature structure. The samples are then examined microscopically. This method is difficulty to apply to metals at high temperatures because the rapidly cooled samples do not always retain their high temperature structure, and considerable skill is then required to interpret the observed microstructure correctly.

X-ray diffraction: Since this method measures lattice dimensions, it will indicate the appearance of a new phase either by the change in lattice dimension or by the appearance of a new crystal structure. This method is simple, precise, and very useful in determining the changes in solid solubility with temperature.

Gibbs Phase Rule

- The phase rule connects the Degrees of Freedom, the number of components in a system and the numberof phases present in a system via a simple equation.
- To understand the phase rule one must understand the variables in the system along with the degrees of freedom.
- We start with a general definition of the phrase "degrees of freedom".

Degrees of Freedom: The degree of freedom, F, are those externally controllable conditions of temperature, pressure, and composition, which are independently variable and which must be specified in order to completely define the equilibrium state of the system.

For a system in equilibrium

$$F = C - P + 2$$

or

$$F - C + P = 2$$

F – Degrees of Freedom
C – Number of Components
P – Number of Phases

The degrees of freedom cannot be less than zero so that we have an upper limit to the number of phases that canexist in equilibrium for a given system.

Variables in a phase diagram

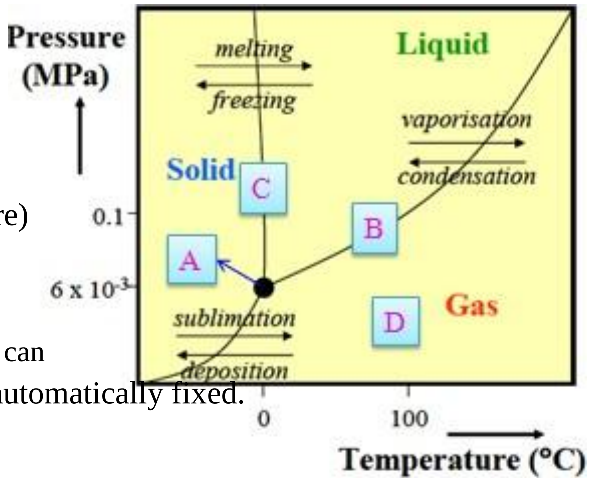
- C – No. of components
- P – No. of phases
- F – No. of degrees of freedom
- Variables in the system = Composition variables + Thermodynamic variables
- Composition of a phase specified by (C – 1) variables (*If the composition is expressed in %ages then the total is 100% → there is one equation connecting the composition variables and we need to specify only (C - 1) composition variables)*
- No. of variables required to specify the composition of all phases: P(C – 1) (*as there are P phases and each phase needs the specification of (C – 1) variables*)

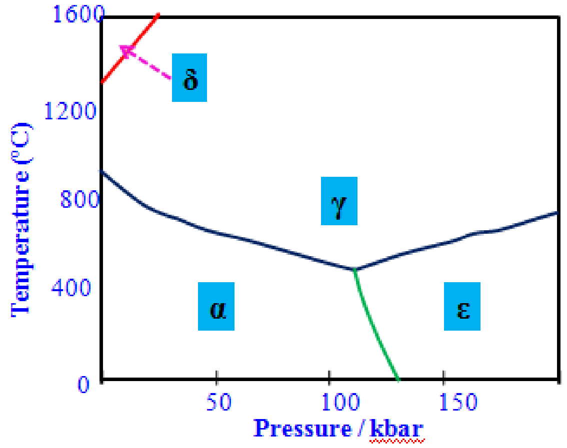
- Thermodynamic variables = P + T (usually considered) = 2 (*at constant pressure (e.g. atmosphericpressure) the thermodynamic variable becomes 1)*
- Total no. of variables in the system = P (C – 1) + 2
- F < no. of variables → F < P (C – 1) + 2For a system in equilibrium the chemical potential of eachspecies is same in all the phases
- If α, β, γ… are phases, then: $\mu_A(\alpha) = \mu_A(\beta) = \mu_A(\gamma)$…..
- *Suppose there are 2 phases (α and β phases) and 3 components (A, B, C) in each phase then :* $\mu_A(\alpha) = \mu_A(\beta)$, $\mu_B(\alpha) = \mu_B(\beta)$, $\mu_C(\alpha) = \mu_C(\beta)$ *→ i.e. there are three equations. For each component there are (P – 1) equations and for C components the total number of equations is C(P – 1). In the above example the number of equations is 3(2 – 1) = 3 equations.*
- F = (Total number of variables) – (number of relations between variables)
- = [P(C – 1) + 2] – [C(P – 1)] = C – P + 2
- *In a single phase system F = Number of variables*
- P↑ → F↓ (For a system with fixed number of components as the number phases increases the degrees of freedom decreases.

Unary Phase Diagram

- Let us start with the simplest system possible: the unary system wherein there is just one component.
- Though there are many possibilities even in unary phase diagram (in terms of the axis and phases), weshall only consider a T-P unary phase diagram.
- Let us consider the water (H_2O) unary
- Phase diagram
- The Gibbs phase rule here is: F=C-P+2
- (2 is forT&P) (no composition variables here)
- Along the 2 phase co-existence (at B & C)

  Lines the degree of freedom (F) is 1→ i.e. we can choseeither T or P and the other will beautomatically fixed.
- The 3 phase co-existence points (at A) are
- Invariant points with F=0. (Invariant point implies They arefixed for a given system).
- The single phase region at point D, T and P can both be varied while still being in the single phaseregion with F = 2.

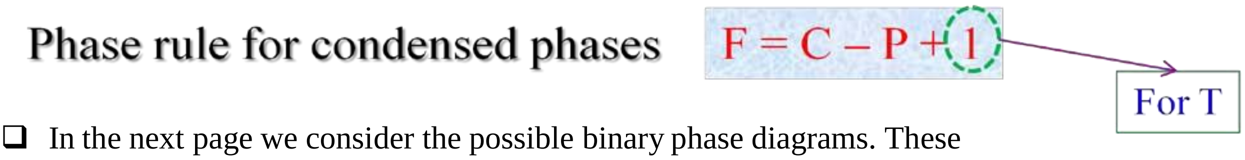




- The above figure represents the phase diagram for pure iron. The triple point temperature and pressure are 490ºC and 110 kbars, respectively. α, γ and ε refer to ferrite, austenite and ε-iron, respectively. δ is simply the higher temperature designation of α.

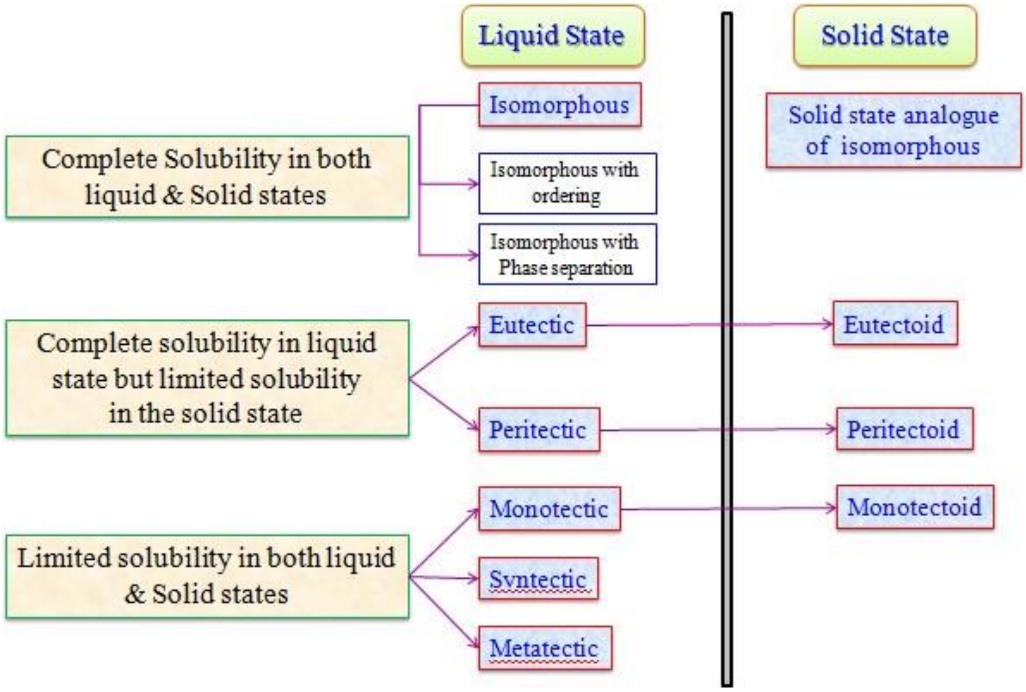
Binary Phase Diagram

- Binary implies that there are two components.
- Pressure changes often have little effect on the equilibrium of solid phases (unless of course weapply ‘huge’ pressures).
- Hence, binary phase diagrams are usually drawn at 1 atmosphere pressure.
- The Gibbs phase rule is reduced to:
- Variables are reduced to : $F = C - P + 1$ *(1 is for T).*
- T & Composition (*these are the usual variables in materials phase diagrams)*


Phase rule for condensed phases $F = C - P + 1$

For T

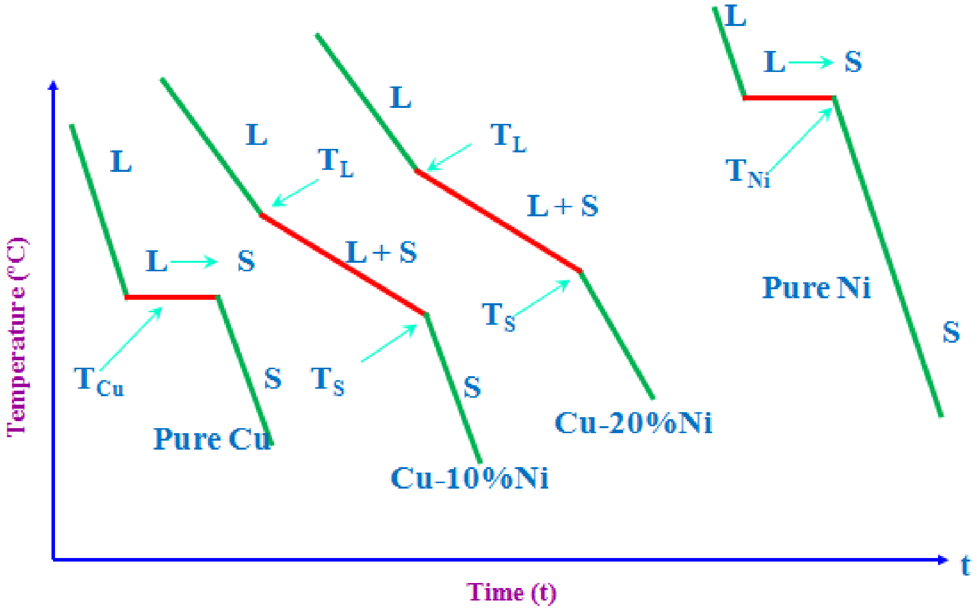
- In the next page we consider the possible binary phase diagrams. These havebeen classified based on:
  - ✓ Complete solubility in both liquid & solid states
  - ✓ Complete solubility in both liquid state, but limited solubility in the solid state
  - ✓ Limited solubility in both liquid & solid states



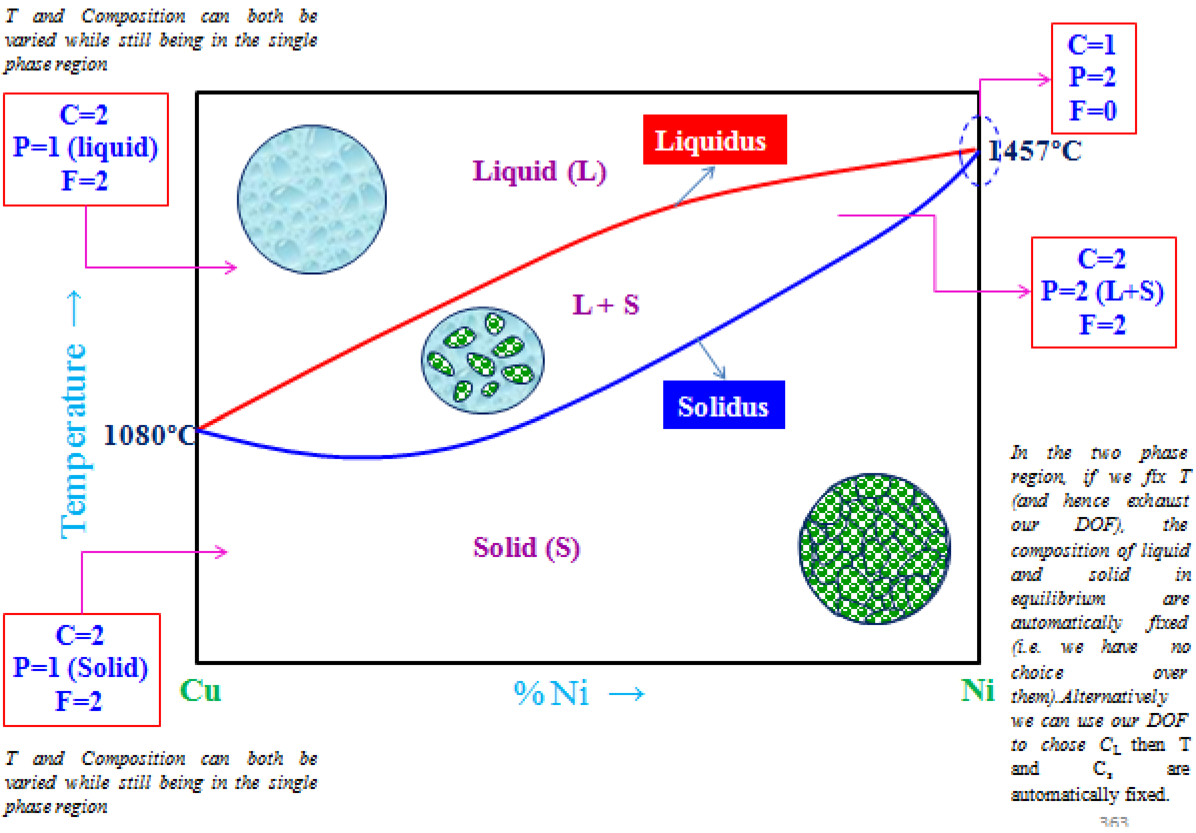
Isomorphous Phase Diagram

- Isomorphous phase diagrams form when there is complete solid and liquid solubility.
- Complete solid solubility implies that the crystal structure of the two components have to besame and Hume-Rothery rules to be followed.
- Examples of systems forming isomorphous systems: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3-Cr_2O_3
- Both the liquid and solid contain the components A and B.
- In binary phase diagrams between two single phase regions there will be a two phase region→ In the isomorphous diagram between the liquid and solid state there is the (Liquid + Solid) state.
- The Liquid + Solid state is NOT a semi-solid state→ it is a solid of fixed composition andstructure, in equilibrium with a liquid of fixed composition.
- In some systems (e.g. Au-Ni system) there might be phase separation in the solid state (i.e.,thecomplete solid solubility criterion may not be followed→ these will be considered as a variation of the isomorphous system (with complete solubility in the solid and the liquid state.

Cooling curves: Isomorphous system



Isomorphous Phase Diagram



T and Composition can both be varied while still being in the single phase region

T and Composition can both be varied while still being in the single phase region

In the two phase region, if we fix T (and hence exhaust our DOF), the composition of liquid and solid in equilibrium are automatically fixed (i.e. we have no choice over them). Alternatively we can use our DOF to chose C_L then T and C_s are automatically fixed.

Tie line and Lever rule

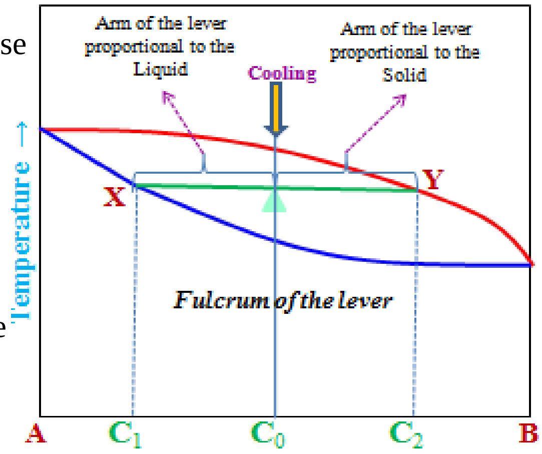
Chemical Composition of Phases: To determine the actual chemical composition of the phases of an alloy, in equilibrium at any specified temperature in a two phase region, draw a horizontal temperature line, called a *tie line*, to the boundaries of the field . These points of intersection are dropped to the base line, and the composition is read directly.

Relative Amounts of Each Phase:

- To determine the relative amounts of the two phases in equilibrium at any specified temperature in a twophase region, draw a vertical line representing the alloy and a horizontal temperature line to the boundaries of the field.
- The vertical line will divide the horizontal line into two parts whose lengths are inversely proportional tothe amount of the phases present. This is also known as *Lever rule.*
- The point where the vertical line intersects the horizontal line may be considered as the *fulcrum* of a lever system.
- The relative lengths of the lever arms multiplied by the amounts of the phases present must balance.

Tie line and Lever rule

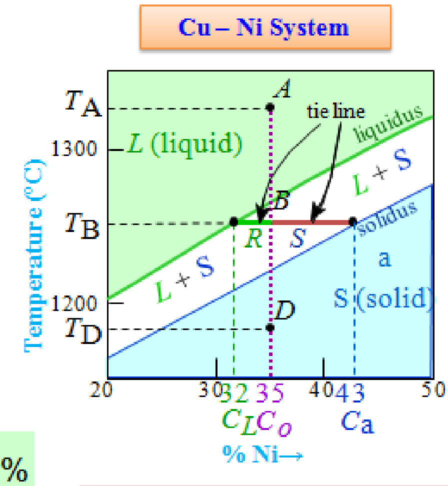
- We draw a horizontal line (called the Tie Line)at the temperature of interest (say T_0). Let Tie line is XY.
- Solid (crystal) of composition C_1 coexists with liquid of composition C_2
- Note that tie lines can be drawn only in the two phase Coexistence regions (fields). Though they may be extended to mark the temperature.
- To find the fractions of solid and liquid we use leverrule.
- The portion of the horizontal line in the two phase region is akin to 'lever' with the fulcrum at the nominal composition (C_0)
- The opposite arms of the lever are proportional to the fraction of the solid and liquid phase present (this is lever rule).



$$f_{liquid} = \frac{C_0 - C_1}{C_2 - C_1}$$

$$f_{Solid} = \frac{C_2 - C_0}{C_2 - C_1}$$

Example



At C_O = 35 wt% Ni

At T_A: Only Liquid (L)

W_{liquid} = 100 wt%, W_{solid} = 0

At T_D: Only Solid (S)

W_L = 0, W_{solid} = 100 wt%

At T_B: Both S and L

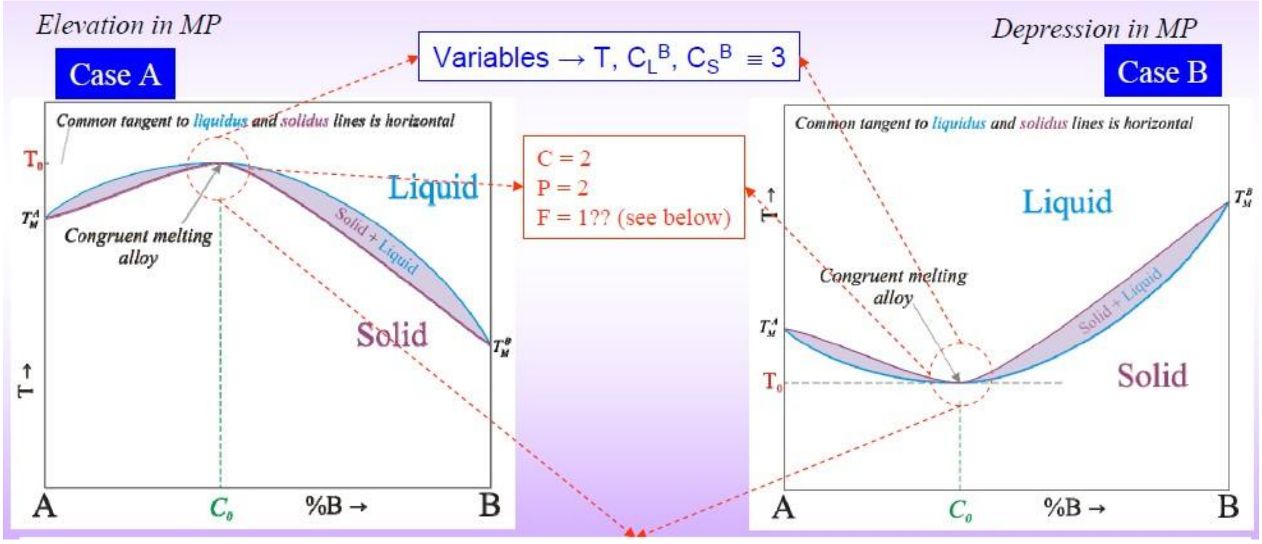
$$\boxed{W_L = \frac{S}{R+S}} = \frac{43-35}{43-32} = 73 wt\%$$

$$\boxed{W_S = \frac{R}{R+S}} = 27 \text{ wt\%}$$

Notice: as in a lever "the opposite leg" controls with a balance (fulcrum) at the 'base composition' and R+S = tie line length = difference in composition limiting phase boundary, at the temp of interest

Variations of Isomorphous System

An alloy typically melts over a range of temperatures. However, there are special compositions which can melt at a single temperature like a pure metal. There is no difference in the liquid and solid composition. It begins and ends solidification at a constant temperature with no change in composition, and its cooling curve will show a horizontal line. Such alloys are known as a **congruent-melting alloys,** sometimes known as a **pseudo- eutectic alloy.** Ex: Cu-Au, Ni-Pd.

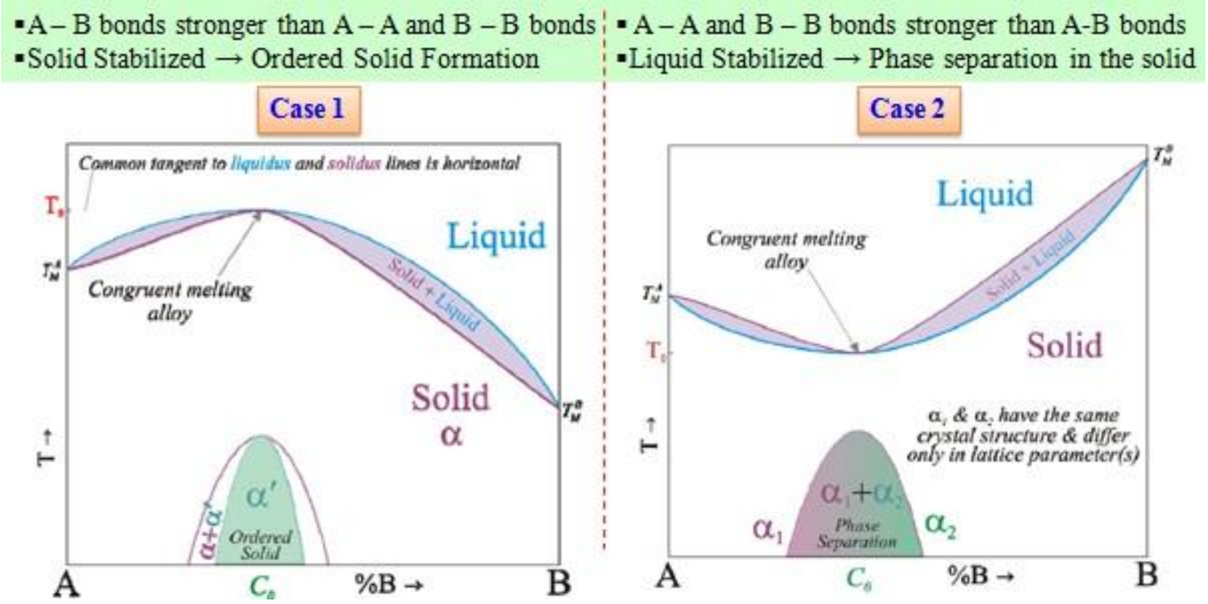


- ❑ Congruently melting alloys → just like a pure metal
- ❑ Is the DOF 1? No: in requiring that $C_L^B = C_S^B$ we have exhausted the degree of freedom. Hence T is automatically fixed→ DOF is actually Zero..!

Variations of Isomorphous System

- Elevation in the MP means that the solid state is 'more stable' (*crudely speaking the ordered state ismore stable*) → ordering reaction is seen at low T.

- Depression in MP 'means' the liquid state (disordered) is more stable→ phase separation is seen at low T. (*phase separation can be thought of as the opposite of ordering. Ordering (compound formation)occurs for –ve values for* ΔH_{mix}).



Equilibrium Cooling

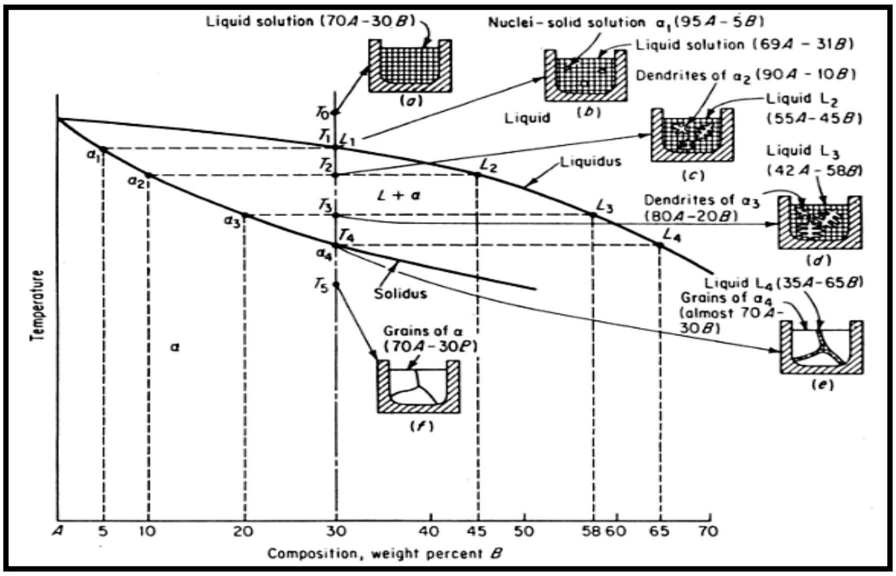


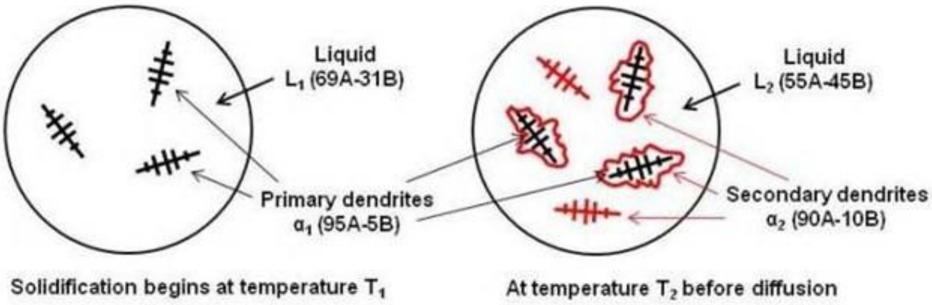
Figure: The above figure represents the very slow cooling, under equilibrium conditions, of a particularalloy 70A-30B will now be studied to observe the phase changes that occur

- This alloy at temperature T_0 is a homogeneous single-phase liquid solution (*a*) and remains so until temperature $T_1$is reached. Since $T_1$is on the liquidus line, freezing or solidification now begins.

- The first nuclei of solid solution to form α_1 will be very rich in the higher melting point metal A and will be composed of 95A-5B (*by tie line rule).* Since the solid solution in forming takes material very rich in A from the liquid, the liquid must get richer in B. Just after the start of solidification, the composition of the liquid is approximated as 69A-31B (b).

- When the lower temperature T_2 is reached, the liquid composition is at L_2. The only solid solution in equilibrium with L_2 and therefore the only solid solution forming at T_2 is α_2. Applying tie line rule, α_2 is composed of 10B. Hence, as the temperature is decreased, not only does the liquid composition become richer in B but also the solid solution.

- At T_2 ,crystals of α_2 are formed surrounding the α_1 composition cores and also separate dendrites of α_z
  (*see figure in below).*



Solidification begins at temperature T_1 At temperature T_2 before diffusion

Schematic Representation of the Alloy 70A-30B at Temperatures T_1 and T_2

- In order for equilibrium to be established at T_2, the entire solid phase must be a composition α_2. This requires diffusion of B atoms to the A-rich core not only from the solid just formed but also from the liquid. This is possible in crystal growth (c).

- The composition of the solid solution follows the solidus line while the composition of liquid followsthe liquidus line, and both phases are becoming richer in B.

- At T_3 (d), the solid solution will make up approximately three-fourths of all the material present.

- Finally, the solidus line is reached at T_4, and the last liquid L_4, very rich in B, solidifies primarily at the grain boundaries (e).

- However, diffusion will take place and all the solid solution will be of uniform composition α(70A-30B), which is the overall composition of the alloy (f).

- There are only grains and grain boundaries. There is no evidence of any difference in chemical composition inside the grains, indicating that diffusion has made the grain homogeneous.

- The very slow cooling , under equilibrium conditions, of particular alloy 65Cu - 35Ni will now be studied.

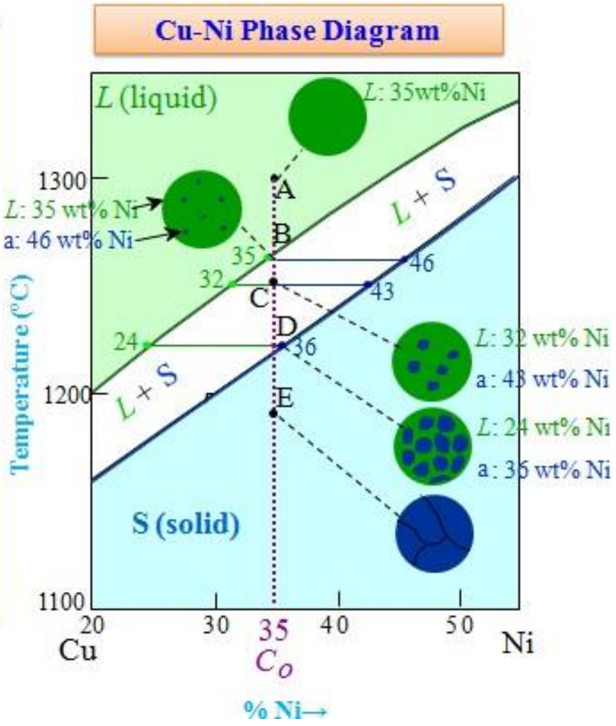
  A – Homogeneous single phase (Liquid)

  B - ‘B’ is on the liquidus line, solidification now begins.

  C – Solid surrounded by liquid crystals.

  D – ‘D’ is on the solidus line, solidification now ends.

  E – Homogeneous single phase (Solid)

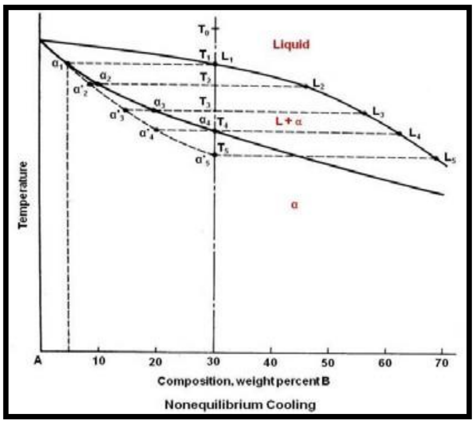


Non Equilibrium Cooling - Coring

- In actual practice it is extremely difficult to cool under equilibrium conditions. Since diffusion in the solid state takes place at a very slow rate, it is expected that with ordinary cooling rates there will be some difference in the conditions as indicated by the equilibrium diagram.

- Consider again 70A-30B alloy, solidification starts atT_1 forming a solid solution of composition α_1 .

- At T_2 the liquid is L_2 and the solid solution now Forming is of composition α_2 . Since diffusion is too slow To keep pace with crystal growth, not enough time will Be allowed to achieve uniformity in the solid, and average composition will be between α_1 and α_2,



- As the temperature drops, the average composition of the solid solution will depart still further from equilibrium conditions. It seems that the composition of the solid solution is following a “nonequilibrium” solidus line α_1 to α'_5, shown dotted lines in figure.

- The liquid, on the other hand, has essentially the composition given by the liquidus line, since diffusion is relatively rapid in liquid. At T_3 the average solid solution will be of composition α'_3 instead of α_3.

- Under equilibrium cooling, solidification should be complete at T_4 ; however, since the average composition of the solid solution α'_4 has not reached the composition of the alloy, some liquid must still remain. Applying lever rule at T_4 gives $\alpha'_4 = 75\%$ and $L_4 = 25\%$.

- Therefore, solidification will continue until T_5 is reached. At this temperature the composition of the solid solution α'_5 coincides with the alloy composition, and solidification is complete. The last liquid to solidify, L_5, is richer in B than the last liquid to solidify under equilibrium conditions.

- *The more rapidly the alloy is cooled the greater will be the composition range in the solidified alloy. Since the rate of chemical attack varies with composition, proper etching will reveal the dendritic structure microscopically (see below figure). The final solid consists of a "cored" structure with a higher-melting central portion surrounded by the lower-melting, last-to-solidify shell. The above condition is referred to as coring or dendritic segregation.*

- To summarize, nonequilibrium cooling results in an increased temperature range over which liquid andsolid are present; Since diffusion has not kept pace with crystal growth, there will be a difference in chemical composition from the center to the outside of the grains. The faster the rate of cooling, the greater will be the above effects.

Eutectic Phase Diagram

- Very few systems exhibit an isomorphous phase diagram (usually the solid solubility of one component in another is limited).

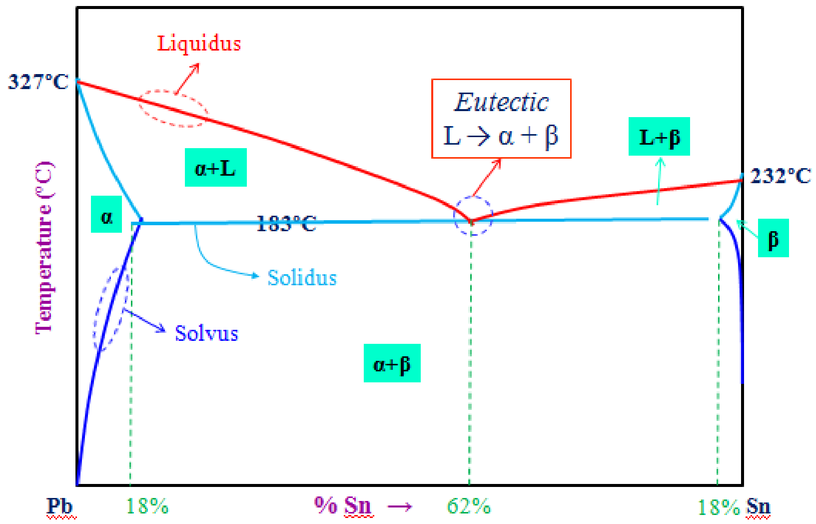
- Often the solid solubility is severely limited – through the solid solubility is never zero (due to entropic reasons).

- In a Simple eutectic system (binary), there is one composition at which the liquid freezes at a single temperature. This is in some sense similar to a pure solid which freezes at a single temperature (unlike a pure substance the freezing produces a two solid phases both of which contain both the components).

- The term Eutectic means easy melting→ The alloy of eutectic composition freezes at a lower temperature than the melting point s of the constituent components.

- *This has important implifications→ e.g. the Pb -Sn eutectic alloy melts at 183 ºC, which is lower than the melting points of both Pb (327ºC) and Sn (232ºC)→ Can be used for soldering purposes (as we want to input least amount of heat to solder two materials).*

- In the next page we consider the Pb-Sn eutectic phase diagram.

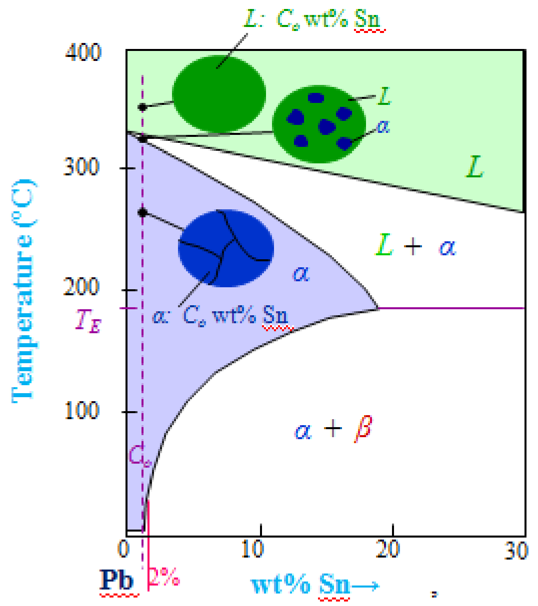


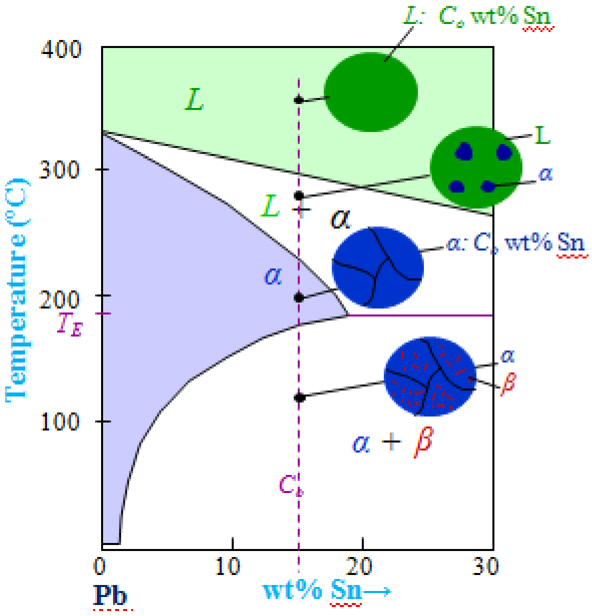
Eutectic reaction at 183°C

L → α + β

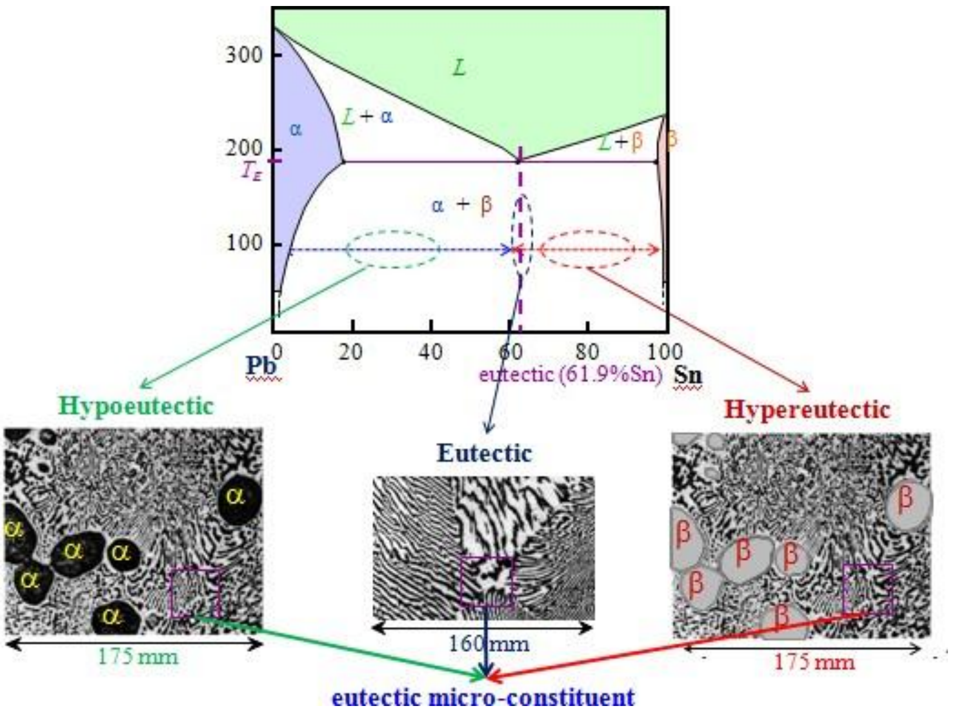
62%Sn → 18%Sn + 97%Sn

Microstructural Characteristics of Eutectic System





- ❑ To reiterate an important point: Phase diagram do not contain microstructural information (i.e. they cannot tell you what the microstructures produced by cooling is. Often microstructural information is overlaid on phase diagram for convenience. Hence, strictly cooling is not in the domain of phase diagram – but we can overlay such information keeping in view the assumptions involved.



Application of Lever rule in Eutectic System

Solved Example

For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find the phases present: α and Liquid, Composition of phases

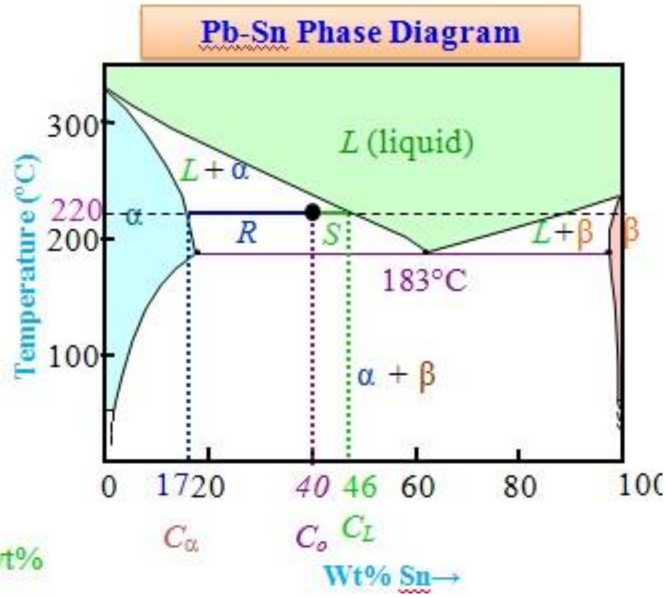
$C_O = 40$ wt% Sn
$C_\alpha = 17$ wt% Sn
$C_L = 46$ wt% Sn

The relative amount of each phase by using lever rule

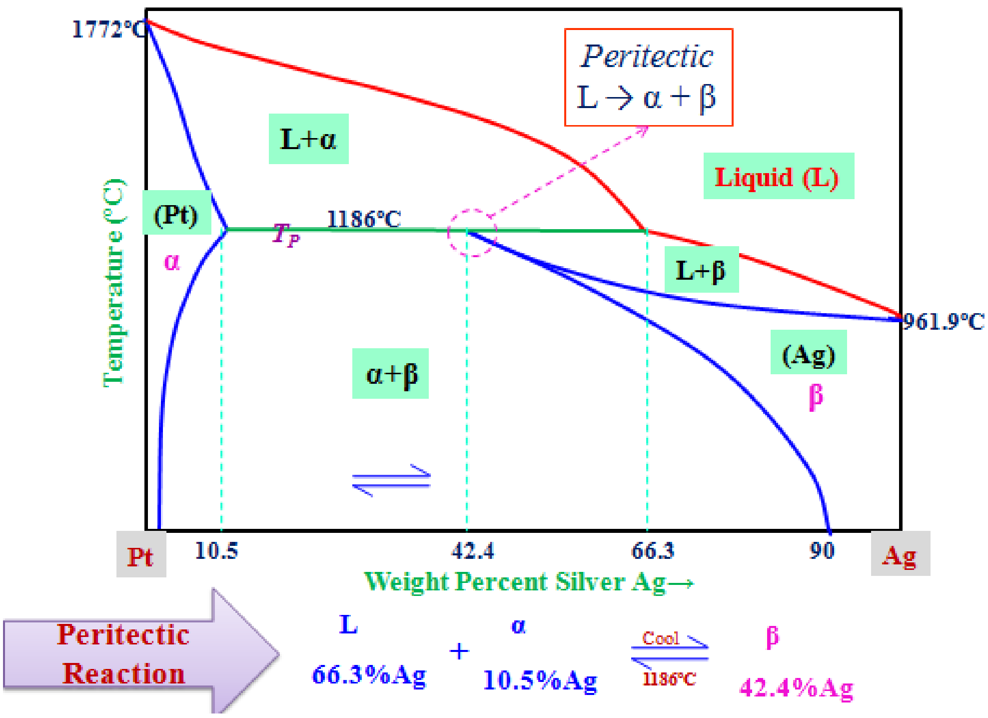
$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$

$$= \frac{6}{29} = 21 \text{ wt\%}$$

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



Peritectic Phase Diagram



- Like the eutectic system, the Peritectic reaction is found in systems with complete liquid solubility but limited solid solubility.

- In the Peritectic reaction the liquid (L) reacts with one solid (α) to produce another solid (β). L+α → β

- Since the solid β forms at the interface between the L and the α, further reaction is dependent on solid state diffusion. Needless to say this becomes the rate limiting step and hence it is difficult to ‘equilibrate’ peritectic reactions (as compared to say eutectic reactions).

- In some Peritectic reactions (e.g. the Pt-Ag system – previous page). The (pure) β phase is not stable below the Peritectic temperature (T_P = *1186* °C for Pt- Ag system) and splits into a mixture of (α+β) just below T_P.

Monotectic Phase Diagram

- In all the types discussed previously, it was assumed that there was complete solubility in the liquid state. It is quite possible, however, that over a certain composition range two liquid solutions are formedthat are not soluble in each other.

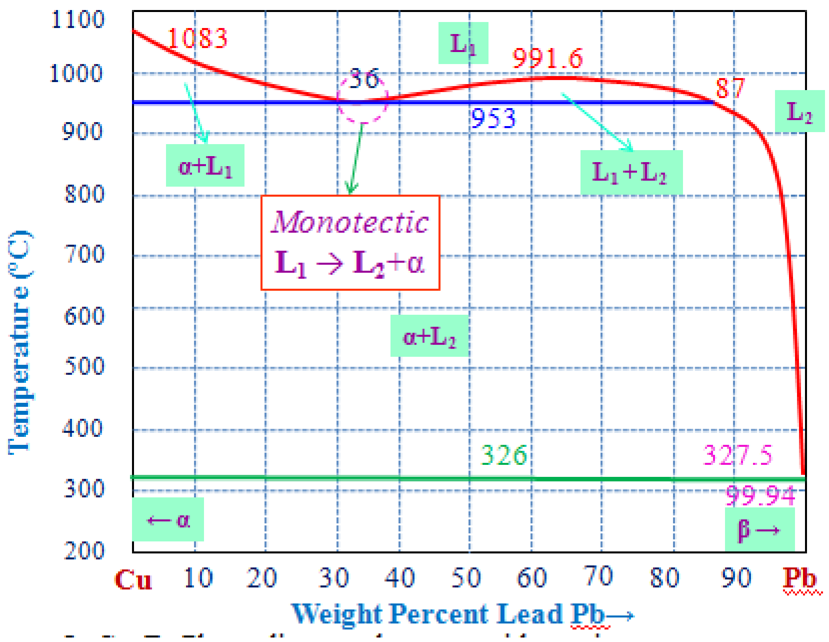
- Another term for solubility is miscibility. Substances that are not soluble in each other, such as oil and water, are said to be immiscible. Substances that are partly soluble in each other are said to show a miscibility gap, and this is related to Monotectic Systems.

- When one liquid forms another liquid, plus a solid, on cooling, it is known as a *Monotectic Reaction.*

- It should be apparent that the Monotectic reaction resembles the eutectic reaction, the only difference being that one of the products is a liquid phase instead of a solid phase.

- *An* example of an alloy system showing a Monotectic reaction is that between *copper and lead* given innext page. Notice that in this case the $L_1 + L_2$ is closed.

- Also, although the terminal solids are indicated as α and β, the solubility is actually so small that theyare practically the pure metals, copper and lead.



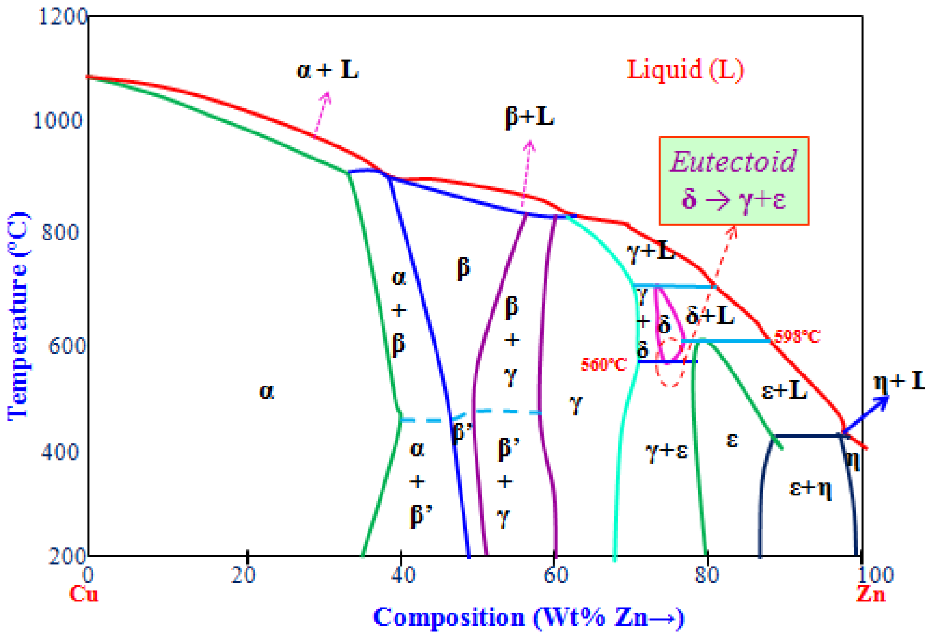
The Eutectoid Reaction

- This is a common reaction in the solid state. It is very similar to the eutectic reaction but does not involve the liquid . In this case, a solid phase transforms on cooling into two new solid phases. Thegeneral equation may be written as..!

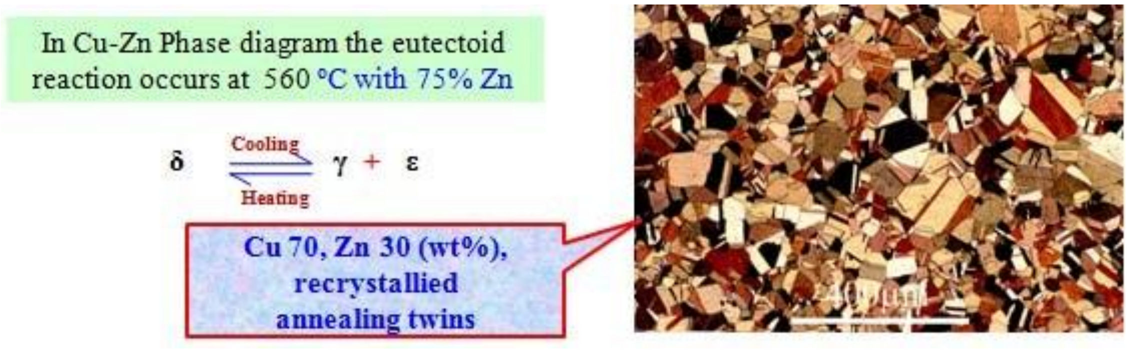
- The resultant Eutectoid mixture is extremely fine, just like the eutectic mixture. Under the microscope both mixtures generally appear the same, and it is not possible to determine microscopically whether themixture resulted from a eutectic reaction or eutectoid reaction.

- An equilibrium diagram of Cu-Zn, illustrating the eutectoid reaction is shown in figure.

- In copper (Cu) – Zinc (Zn) system contains two terminal solid solutions i.e. these are extreme ends ofphase diagram α and η, with four intermediate phases called β, γ, δ and ε. The β' phase is termed an ordered solid solution, one in which the copper and zinc atoms are situated in a specific and ordered arrangement within each unit cell.



- In the diagram, some phase boundary lines near the bottom are dashed to indicate that there positions have not been exactly determined. The reason for this is that at low temperatures, diffusion rates are very slow and inordinately long times are required for the attainment of equilibrium.
- Again only single- and two- phase regions are found on the diagram, and the same and we can utilize the lever rule for computing phase compositions and relative amounts.
- The commercial material brasses are copper-rich copper-zinc alloys: for example, cartridge brass has a composition of 70 wt% Cu-30 wt% Zn and a microstructure consisting of a single α phase.



In Cu-Zn Phase diagram the eutectoid reaction occurs at 560 °C with 75% Zn

$$\delta \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \gamma + \varepsilon$$

Cu 70, Zn 30 (wt%), recrystallied annealing twins

The Peritectoid Reaction

- This is a fairly common reaction in the solid state and appears in many alloy systems. The peritectoid reaction may be written as

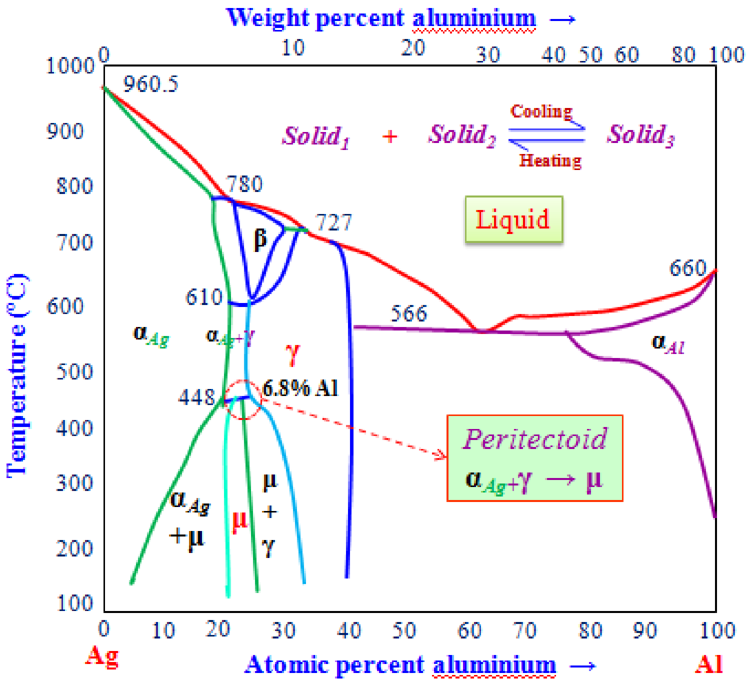
$$Solid_1 + Solid_2 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} Solid_3$$

- The new solid phase is usually an intermediate alloy, but it may also be a solid solution .The peritectoid reaction has the same relationship to the peritectic reaction as the eutectoid has to the eutectic. Essentially, it is the replacement of a liquid by a solid.

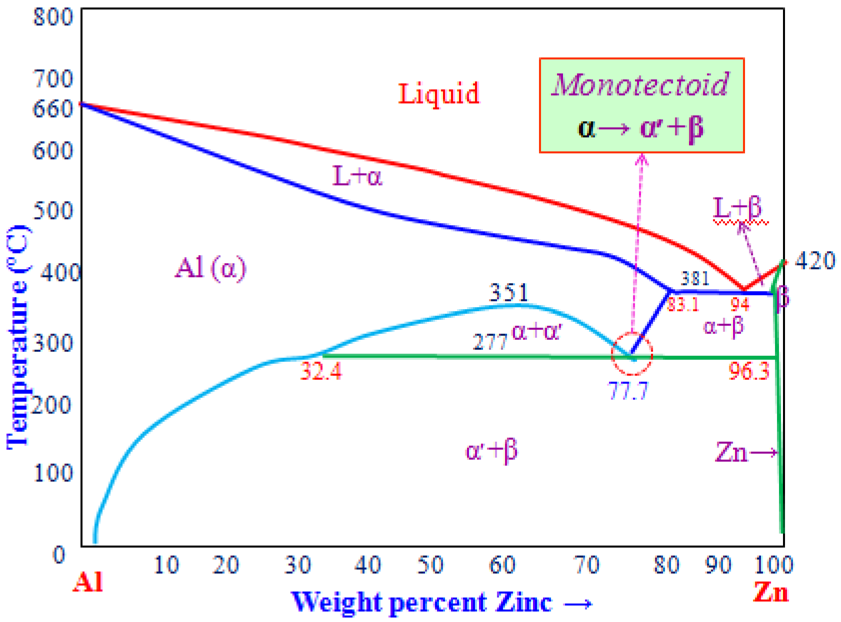
- The peritectoid reaction occurs entirely in the solid state and usually at lower temperatures than the peritectic reaction, the diffusion rate will be slower and there is less likelihood that equilibrium structures will be reached.

- Consider Silver (Ag) – Aluminium (Al) phase diagram (*in next page*) containing a peritectoid reaction.

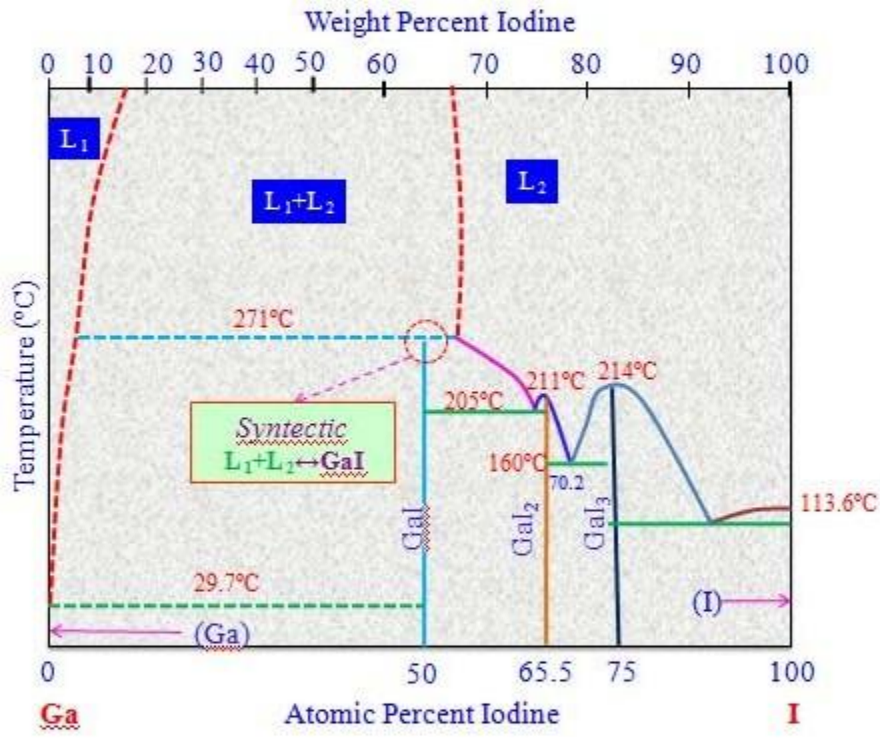
- If a 7% Al alloy is rapidly cooled from the two phase area just above the peritectoid temperature the twophases will be retained, and the microstructure will show a matrix of γ with just a few particles of α. When we cool at below the peritectoid temperature by holding we get single phase μ.



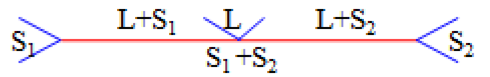
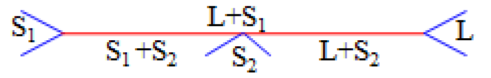
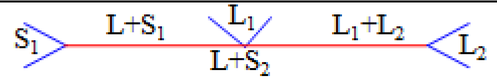
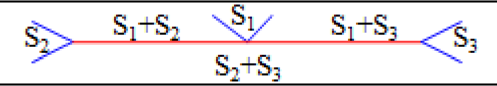
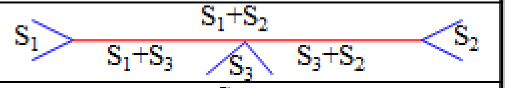
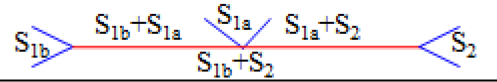
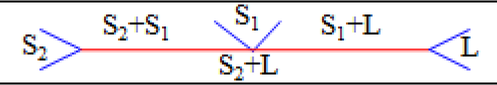
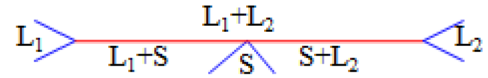
Monotectoid Reaction : Al-Zn Phase Diagram



Syntectic Reaction : Ga – I Phase Diagram

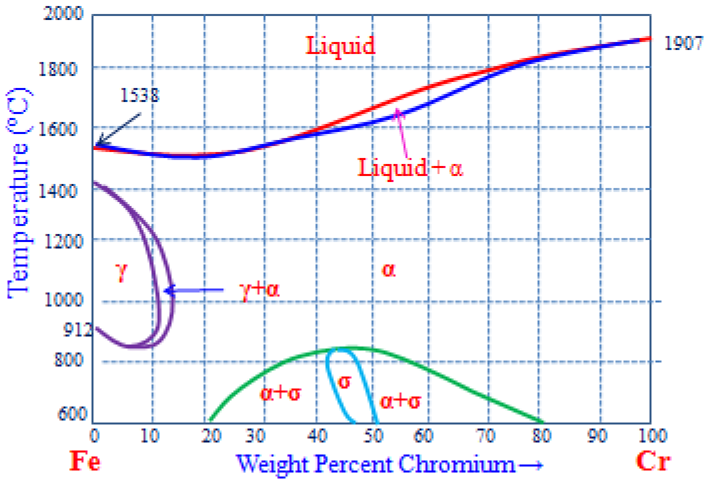


Summary of Invariant reactions

Name of reaction	Phase equilibrium	Schematic representation
Eutectic	$L \leftrightarrow S_1 + S_2$	
Peritectic	$S_1 + L \leftrightarrow S_2$	
Monotectic	$L_1 \leftrightarrow S_1 + L_2$	
Eutectoid	$S_1 \leftrightarrow S_2 + S_3$	
Peritectoid	$S_1 + S_2 \leftrightarrow S_3$	
Monotectoid	$S_{1a} \leftrightarrow S_{1b} + S_2$	
Metatectic	$S_1 \leftrightarrow S_2 + L$	
Syntectic	$L_1 + L_2 \leftrightarrow S$	

Allotropic Transformations

- As we discussed earlier that several metals may exist in more than one type of crystal structure depending upon temperature , Iron, Tin, Manganese and Cobalt are examples of metals which exhibit this property , known as *Allotropy*.
- On an equilibrium diagram, this allotropic change is indicated by a point or points on the vertical line which represents the pure metal. This is illustrated in below figure. In this diagram, the gamma solid solution field is 'looped'. The pure metal Fe and alloys rich in Fe undergo two transformations.



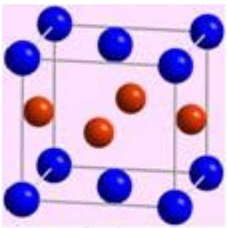
Order-disorder Transformations

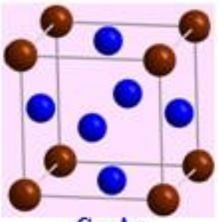
- Ordinarily in the formation of substitutional type of solid solution the solute atoms do not occupy any specific position but are distributed at random in the lattice structure of the solvent. The alloy is said to be in a 'disordered' condition.

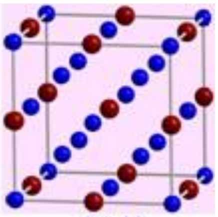
- Some of these random solid solutions, if cooled slowly, undergo a rearrangement of the atoms where the solute atoms move into definite positions in the lattice. This structure is known as an *ordered solid solution or superlattice.*

- Ordering is most common in metals that are completely soluble in the solid state, and usually the maximum amount of ordering occurs at a simple atomic ratio of the two elements.

- For this reason, the ordered phase is sometimes given a chemical formula, such as AuCu and $AuCu_3$ in the gold-copper alloy system. On the equilibrium diagram, the ordered solutions are frequently designated as α', β', etc. or α ,′α , ′etc., and the area in which they are found is usually bounded by a dot-dash line.


CuAu


Cu_3Au


Fe_3Al

- When the ordered phase has the same lattice structure as the disordered phase, the effect of ordering on mechanical properties is negligible. Hardening associated with the ordering process is most pronounced in those systems where the shape of the unitcell is changed by ordering.

- Regardless of the structure formed as a result of ordering, an important property change produced, even in the absence of hardening, is a significant reduction in electrical resistance. Notice the sharp decrease in electrical resistivity at the compositions which correspond to the ordered phases AuCu and $AuCu_3$.

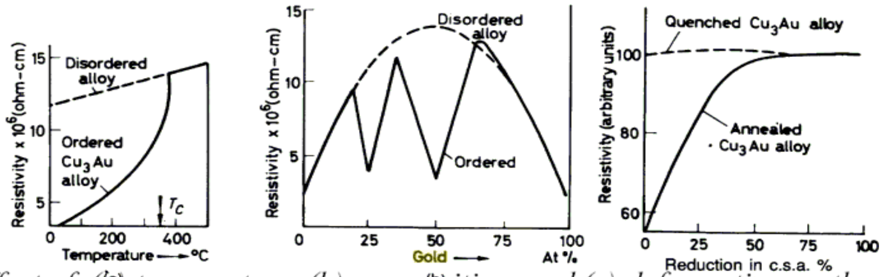
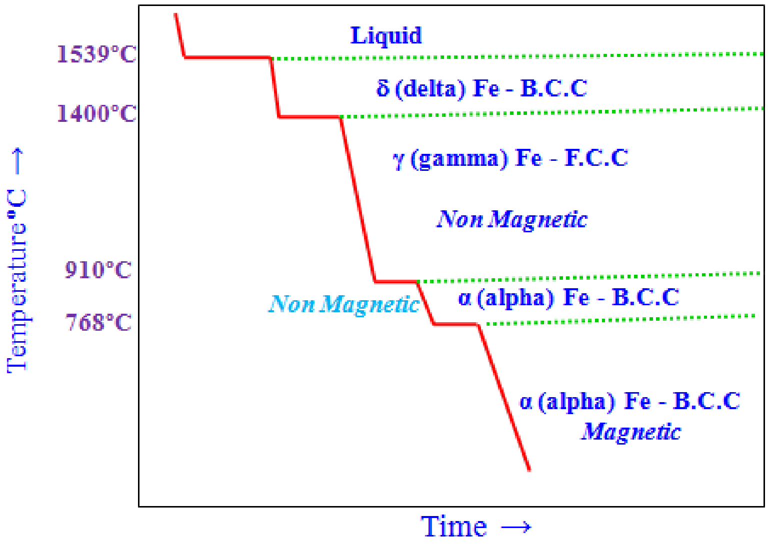


Figure : Effect of (a) temperature, (b) composition, and (c) deformation on the resistivity of copper-gold alloys

Allotropic Transformations in Iron

- Iron is an allotropic metal, which means that it can exist in more than one type of lattice structure depending upon temperature. A cooling curve for pure iron is shown below:



Iron – Cementite Phase Diagram

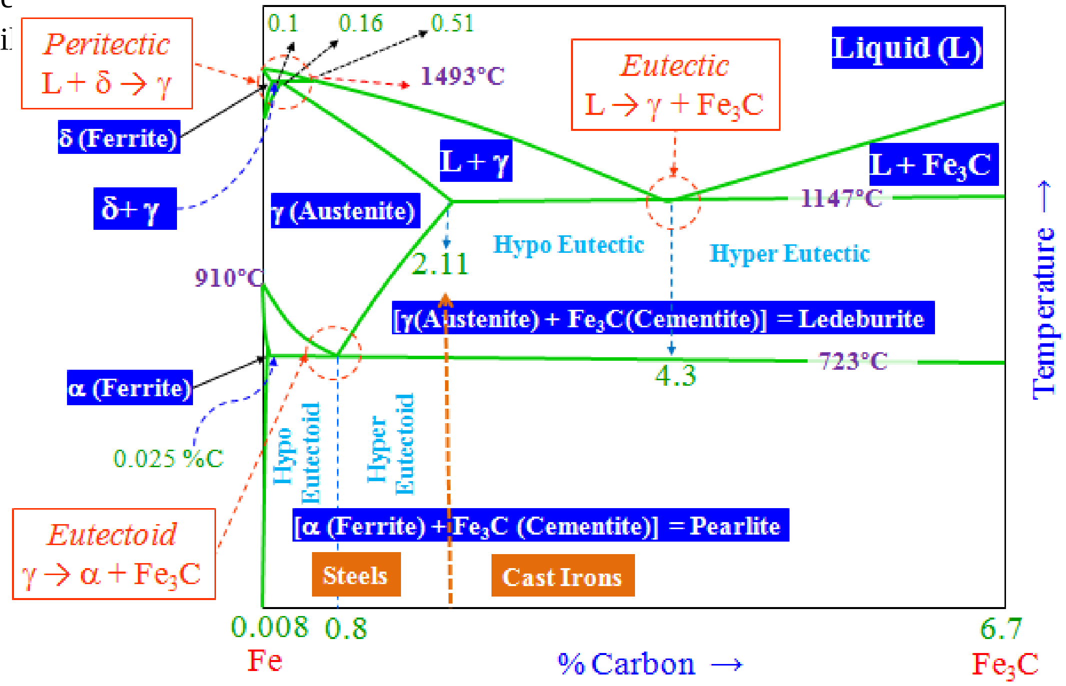
- The Fe-C (or more precisely the Fe-Fe_3C) diagram is an important one. Cementite is a metastable phase and 'strictly speaking' should not be included in a phase diagram. But the decomposition rate of cementite is small and hence can be thought of as 'stable enough' to be included in a phase diagram. Hence, we typically consider the Fe-Fe_3C part of the Fe-C phase diagram.

- A portion of the Fe-C diagram – the part from pure Fe to 6.67 wt.% carbon (*corresponding to cementite,Fe_3C) – is technologically very relevant.*

- Cementite is not a equilibrium phase and would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.

- Compositions upto 2.1%C are called steels and beyond 2.1% are called cast irons. *In reality the calssification should be based on 'castability' and not just on carbon content.*

- Heat treatments can be done to alter the properties of the steel by modifying the microstructure → we wi



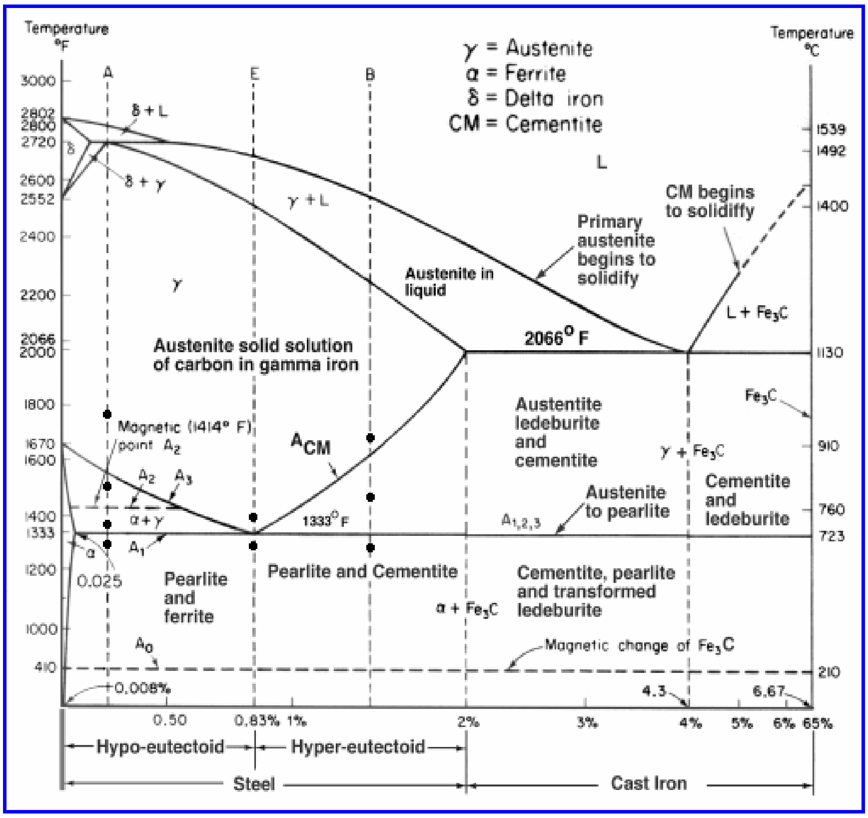
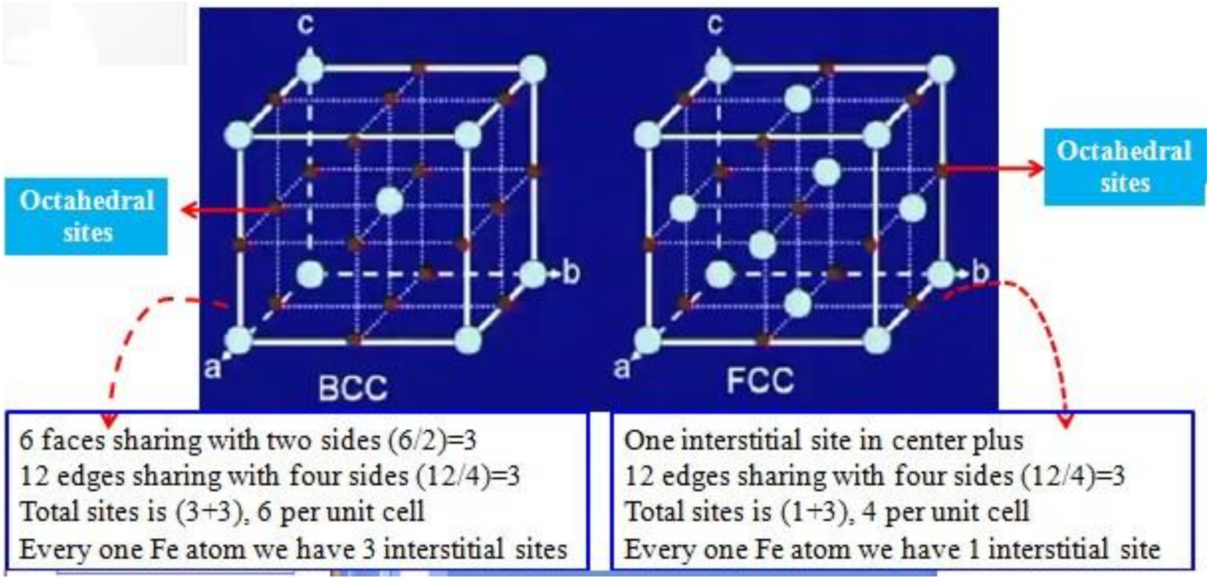


Figure: Iron – Cementite Phase

DiagramCarbon Solubility in Iron

Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice?



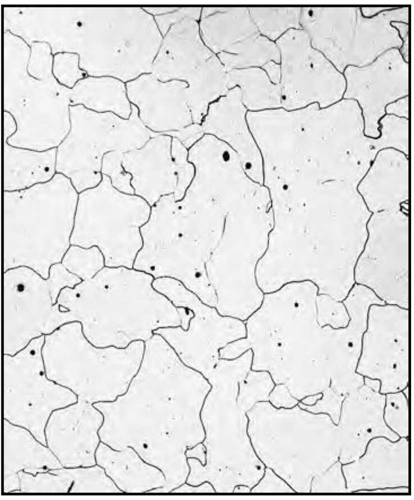
6 faces sharing with two sides (6/2)=3
12 edges sharing with four sides (12/4)=3
Total sites is (3+3), 6 per unit cell
Every one Fe atom we have 3 interstitial sites

One interstitial site in center plus
12 edges sharing with four sides (12/4)=3
Total sites is (1+3), 4 per unit cell
Every one Fe atom we have 1 interstitial site

Characteristics of phases appeared in Fe-Fe_3C phase diagram

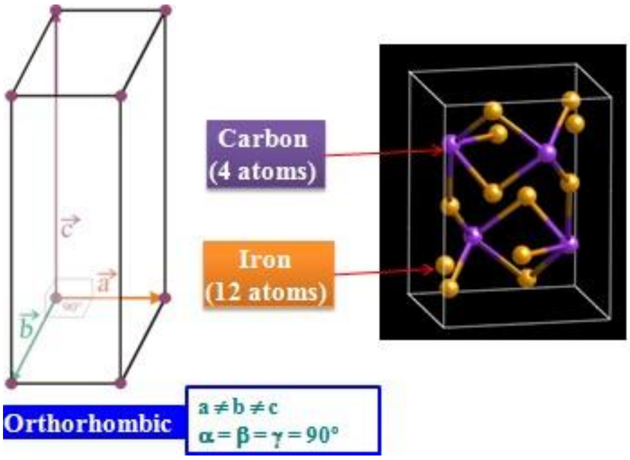
Ferrite (α)

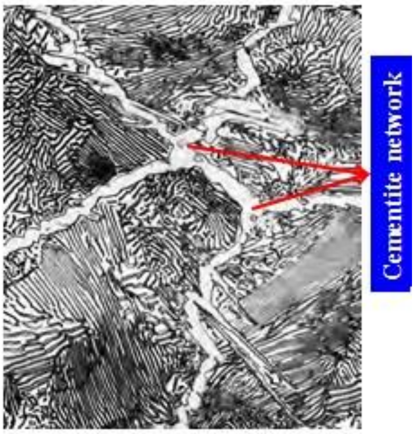
- It is an interstitial solid solution of a small amount of Carbon dissolved in α iron. The maximum solubility is 0.025%C at 723ºC and it dissolves only 0.008%C at room temperature. *It is the softest structure that appears on the diagram*
- The crystal structure of ferrite (α) is B.C.C
- Tensile strength – 40,000 psi or 275 Mpa
- Elongation – 40% in 2 in.
- Hardness - < 0 HRC or < 90 HRB



Cementite (Fe_3C)

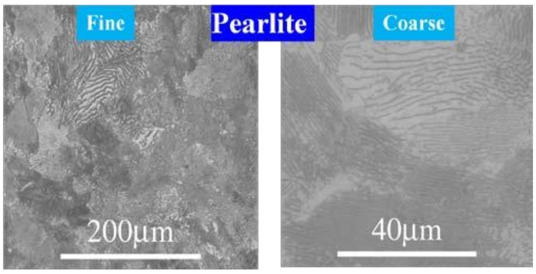
- Cementite or iron carbide, chemical formula Fe_3C, contains 6.67%C by weight and it is a metastablephase.
- It is typically hard and brittle interstitial compound of low tensile strength (approx. 5000 psi) but highcompressive strength.
- It is the hardest structure that appears on the diagram.
- Its crystal structure is orthorhombic





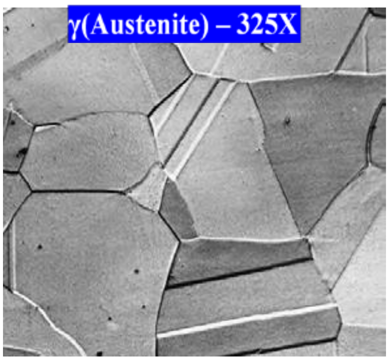
Pearlite (α + Fe_3C)

- Pearlite is the eutectoid mixture containing 0.80 %C and is formed at 723ºC on very slow cooling.
- It is very fine Pearlite or lamellar mixture of ferrite and cementite.
- The fine fingerprin mixture called pearlite is shown in below figure.
- Tensile strength – 120,000 psi or 825 Mpa
- Elongation – 20 percent in 2 in.
- Hardness – HRC 20, HRB 95-100, or BHN 250-300



Austenite (γ)

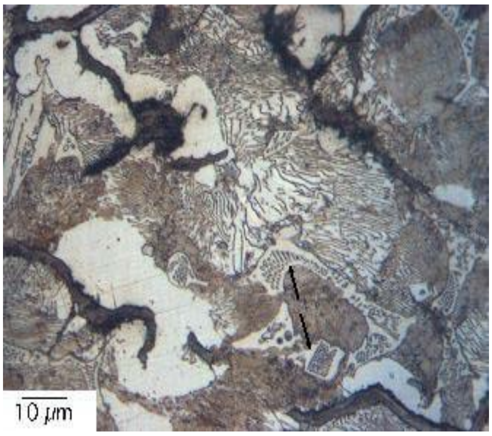
- It is an interstitial solid solution of a small amount of carbon dissolved in γ iron. The maximum solubility is 2.1%C at 1147ºC.
- The crystal structure of Austenite (γ) is F.C.C
- Tensile strength – 150,000 psi or 1035 Mpa
- Elongation – 10% in 2 in.
- Hardness - 40 HRC and Toughness is high.



Ledeburite (γ+ Fe_3C)

- Ledeburite is the eutectic mixture of austenite

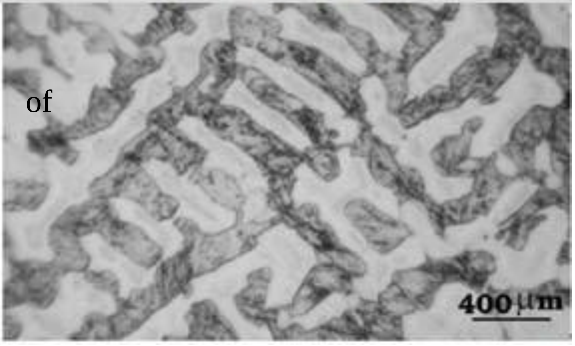
  and cementite.It contains 4.3%C and is formed at 1147ºC
- Structure of ledeburite contains small islands of
- austenite aredispersed in the carbide phase.
- Not stable at room temperature



Ferrite (δ)

- Interstitial solid solution of carbon in iron of Body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89Å) having solubility limit of 0.09 wt% at 1495°C with respect to austenite. The stability of the phase ranges between 1394-1539°C.

δ-ferrite in dendrite form in as-cast Fe-0.4C-2Mn-0.5Si-2 Al0.5Cu



- This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel especially duplex stainless steel.

Invariant Reactions in Fe-Fe_3C Phase Diagram

Peritectic Reaction

- The invariant peritectic reaction in Fe-Fe_3C diagram is given by

$$\underset{0.51\%C}{L} + \underset{0.1\ \%C}{\delta\text{-ferrite}} \underset{1495^{o}C}{\overset{\text{Cool}}{\rightleftharpoons}} \underset{0.17\%C}{\text{Austenite }(\gamma)}$$

- Thus Liquid, wt% is

$$L = \frac{0.16 - 0.1}{0.51 - 0.1} \times 100 = 14.63\%$$

- Thus δ ferrite, wt % is

$$\delta(\,ferrite) = \frac{0.51 - 0.16}{0.51 - 0.1} \times 100 = 85.37\%$$

- Fe-0.16%C steel is a peritectic steel because only this steel undergoes above reaction completely.
- Peritectic reaction is of some importance during freezing of steels (carbon from 0.1 to 0.51% particularly under fast cooling conditions, when micro segregation may result, otherwise no commercial heat treatment is done in this region.
- Unfortunately these temperatures are attained during heating of steels for forging or rolling etc., then severe overheating and burning results in steels turning them to scrap form.

Eutectic Reaction

- The invariant Eutectic reaction in Fe-Fe_3C diagram is given by

$$\underset{0.17\%C}{\textbf{Liquid (L)}} \underset{1147^{o}C}{\overset{\text{Cool}}{\rightleftharpoons}} \underset{2.11\%C}{\textbf{Austenite }(\gamma)} + \underset{6.67\ \%C}{\textbf{Cementite}}$$

- Thus Austenite, wt% is $\gamma = \dfrac{6.67-4.3}{6.67-2.11} \times 100 = 51.97\%$

- Thus cementite, wt % is $Fe_3C = \dfrac{4.3-2.11}{6.67-2.11} \times 100 = 48.03\%$

- Fe-4.3%C alloy is called eutectic cast iron as it is the lowest melting point alloy, which is single phase liquid (100%) of 4.3% carbon at the eutectic temperature, 1147°C just attained and undergoes eutectic reaction completely at this constant eutectic temperature to give a mixture of two different solids, namely austenite and cementite, solidifying simultaneously. The eutectic mixture called *Ledeburite*.
- As Fe-C alloys having more than 2.11% carbon are classed as cast irons, the Fe-C alloys having carbon between 2.11 and 4.3% are called *hypo eutectic cast irons*, where as those having carbon between 4.3% and 6.67% are called *hypereutectic cast irons*. Alloys of Fe with 4.3% carbon is called *eutectic cast iron*.

Eutectoid Reaction

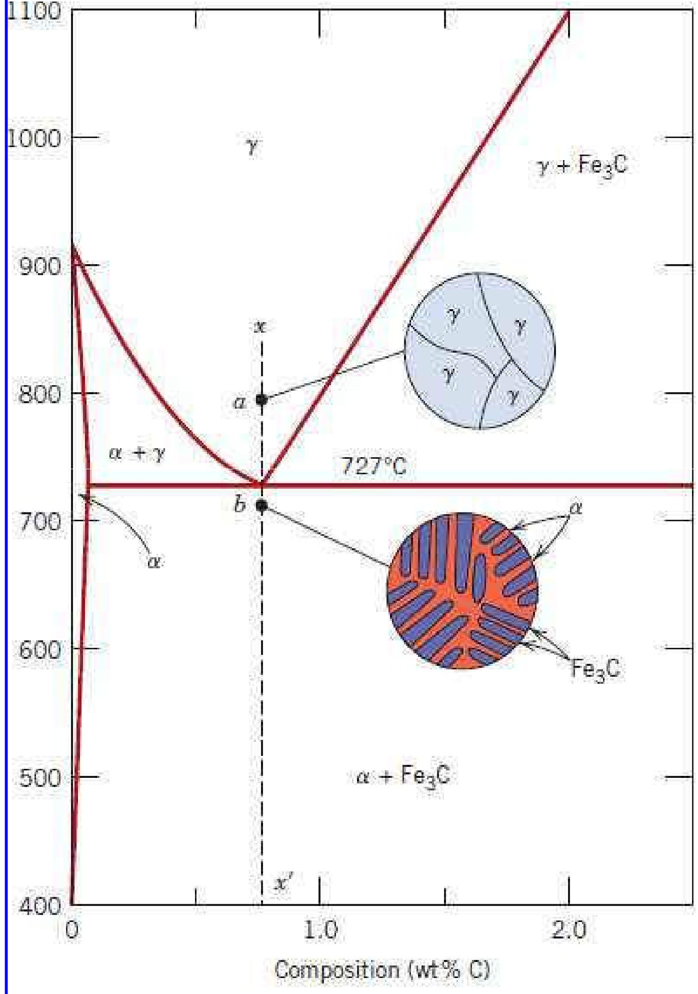
- ❑ The invariant Eutectoid reaction in Fe-Fe_3C diagram is given by

$$\underset{0.8\%C}{\textbf{Austenite }(\gamma)} \underset{727^{o}C}{\overset{\text{Cool}}{\rightleftharpoons}} \underset{0.02\%C}{\textbf{Ferrite }(\alpha)} + \underset{6.67\ \%C}{\textbf{Cementite}}$$

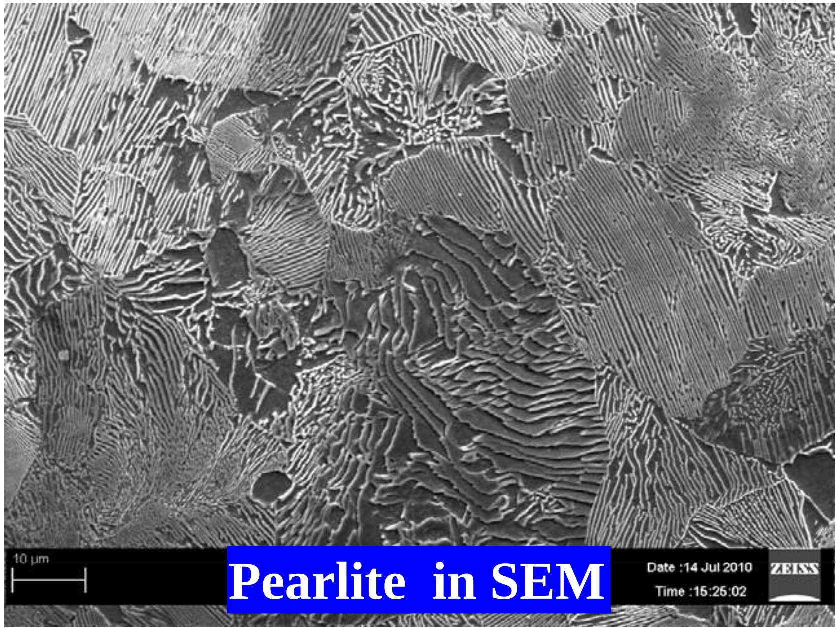
- ❑ Thus Ferrite, wt% is $$\alpha = \frac{6.67-0.8}{6.67-0.02}\times 100 = 88\%$$
- ❑ Thus cementite, wt % is $$Fe_3C = \frac{0.8-0.02}{6.67-0.02}\times 100 = 12\%$$
- ❑ During cooling austenite of 0.8% at constant eutectoid temperature, 727°C undergoes eutectoid transformation to form a mixture of ferrite (C%=0.02%) and cementite i.e., there are alternate lamellae of ferrite and cementite .
- ❑ This eutectoid mixture of ferrite and cementite is called PEARLITE, because of its pearly appearance under optical microscope.
- ❑ The weight % of these phases are thus 8:1. The densities are (α-7.87 gm/cm^3) and (Fe_3C- -7.70 gm/cm^3) are quite comparable. Thus the Volume % also approx 8:1. Thus ferrite lamilla is 8 times thicker than cementite lamilla. as the two boundaries of cementite plate are close together, they may not resolved separately under the microscope, instead of two lines, it appears a single dark line.

Eutectoid Reaction

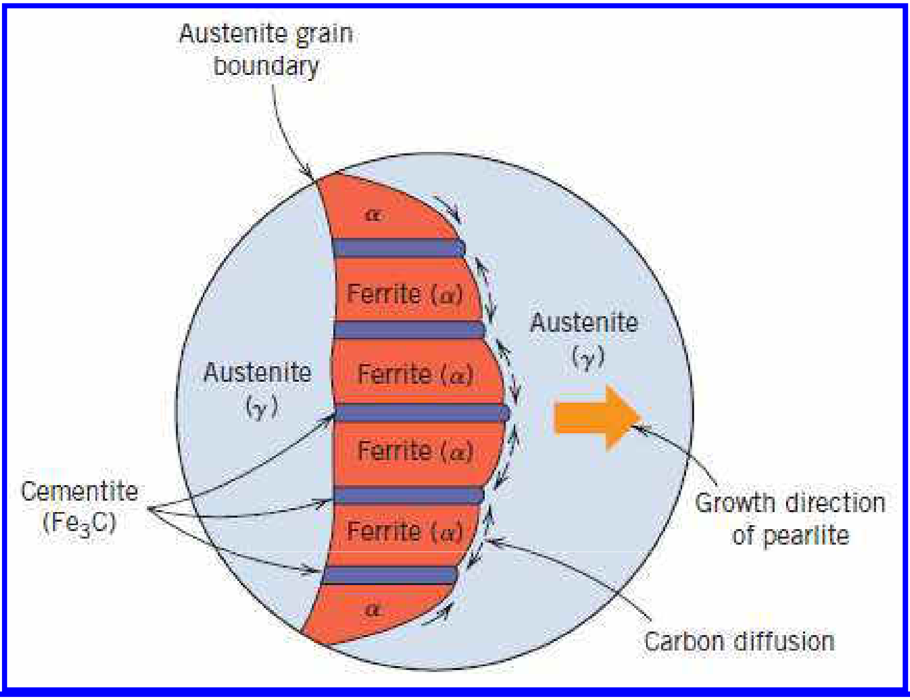
- Phase changes that occur upon passing from the γ region into the α+ Fe_3C phase field.
- Consider, for example, an alloy of eutectoid composition (0.8%C) as it is cooled from a temperature within the γ phase region, say 800ºC – that is, beginning at point ‘a’ in figure and moving down vertical xx’. Initially the alloy is composed entirely of the austenite phase having composition 0.8 wt.% C and then transformed to α+ Fe_3C [pearlite]
- The microstructure for this eutectoid steel that is slowly cooled through eutectoid temperature consists of alternating layers or lamellae of the two phases α and Fe_3C
- The pearlite exists as grains, often termed “colonies”; within each colony the layers are oriented in essentially the same direction, which varies from one colony to other.
- The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which appear dark.



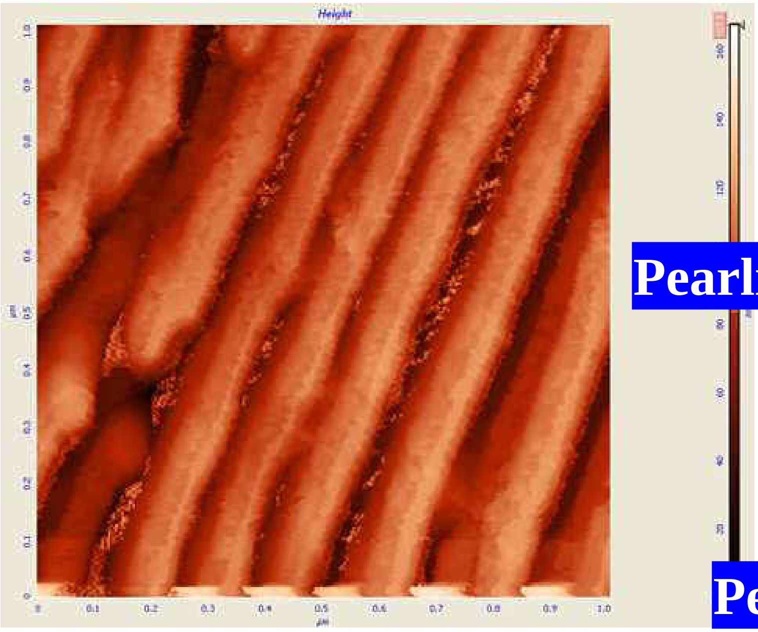
Eutectoid Structure



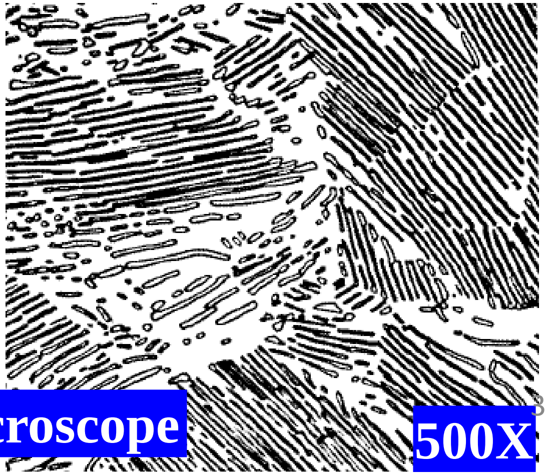
Pearlite in SEM



Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows



Pearlite in AFM

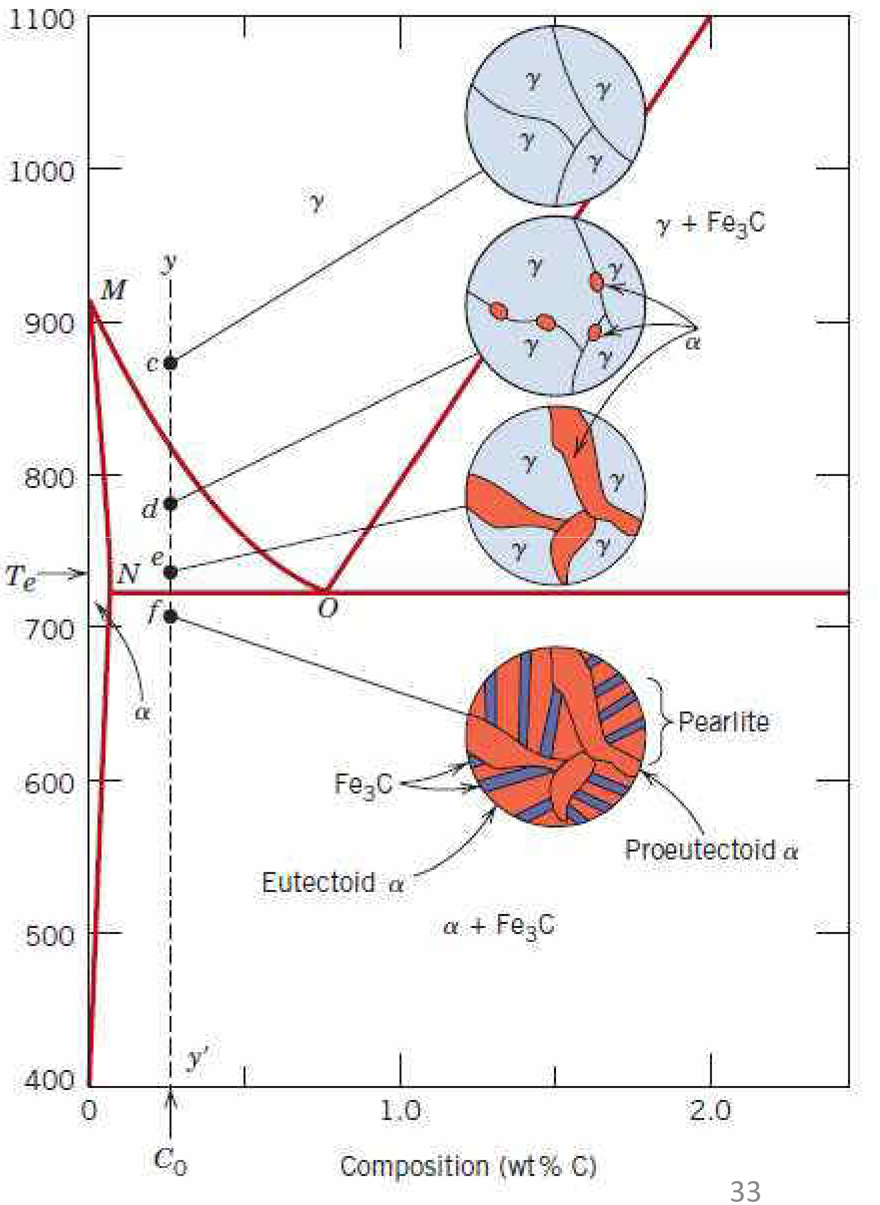


Pearlite in optical microscope

500X

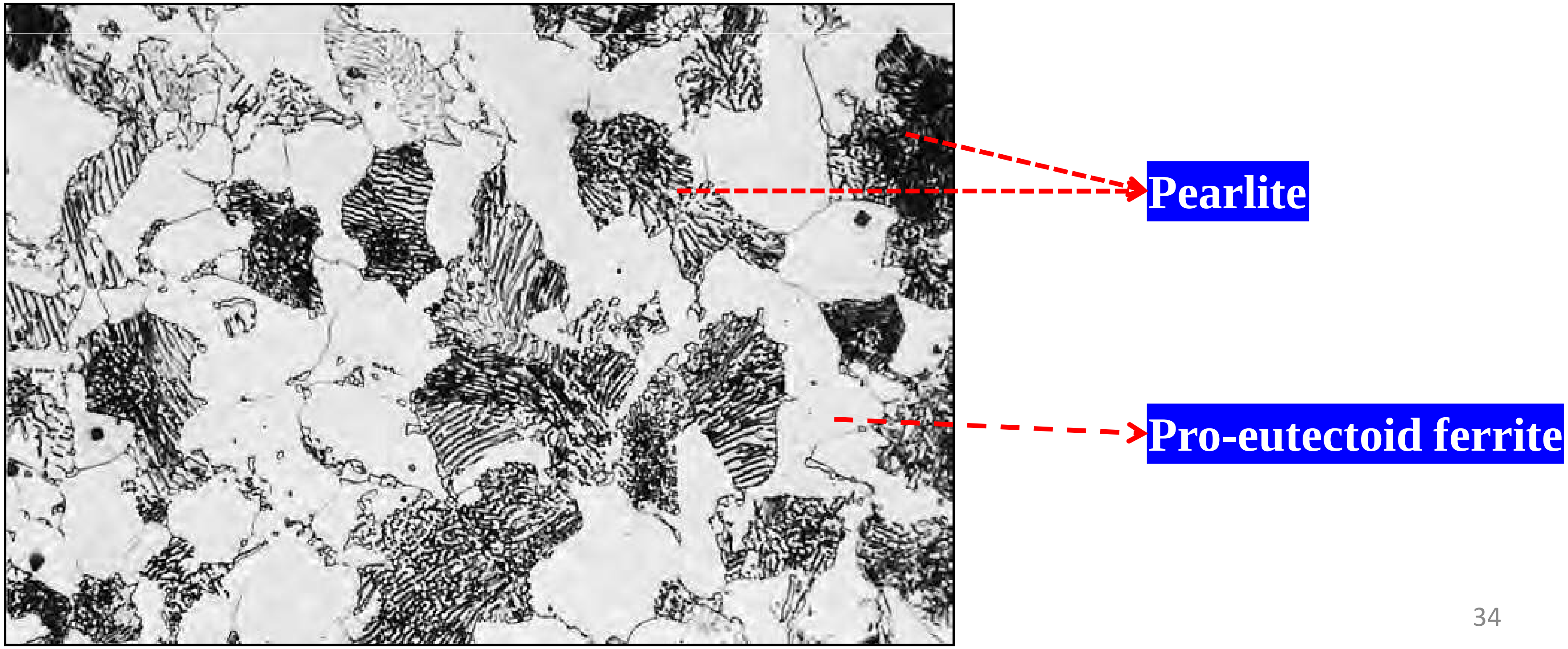
Hypo Eutectoid Region

- Hypo eutectoid region – 0.008 to 0.8 %C
- Consider vertical line yy’ in figure, at about 875ºC, point c, the microstructure will consist entirely of grains of the γ phase.
- In cooling to point d, about 775ºC, which is within the α+γ phase region, both these phases will coexist as in the schematic microstructure Most of the small α particles will form along the original γ grain boundaries.
- Cooling from point d to e, just above the eutectoid but still in the α+γ region, will produce an increased fraction of the α phase and a microstructure similar to that also shown: the α particles will have grown larger.



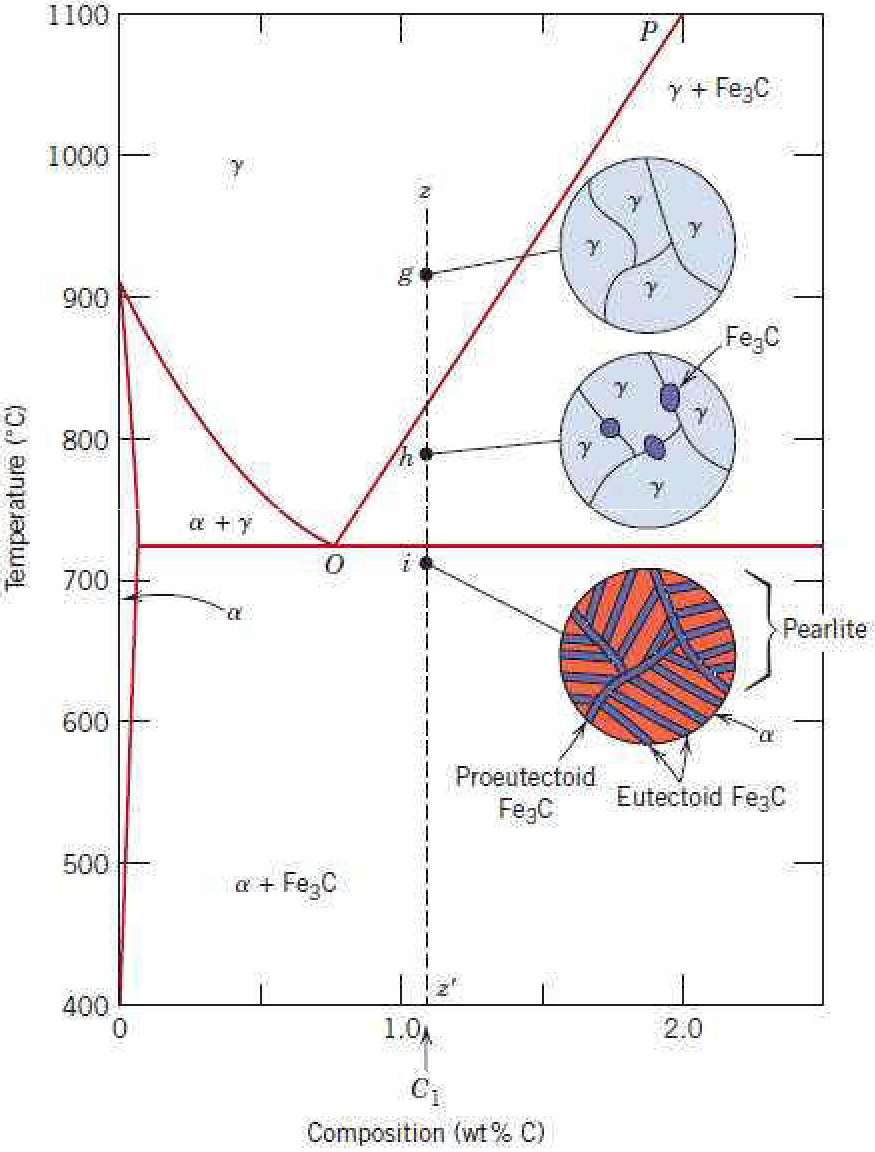
Hypo Eutectoid Region

- Just below the eutectoid temperature, at point f, all the γ phase that was present at temperature e will transform pearlite. Virtually there is no change in α phase that existed at point e in crossing the eutectoid temperature – it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies.
- Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the α+γ phase region. The ferrite that is present in the pearlite is called eutectoid ferrite, whereas the other, is termed proeutectoid (meaning pre- or before eutectoid) ferrite.

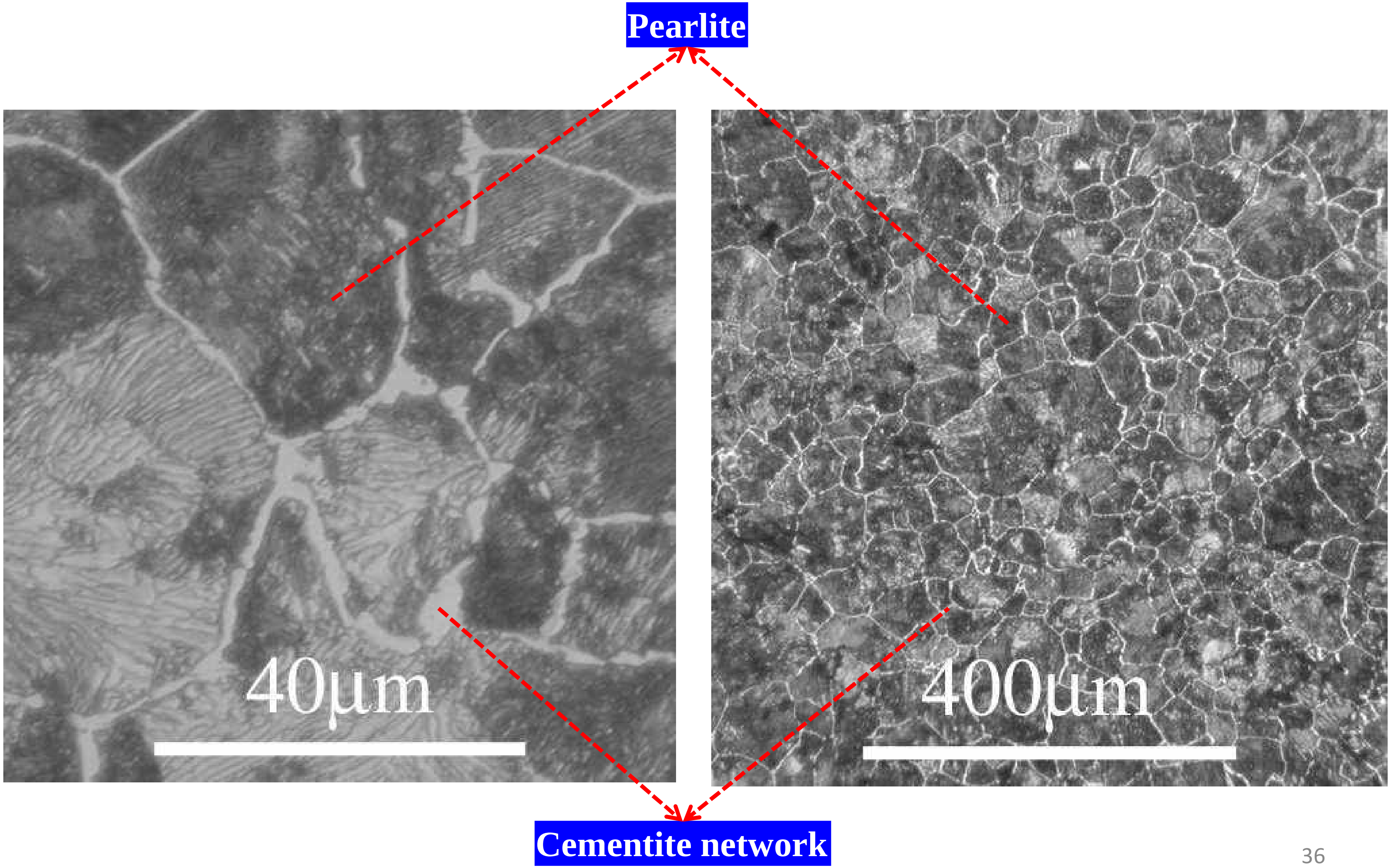


Hyper Eutectoid Region

- ☐ Hyper eutectoid region – 0.8 to 2.1 %C
- ☐ Consider an alloy of composition C_1 in figure that, upon cooling, moves down the line zz'. At point g only the γ phase will be present and the microstructure having only gamma grains.
- ☐ Upon cooling into the γ+ Fe_3C phase field – say to point h – the cementite phase will began to form along the initial γ grain boundaries, similar to the α phase in point d. this cementite is called *proeutectoid cementite* that which forms before the eutectoid reaction.
- ☐ As the temperature is lowered through the eutectoid to point I, all remaining austenite of eutectoid composition is converted into pearlite; thus the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents.



Hypo Eutectoid Region

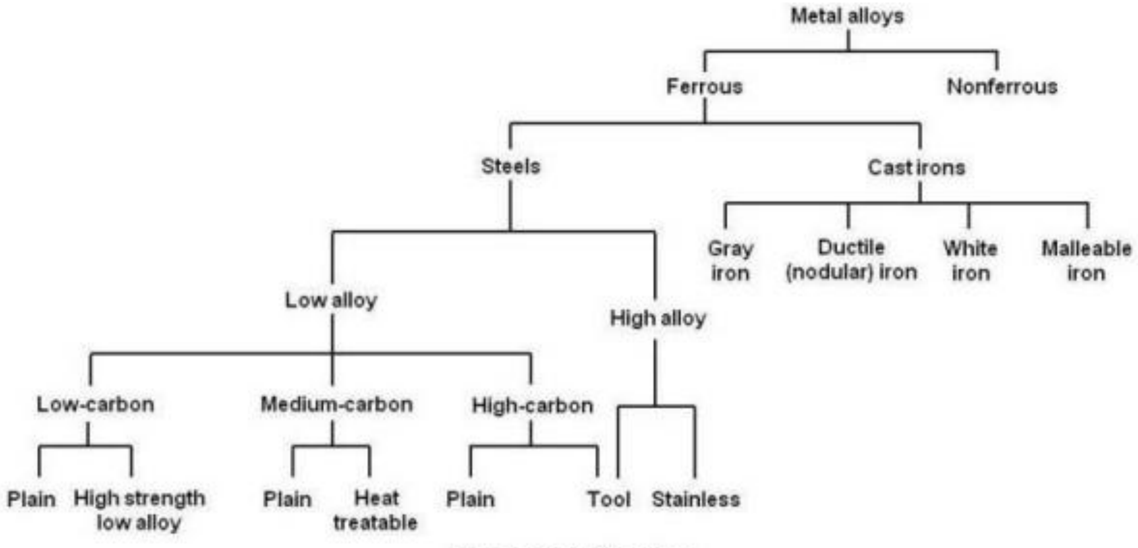


Pearlite

Cementite network

CHAPTER 2

Ferrous Materials and Non-Ferrous Metals and Alloy



Metals Classification

Ferrous metals and its alloys: These are metals and alloys containing a high proportion of the element iron. They are the strongest materials available and are used for applications where high strength is required at relatively low cost and where weight is not of primary importance ferrous metals and alloys contain iron. Ferrous metals include carbon steel, stainless steel and cast iron. These metals are primarily used for their tensile strength and durability. Most ferrous metals have magnetic properties, which makes them useful in electrical appliances. Ferrous metals can be easily recycled. Most ferrous metals and alloys are vulnerable to rust when exposed to atmosphere.

Cast iron

Cast iron is a group of iron-carbon alloys with a carbon content of more than 2 to 4 percent. In addition, varying amounts of silicon from 1 to 3% by weight and manganese as well as traces of impurities such as sulfur and phosphorus. Cast iron is made by reducing Iron Ore in a Blast Furnace The liquid iron is poured or cast and hardened into crude ingots called pigs, and the pigs are then remelted along with scrap and alloying elements in cupola furnaces and recast into molds to produce a variety of products. The alloying ingredients affect its color when breaks: white cast iron has carbide impurities that allow cracks to pass easily, gray cast iron has graphite flakes that deflect a passing crack and initiate countless new cracks as the material breaks, and ductile cast iron has spheroidal graphite “nodules” that stop the crack prevent further progress.

With the exception of malleable iron, cast iron tends to be brittle. With its relatively low melting point, good fluidity, castability, excellent machinability, deformation resistance, and wear resistance, cast iron has become an engineering material with a wide range of applications. Cast iron is used in pipes, machinery, and automotive parts such as cylinder heads, cylinder blocks, and gearboxes. It is resistant to oxidation damage but difficult to weld.

Properties of Cast Iron

A few common mechanical properties for cast iron include:

- **Hardness.** Cast iron is hard and it can be hardened by heating and sudden cooling. This makes it quite durable. Mild steel can be hardened and tempered by using relevant processes.
- **Toughness.** Material's ability to absorb energy
- **Ductility.** Material's ability to deform without fracture
- **Elasticity.** Material's ability to return to its original dimensions after it has been deformed
- **Malleability.** Material's ability to deform under compression without rupturing
- **Tensile strength.** The greatest longitudinal stress a material can bear without tearing apart
- **Fatigue strength.** The highest stress that a material can withstand for a given number of cycles without breaking
- **Melting Point.** Cast iron has a lower melting point (12000C) as compared to the melting point of mild steel which lies in the range of 13000C and 14000C.
- **Castability.** Cast iron is easier to work with when it comes to casting shapes out of the material. Due to the extra carbon present in cast iron, its molten form is more fluid and this makes it easier to cast the material into complex shapes.
- **Machinability.** Cast iron is almost elastic up to ultimate tensile strength and produce discontinuous chips which break away from the sample easily. This helps to improve the cutting ability. Due to this, cast iron is the preferred material when it comes to high machinability and strength.

Carbon can occur in C.I's as:

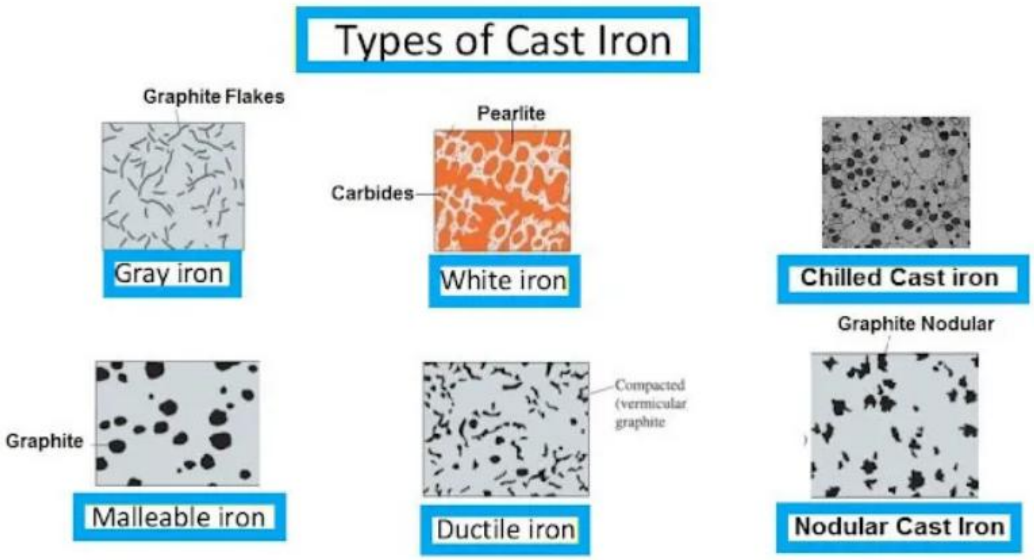
- combined carbon (Fe_3C) or free carbon (graphite)

Shape and distribution of free carbon also important Parameters that influence are:

- Carbon content,
- Alloy and impurity content,
- Cooling rate during and after freezing,
- Heat treatment after casting

Types of Cast Iron

1. White Cast Iron (combined carbon Fe_3C)
2. Malleable Cast Iron (free carbon as irregular particles)
3. Chilled Cast Iron (white cast iron at the surface and gray cast iron at the interior)
4. Grey Cast Iron (Flake Graphite)
5. Spheroidal Graphite (SG) / Ductile Cast Iron / Nodular Cast Iron (free carbon as spheroids)
6. Alloy Cast Iron



White Cast Iron

The most common abrasion-resistant ferrous materials having carbon greater than 2wt% in the form of cementite is called **white cast iron**. White faceted fracture due to the presence of cementite is of main characteristics of white cast iron.

Structure of White Cast Iron: This microstructure depicts the Pearlitic matrix with a continuous thick cementite matrix formed in result of the eutectic reaction. The presence of a thick network is the main reason for the brittleness of respective microstructure

White cast iron application: White cast irons are used in abrasion-resistant parts where its brittleness is of minimum concern such as shell liners, slurry pumps, ball mills, lifter bars, extrusion nozzles, cement mixers, pipe fittings, flanges, crushers and pump impellers

White cast iron Properties: White cast iron has a light appearance due to the absence of graphite. It has a high compressive strength and retains good hardness and strength at higher temperatures. The presence of different carbides, depending on the alloy content, makes white cast irons extremely hard and abrasion resistant but very brittle.

Is white cast iron weldable?

White cast iron contains a strong continuous network of carbides that are difficult to weld. Welding is normally not recommended for white cast iron. The structure of white cast iron also contains martensite. This combination of carbides and various hard matrix phases is prone to heat cracking. Welding and immediate cooling result in cracks in cast iron, that’s why white iron is not recommended for welding.

Following are common repair methods which can be adopted for white cast iron;

— Addition of welding inserts
— Addition of Heli coil inserts
— Bolting
— Epoxy

Why White cast iron is hard and brittle?

White iron is extremely hard and brittle. The answer lies in its microstructure. The microstructure consists of a thick continuous network of carbides embedded in the Pearlitic or martensitic matrix. This carbide network is extremely hard and resists any plastic deformation. This is the main reason for white cast iron to be hard and brittle. When crack generates within carbide network, crack flows immediately and no other micro cracks are generated. That's why the surface of fractured white cast iron appears white.

MALLEABLE CAST IRON

Malleable iron is cast as white iron, the structure being a metastable carbide in a pearlitic matrix. Through an annealing heat treatment, the brittle structure as first cast is transformed into the malleable form. Carbon agglomerates into small roughly spherical aggregates of graphite leaving a matrix of ferrite or pearlite according to the exact heat treatment used. Three basic types of malleable iron are recognized within the casting industry: blackheart malleable iron, whiteheart malleable iron and pearlitic malleable iron.

Mechanical properties of malleable iron

Malleable iron, like ductile iron, possesses considerable ductility and toughness because of its combination of nodular graphite and low-carbon metallic matrix. Because of the way in which graphite is formed in malleable iron, however, the nodules are not truly spherical as they are in ductile iron but are irregularly shaped aggregates. Malleable iron and ductile iron are used for some of the applications in which ductility and toughness are important. In many cases, the choice between malleable and ductile iron is based on economy or availability rather than on properties. In certain applications, however, malleable iron has a distinct advantage. It is preferred for thin-section castings:

- for parts that are to be pierced, coined, or cold formed,
- for parts requiring maximum machinability,
- for parts that must retain good impact resistance at low temperatures, and
- for parts requiring wear resistance (martensitic malleable iron only).

APPLICATION:-

It is often used for small castings requiring good tensile strength and the ability to flex without breaking (ductility). Uses include electrical fittings, hand tools, pipe fittings, washers, brackets, fence fittings, power line hardware, farm equipment, mining hardware, and machine parts. Before the widespread use of malleable iron in everyday items, heavy-duty bench vises were made from cast steel. The use of cast steel has rapidly declined in most application due to its poor castability, and hence high-quality cast vises (as opposed to forged ones), among other tools and machine elements, are now almost exclusively made of malleable Iron.

Chilled Cast Iron

Quick cooling is generally known as chilling and the iron so produced is "chilled iron". The outer surface of all castings always gets chilled to a limited depth about (1 to 2 mm) during pouring and solidification of molten metal after coming in contact with cool sand of mould. Sometimes the casting is chilled intentionally and some becomes chilled accidentally to a small depth. Chills are employed on any faces of castings which are required to be hard to withstand wear and friction. Chilled castings are used in producing stamping dies and crushing rolls railway, wheels cam followers, and so on.

GRAY CAST IRON

Gray cast iron is the oldest and most common type of iron in existence and probably what most people think of when they hear the term “cast iron”. The carbon and silicon contents of gray cast irons vary between 2.5 and 4.0 wt% and 1.0 and 3.0 wt%, respectively. Gray cast iron have also an excellent damping capacity, which is given by the graphite because it absorbs the energy and converts it into heat. A large damping capacity is desirable for materials used in structures where unwanted vibrations are induced during operation such as machine tool bases or crankshafts.

Gray cast iron is characterised by its graphitic microstructure, which causes fractures of the material to have a gray appearance. This is due to the presence of graphite in its composition. In gray cast iron the graphite forms as flakes, taking on a three dimensional geometry.

Gray cast iron Properties

Gray cast iron has also an excellent damping capacity, which is given by the graphite because it absorbs the energy and converts it into heat. A large damping capacity is desirable for materials used in structures where unwanted vibrations are induced during operation such as machine tool bases or crankshafts. Materials like brass and steel have small damping capacities allowing vibration energy to be transmitted through them without attenuation.

Gray cast iron has less tensile strength and shock resistance than steel, but its compressive strength is comparable to low- and medium-carbon steel. Gray cast iron has good thermal conductivity and specific heat capacity; therefore it is often used in cookware and brake rotors.

APPLICATION

- Gears
- Hydraulic components
- Automotive suspension components
- Pumps
- Stove parts
- Steering knuckles
- Tractor parts
- Valves
- Truck suspension components
- Other truck parts
- Wind turbine housings.
- Weights and counter-weights
- Machinery bases

What is the Microstructure of Grey Cast Iron

Grey iron has graphite flakes entwined with the rest of the structure. Unhardened grey iron is “fragile” compared to other cast metals. The graphite flakes create areas of weakness in the metal where fractures can begin that will split the metal. This propensity to fracture is why grey iron has low tensile and impact strength. Yet the graphite flakes are what create great wear resistance because as friction occurs the graphite acts as a lubricant. The graphite structure also has great vibration dampening properties because the structure created by the graphite flakes helps cancel out vibrations.

Nodular Cast Iron

It is also known as “spheroidal graphite iron” or ductile iron or High strength “Cast iron”. This nodular cast iron is obtained by adding magnesium to the molten cast iron. The magnesium converts the graphite of cast iron from flake to spheroidal or nodular form. In this manner, the mechanical properties are considerably improved. The strength increases, yield point improves and brittleness is reduced. Such castings can even replace steel components. Outstanding characteristics of nodular cast iron are high fluidity which allows the castings of intricate shape. This cast iron is widely used in castings where density as well as pressure tightness is a highly desirable quality. The applications include hydraulic cylinders, valves, pipes and pipe fittings, cylinder head for compressors, diesel engines, etc.

Alloy Cast Iron

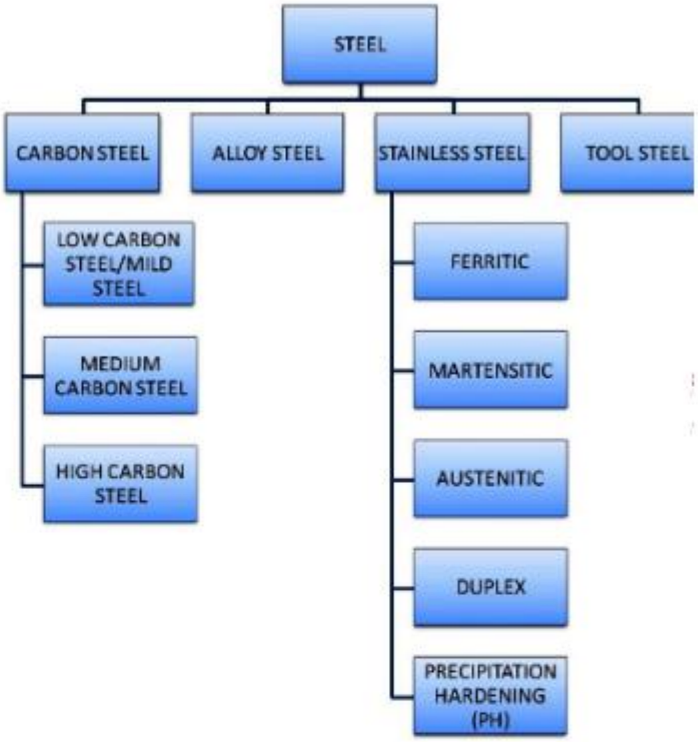
Alloying elements are added to cast iron to overcome inherent deficiencies in ordinary cast iron to provide requisite characteristics for special purposes. The alloy cast iron is 20 Manufacturing Processes extremely tough, wear resistant and non-magnetic steel about 12 to 14 per cent manganese should be added.

1. **Nickel**: It may be termed as one of the most important alloying elements. It improves tensile strength, ductility, and toughness and corrosion resistance.
2. **Chromium**: Its addition to steel improves toughness, hardness and corrosion resistance.
3. **Boron**: It increases harden ability and are therefore very useful when alloyed with low carbon steels.
4. **Cobalt**: It is added to high speed steels to improve hardness, toughness, tensile strength, thermal resistance and magnetic properties. It acts as a grain purifier.
5. **Tungsten**: Tungsten improves hardness, toughness, wear resistance, shock resistance, magnetic reluctance and ability to retain hardness at elevated temperatures. It provides hardness and abrasion resistance properties to steel.
6. **Molybdenum**: It improves wear resistance, hardness, thermal resistance, ability to retain mechanical properties at elevated temperatures and helps to inhibit temper brittleness.
7. **Vanadium**: It increases tensile strength, elastic limit, ductility, shock resistance and also acts as a de-gaser when added to molten steel. It provides improvement to hardenability of steel.
8. **Titanium**: It is a very good deoxidizer and promotes grain growth. It is the strongest carbide former. Titanium is used to fix carbon in stainless steel and thus prevents the precipitation of chromium-carbide.
9. **Niobium**: It improves ductility, decreases hardenability and substantially improves the impact strength. It also promotes fine grain growth.

Steel

Steel is an **alloy of Iron** and the principal (main) alloying element is **Carbon.** However, there are some exceptions to this definition like interstitial-free (IF) steels and type 409 ferritic stainless steels, in which carbon is considered as an impurity. When different elements are mixed in smaller quantities in the base element, the resulting product is called an alloy of the base element. Hence steel is an alloy of Iron because Iron is the base element (main constituent) in steel and the principal alloying element is Carbon. Some other elements such as **Manganese, Silicon, Nickel, Chromium, Molybdenum,**

Vanadium, Titanium, Niobium, Aluminum, etc. are also added in varying quantities to produce different grades (or types) of Steel



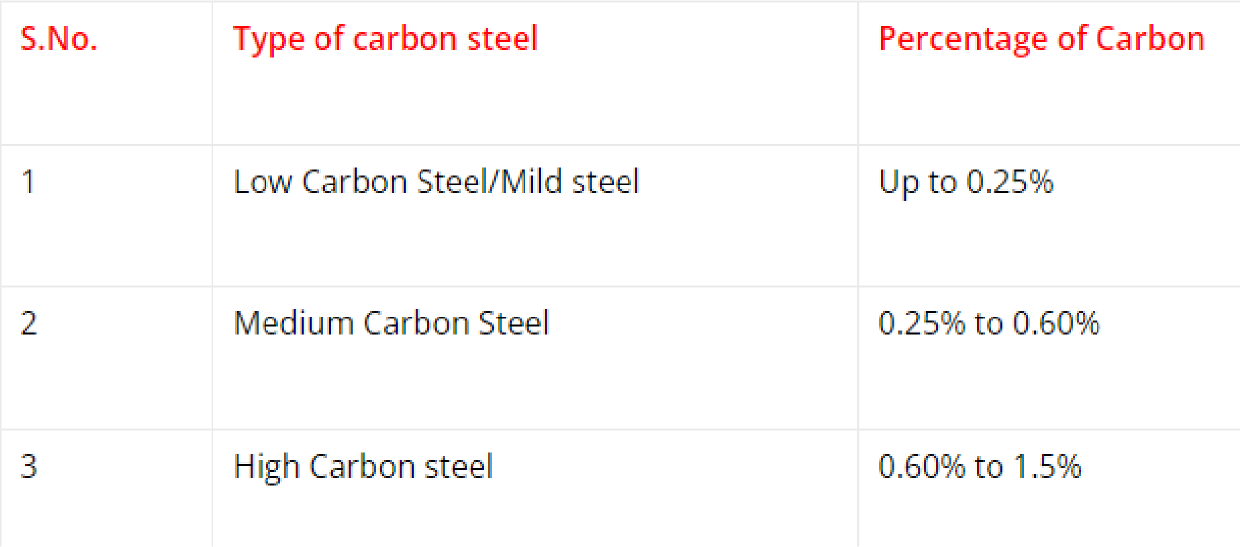
Based on the chemical compositions, Steel can be categorized into four (04) basic types:

- **Carbon Steel**
- **Stainless Steel**
- **Alloy Steel**
- **Tool Steel**

Carbon Steel:

Carbon steel is the most utilized steel in the industries and accounts for more than 90% of the total steel production. Based on the carbon content, Carbon steels are further classified into three groups.

- **Low Carbon Steel/Mild Steel**
- **Medium Carbon Steel**
- **High Carbon steel**



S.No.	Type of carbon steel	Percentage of Carbon
1	Low Carbon Steel/Mild steel	Up to 0.25%
2	Medium Carbon Steel	0.25% to 0.60%
3	High Carbon steel	0.60% to 1.5%

Low-carbon steel

Low-carbon steel is the most widely used form of carbon steel. These steels usually have a carbon content of less than 0.25 wt.%. They cannot be hardened by heat treatment (to form martensite) so this is usually achieved by cold work.
Carbon steels are usually relatively soft and have low strength. They do, however, have high ductility, making them excellent for machining, welding and low cost.

High-strength, low-alloy steels (HSLA) are also often classified as low-carbon steels, however, also contain other elements such as copper, nickel, vanadium and molybdenum. Combined, these comprise up to 10 wt.% of the steel content. High-strength, low-alloy steels, as the name suggests, have higher strengths, which is achieved by heat treatment. They also retain ductility, making them easily formable and machinable. HSLA are more resistant to corrosion than plain low-carbon steels.
Low carbon steels are often used in automobile body components, structural shapes (I-beams, channel and angle iron), pipes, construction and bridge components, and food cans.

Medium-carbon steel

Medium-carbon steel has a carbon content of 0.25 – 0.60 wt.% and a manganese content of 0.60 – 1.65 wt.%. The mechanical properties of this steel are improved via heat treatment involving autenitising followed by quenching and tempering, giving them a martensitic microstructure.
Heat treatment can only be performed on very thin sections, however, additional alloying elements, such as chromium, molybdenum and nickel, can be added to improve the steels ability to be heat treated and, thus, hardened.
Hardened medium-carbon steels have greater strength than low-carbon steels, however, this comes at the expense of ductility and toughness.

As a result of their high strength, resistance to wear and toughness, medium-carbon steels are often used for railway tracks, train wheels, crankshafts, and gears and machinery parts requiring this combination of properties

High-carbon steel

High-carbon steel has a carbon content of 0.60– 1.25 wt.% and a manganese content of 0.30 – 0.90 wt.%. It has the highest hardness and toughness of the carbon steels and the lowest ductility. High-carbon steels are very wear-resistant as a result of the fact that they are almost always hardened and tempered.

Tool steels and die steels are types of high-carbon steels, which contain additional alloying elements including chromium, vanadium, molybdenum and tungsten. The addition of these elements results in the very hard wear-resistant steel, which is a result of the formation of carbide compounds such as tungsten carbide (WC).

Due to their high wear-resistance and hardness, high-carbon steels are used in cutting tools, springs high strength wire and dies.

Stainless Steel:

Stainless steel is an alloy steel that contains 10.5% Chromium (Minimum). Stainless steel exhibits corrosion resistance properties, due to the formation of a very thin layer of $Cr2O3$ on its surface. This layer is also known as the passive layer. Increasing the amount of Chromium will further increase the corrosion resistance of the material. In addition to Chromium, Nickel and Molybdenum are also added to impart desired (or improved) properties. Stainless steel also contains varying amounts of Carbon, Silicon, and Manganese.

Stainless steels are further classified as;

1. Ferritic Stainless Steels
2. Martensitic Stainless Steels
3. Austenitic Stainless Steels
4. Duplex Stainless Steels
5. Precipitation-Hardening (PH) Stainless Steels

Ferritic Stainless Steel: Ferritic steels consist of Iron-Chromium alloys with body-centered cubic crystal structures (BCC). These are generally magnetic and cannot be hardened by heat treatment but can be strengthened by cold working.

Austenitic Stainless Steel: Austenitic steels are most corrosion-resistant. It is non-magnetic and non-heat-treatable. Generally, austenitic steels are highly weldable.

Martensitic Stainless Steel: Martensitic stainless steels are extremely strong and tough but not as corrosion-resistant as the other two classes. These steels are highly machinable, magnetic, and heat-treatable.

Duplex Stainless Steels: Duplex stainless steel consists of a two-phase microstructure consisting of grains of ferritic and austenitic stainless steel (i.e Ferrite + Austenite). Duplex steels are about twice as strong as austenitic or ferritic stainless steels.

Precipitation-Hardening (PH) Stainless Steels: Precipitation-Hardening (PH) Stainless Steels possess Ultra high strength due to precipitation hardening.

Alloy Steel:

In alloy steel, varying proportions of alloying elements are used, to achieve desired (improved) properties such as weldability, ductility, machinability, strength, hardenability and corrosion resistance, etc. Some of the most used alloying elements and their effects are as follows;
Manganese – Increases strength and hardness, decreases ductility and weldability
Silicon – Used as deoxidizers used in the steel making process
Phosphorus – Increases strength and hardness and decreases ductility and notch impact toughness of steel.
Sulfur –Decreases ductility, notch impact toughness, and weldability. Found in the form of sulfide inclusions.
Copper – improved corrosion resistance
Nickel – Increases hardenability and Impact strength of steels.
Molybdenum – Increases hardenability and enhances the creep resistance of low-alloy steels

TOOL STEELS

Tool steels are specially alloyed steels designed for high strength, impact toughness and wear resistance at room and elevated temperatures. They are normally used in forming and machining of metals. So the requirements in a tool steel are that it should be capable of becoming very hard and further that it should be able to retain its hardness at high temperatures normally developed during cutting of materials. This property is known as “red hardness”. Further, tool steel should not be brittle for smooth working.

High Speed Steel (H.S.S.) It is the name given to the most common tool steel. As the name implies, it can cut steel at high cutting speeds. These steels are high in alloy content, have excellent hardenability, maintain their hardness at elevated temperatures around 650°C, are quite resistant to wear and contain relatively large amounts of tungsten or molybdenum, together with chromium, cobalt or vanadium. They are used to produce cutting tools to be operated for various machining operations such as turning, drilling, milling, etc. A typical composition of H.S.S. is tungsten 18%, chromium 4% and vanadium 1%, carbon 0.75 to 0.9% and rest iron.

Molybdenum High Speed Steel This steel contains 6% tungsten, 6% molybdenum, 4% chromium and 2% vanadium and have excellent toughness and cutting ability. The molybdenum high speed steel are better and cheaper than other types of steel. It is particularly utilized in drilling and tapping operations.

IMPORTANT PROPERTIES OF COPPER:-

1. High electrical and thermal conductivity.

2. Good corrosion resistant, mechinability, strength and ease of fabrication.

3. It is having pleasing color and can be welded, brazed, soldered and easily finished by platingor lacquering.

APPLICATIONS:-

1. Most of the copper is used for electrical conductors contains over99.9% copper is identified aselectrolyte tough pitch copper [ETP] or oxygen free high conductivity copper [OFHC]

2.ETP copper also used for roofing, gutters, down-spouts, automobile radiators and gaskets, vats,pressure vessels, distillery and process equipment.

3. Oxygen free copper is used in electronics tubes or similar applications because it makes aperfect seal to glass.

4. Arsenic copper contains about 0.3% arsenic has improved resistance to special corrosiveconditions and is used for certain condenser and heat exchanger applications.

5. Free cutting copper with about 0.6% tellurium has excellent machining properties and is used for bolts, studs, welding tips and electrical parts such as contact pins, switch gears, relays and precession electrical equipment.

6. Silver bearing copper has a silver content of 70 to 30%.Silver raises the recrystallization temperature of copper thus preventing softening during soldering of commu

It is preferred in the manufacture of electric motors for rail road and air craft use.

Copper Alloys:-

The most important commercial copper alloys may be classified as follows

1. Brasses
2. Bronzes
3. Cupronickels
4. Nickel silvers

Brasses:-

Brasses are alloys of copper and zinc and containing more than 5% zinc. Brasses are classified into two types

a. α-Brasses

b. (α+β) Brasses

a. α-Brasses:-

α-brasses are containing up to 36% zinc possess relatively good corrosion resistance and good working properties. The colours of α brasses varies according to copper content from red for high copper alloys to yellow at about 62% copper so, that those α brasses may be divided into two groups yellow α brasses and red brasses.

α-brasses having 5-22% zinc are in reddish colour and are called as red brasses.

α-brasses having zinc content between 20 to 36% are yellow in colour and are called as yellow brasses.

Commercial brasses:

Commercial brasses contain 90% copper and 10% zinc. It is stronger, harder than pure copper and is used for rivits ,screws, jewellary.

Cartridge brass:-

cartridge brass contains 70% cu and 30%zn.It has excellent deep drawing property and is used for making cartridge cases, house hold articles, radiator fins, lamp fixtures etc.

Admirality brass:-

Admirality brass contains 70%cu and 29% zn and1% tin. It has superior corrosion resistance than that of ordinary brass and is extensivity used for propellers and marine works.

Aluminium brasses:

-Aluminium brasses contains 76% cu,22%zn and 2%Al.It has better corrosion resistance than admirality brass and hence extensively used for marine works.

b.(α+β) Brasses:-These contain from 54 to 62% copper. These alloys will consists of two phases α and β’. these β’ phase is harder and more brittle at room temperature than α. Therefore, these alloys are more difficult to cold work than the α-brasses. At elevated temperatures the β phase becomes very plastic and since most of these alloys may be heated into single phase β region, they have excellent hot working process.

Muntz metal:-The most widely used (α+β) brasses is muntz metal which contains 60% cu and 40%zn.It has high strength and excellent hot working properties and is extensively used for marine fittings, condenser heads, radiator cores, springs, chains ete….

Naval brasses:-These contains 60%cu, 39%zn and 11%tin.It has high corrosion and abrasion resistance and is widely used for condenser plates, propeller shafts and marine works.

2.Bronzes:-

Alloys of copper with other elements except zinc are called bronzes. The most important bronzes are alloys of copper and tin, aluminium, silicon or beryllium .These may also contain phosphorous, lead, zinc or nickel.

1. Tin bronzes or phosphor bronzes:-

Tin bronzes are alloys of copper and tin and contain tin between 1 to 11%.These are also called as phosphor bronze .phosphorous invariably present as a de oxidizer in casting.The phosphorous content varies from 0.01 to 0.05%.

These bronzes posses high strength, toughness, high corrosion resistance, low coefficient of friction and do not susceptible to season cracking. These are used for bushes, cottor pins, clutch disks, springs, taps, marine pumps etc….Tin bronzes have good castability and widely used in the foundry.

Gun metal:-

Gun metal contains 88%cu,10%tin and 2%zn.It has considerable strength and toughness and resistance to sea water corrosion. It is used for bushes, nuts, hydraulic fittings, heavy load bearings, marine pumps etc…

Aluminium bronzes:-

Commercial aluminum bronzes contain aluminum between 4 to 11%.Aluminium bronzes containing up to 7.5% Al are generally single phase alloys. while those containing between 7.5 and 11% Al are two phase alloys.

The single phase aluminum bronze have good cold working properties, good strength and good corrosion resistance. These are used for corrosion resistance vessels, nuts, condenser tubes etc…

The properties of two phase aluminum bronzes can be improved by heat treatment. By controlling the composition and by heat treatment the tensile strength of these alloys van be varied from 47 to 95kg/sq mm with elongation gradually decreasing from 70 to 5%.The heat treated aluminum bronzes are used for gears, propellers, pump parts, bearing, bushings ,drawing and forming dies ets….

Silicon bronzes:-

These contains 90-97%cu,1-4%si and small amounts of zinc, iron and manganese. The thermal and electrical conductivity of those alloys is about 10% of that pure copper. Silicon bronzes have mechanical properties comparable to that of mild steel and corrosion resistance comparable to that of pure copper. These are used for storage vessels for chemical and gasses, marine construction, nuts, bolts, rivets etc…

Beryllium bronzes:-

Beryllium bronzes contain 1.5-2.25% of beryllium. These alloys can be easily cast, can be easily hot or cold worked and can be easily welded. Like Al alloys, beryllium bronzes can be age hardened and the hardness obtained will vary between 200 to 400 brinell, depending upon the aging time and also tensile strengths upto142kgl sq.mm can be obtained by suitable heat treatment and cold working. The thermal and electrical conductivities of these alloys is comparable to that of pure copper.

These bronzes are used for diaphragms, springs, surgical and dental instruments, gears, watch parts, screws, bearings etc….

Cupro nickels:-

These are the alloys of copper and nickel and contain upto 30% nickel. The copper-nickel binary phase diagram shows complete solubility. So that all cupronickels are single phase alloys. They are not susceptible to heat treatment and may have their properties altered only by cold working.

These alloys have resistance to corrosion fatigue and also high resistance to the corrosive and erosive action of rapidly moving sea water. They are widely used for condenser distiller, evaporator and heat exchanger tubes for naval vessels and costal power plants.

Nickel silvers (German silver):-

Nickel silvers are alloys of copper, nickel and zinc and contain 20-30% Ni,10-30% zn and the balance copper. The appearance of those alloys is similar silver and posses good corrosion resistant characteristics. These are mainly used for utensils, costume jewellary, name plates etc…

Aluminium & Aluminium alloys:-

Properties of aluinium:-

1. It is ductile and malleable due to FCC structure. It can be worked either hot or cold but afterrecrystallization does not show twins as are seen in cu &cu alloys.

2. It is light in weight (specific gravity 2.7kg/cm3)

3. It has very good thermal & electrical conductivity on weight to weight basis, it carries more electricity than copper.

4. It has excellent ability of getting alloyed with other elements like cu, si, Mg, zn etc….some of the alloys respond to precipitation hardening and some have excellent castability due to this and their light weight & good corrosion resistance and oxidation. They are widely used in automotiveand aeronautic fields.

5. Al has good malleability and formability, high corrosion resistance and high electrical & thermal conductivity.

6. Al ultra pure form of aluminium is used for photo graphic reflectors to take advantage of it's light reflectivity and non tarnishing characteristics.

7. Al is non toxic, non magnetic and non sparking. The non magnetic characterstic makes aluminium useful for electrical shielding purposes such as bus bar housings or enclosures for other electrical equipment.

8. One of the most important characteristics of aluminium is it's machinability & work ability. It can be cast by any know method rolled to any desired thickness, stamped, drawn, span, hammered forged and extruded to almost any conceivable shape.

9. These are extensively used for cooking utensils, various architectural components, food andchemical handling and storage equipment and assemblies.

Aluminium-Magnesium Alloys (Magnalium):-

1. Composition:-5.0% magnesium, 0.5%manganise

Properties:-

1. It is highly resistant to corrosion, machines well.
2. It takes high polish and anodizes well.
3. It has high strength.

Applications:- This type of alloys are used in the marine environments.

2.composition:- 10% magnesium with aluminium.

Properties:-

1. It oxidizes very easily
2. Light weight
3. Machinability good
4. Can be welded

Applications:- These alloys are used for the air craft and automobile components, dairy equipments and architectural work.

Aluminium copper alloys:-

1. These alloys having 4.5%cu and remaining material should be aluminium
2. This is a precipitation hardenable alloy and produces good strength after precipitationhardening.
3. This alloy has a moderate corrosion resistance and very much susceptible to hot tearing.
4. These alloys are mainly used for air craft castings and for other highly stressed parts dueto its good mechinability properties and shock resistance.

Y-Alloys:-

Composition:- 4% cu, 2% Ni, 1.5% magnesium

1. It has an excellent ability to retain the strength at elevated temperatures with faitly goodcorrosion resistance.
2. It can be easily cast and hot worked.

Applications:- These alloys are mainly used for pistons and cylinder heads of diesel and high duty petrol engines.

induminium:-

1. It contain about 5%cu & 1.5% Ni with small amounts Mn, Ti, Sb, Co and Zr.
2. It is superior to y-alloys at elevated temperature service particularly in respect of creepresistance.
3. It is used in aero engines and other continuous elevated temperature service applicationsup to 300°c.

Duralumin:-

It contain 3.5-4.5% cu, 0.4-0.7% Mn, 0.4-0.7% Mg, Fe or si <0.7%, Al balance.

Properties:-

1. it posses high machinability.
2. It is having high tensile strength.
3. Excellent casting & forging properties.

Applications:-

1. Air craft and automobile parts.
2. Al-bars, sheets, tubes and rivets etc…

Titanium & its alloys:-

Major characteristic & properties of Titanium:-

1. Titanium is one of the few allotropic metals i.e it can be exist in two different crystallographic forms. At room temperature it has a close packed hexagonal structure, designated as the Alpha-phase.

   At around 885°c, the alpha phase transforms to body centered cubic structure, known as the beta phase which is stable upto titanium's melting point of about 1680°c.
2. Titanium mechanical properties are closely related to these allotropic phases. For example the beta phase is much stronger but more brittle than the alpha phase.
3. Ti-alloys can be usefully classified into three groups on the basis of allotrophic phases i.e alpha, beta & alpha-beta alloys.
4. Ti & Ti-alloys are having attractive engineering properties. They are about 40% lighter than steel & 60% heavier than aluminium. The combination of moderate weight and high strengths up to 1400kg/cm2, gives titanium alloys the highest strength to weight ratio of any structure metal roughly 30% greater than aluminium &

   This exceptional strength to weight ratio is maintained from -220°c up to 540°c
5. A second outstanding property of titanium material is corrosion resistance. The presence of a thin, tough oxide surface film provides excellent resistance to atmospheric and sea environments as well as a wide range of chemicals, including chlorine and organics containing chlorides. Being near the chloride end of the galvanic series, titanium performs the function of a noble metal.
6. Other notable properties are a higher melting point than iron, low thermal conductivity, low co-efficient of expansion and high electrical resistivity.

Applications:-

These titanium and its alloys are used for surgical implants, marine hard ware, compressors & valve bodies.

Titanium alloys:-

Alpha alloys:-

1. These alloys contain the alloying elements as aluminium, tin, columbium, zirconium, vanadium and molybdenum in amounts varying about 1-10%.
2. They are non heat treatable, having good stability up to 540°c and down as low as -220°c.They have good combination of weldability, strength and toughness.
3. The 5% Al and 25% tin alloy is the most widely used alpha alloy has been employed in numerous space and air craft applications.
4. It has strength at room temperature of 8400kg/cm2, acceptable ductility and is useful at room temperature up to 430 and 540°c. In addition, it has good oxidation resistance and good weldability and formability.

Alpha-Beta alloys:-

This is the largest and most widely used group of titanium alloys. Because these alloys are a two phase combination of alpha & beta alloys, their behaviour falls in a range between the two, single phase alloys.

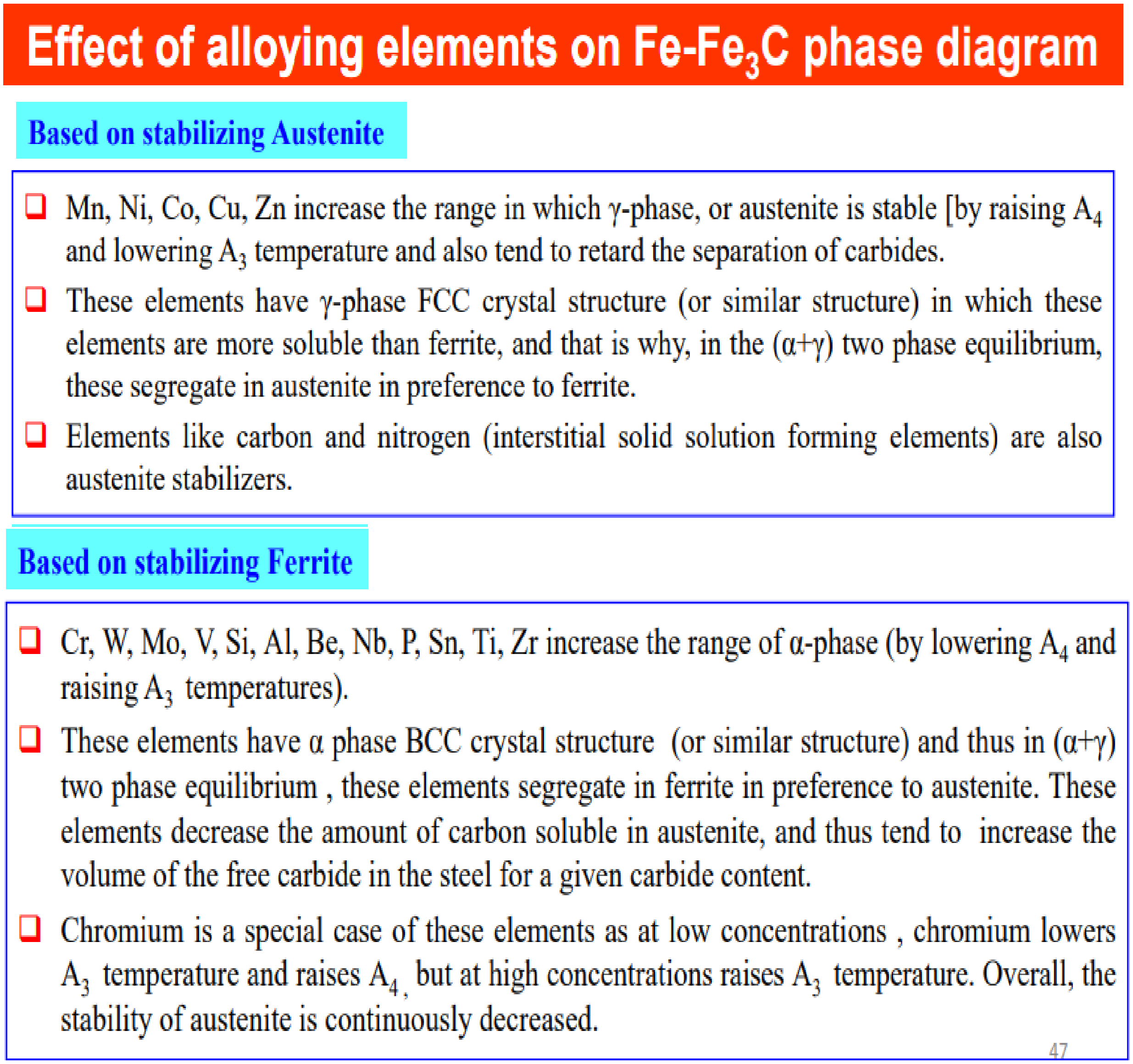
1. They are heat treatable, useful up to 430°c, more formable than alpha alloys, but less tough and more difficult to weld.
2. The most popular alloy in this group is the 6% Al & 4% vanadium. It can be heat treated up to 11,972kg/cm2 has good impact and fatigue strength and unlike other alpha-beta alloys is weldable.
3. The 6% Al, 6% vanadium & 2% tin alloy is heat treatable to higher strength than any other alpha beta alloy(13380kg/cm2)

Beta alloys:-

These beta alloys have exceptional high strength over 14085kg/cm^2. Their lack of toughness and low fatigue strength limits their use. They retain an unusually high percentage of strength up to 320°c but cannot be used at much higher temperature and they become brittle at temperature below -40°c.

UNIT-3

Heat treatment of Alloys



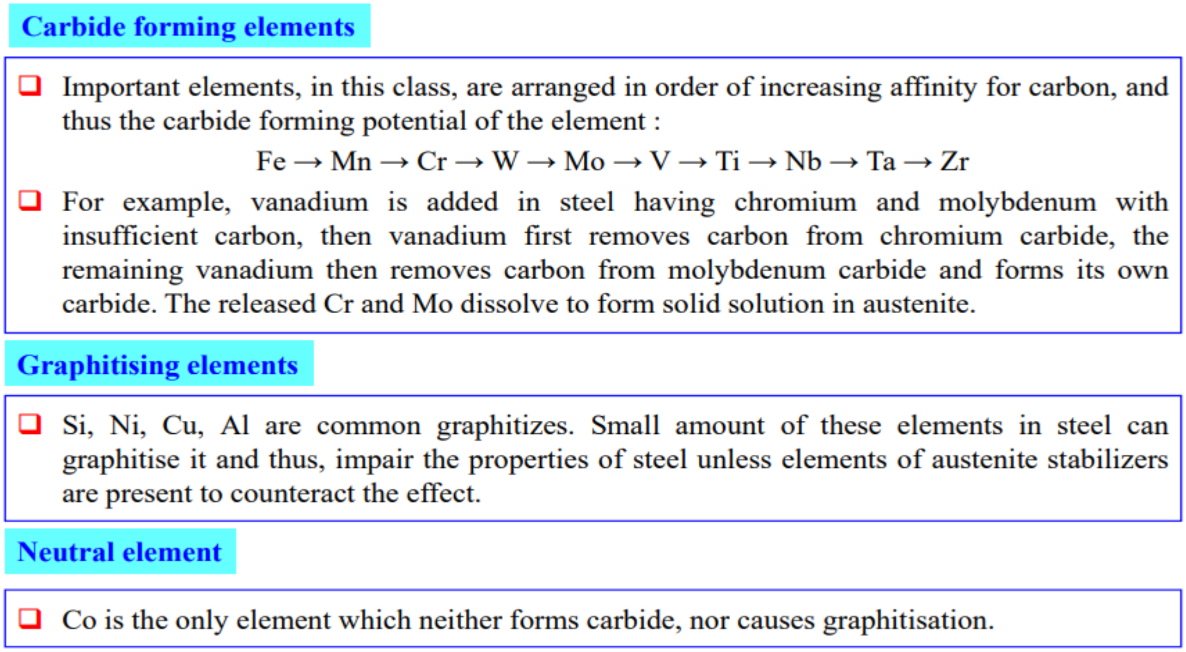
Effect of alloying elements on Fe-Fe_3C phase diagram

Based on stabilizing Austenite

- Mn, Ni, Co, Cu, Zn increase the range in which γ-phase, or austenite is stable [by raising A_4 and lowering A_3 temperature and also tend to retard the separation of carbides.
- These elements have γ-phase FCC crystal structure (or similar structure) in which these elements are more soluble than ferrite, and that is why, in the (α+γ) two phase equilibrium, these segregate in austenite in preference to ferrite.
- Elements like carbon and nitrogen (interstitial solid solution forming elements) are also austenite stabilizers.

Based on stabilizing Ferrite

- Cr, W, Mo, V, Si, Al, Be, Nb, P, Sn, Ti, Zr increase the range of α-phase (by lowering A_4 and raising A_3 temperatures).
- These elements have α phase BCC crystal structure (or similar structure) and thus in (α+γ) two phase equilibrium , these elements segregate in ferrite in preference to austenite. These elements decrease the amount of carbon soluble in austenite, and thus tend to increase the volume of the free carbide in the steel for a given carbide content.
- Chromium is a special case of these elements as at low concentrations , chromium lowers A_3 temperature and raises A_4 , but at high concentrations raises A_3 temperature. Overall, the stability of austenite is continuously decreased.



Carbide forming elements

- Important elements, in this class, are arranged in order of increasing affinity for carbon, and thus the carbide forming potential of the element :

$$Fe \rightarrow Mn \rightarrow Cr \rightarrow W \rightarrow Mo \rightarrow V \rightarrow Ti \rightarrow Nb \rightarrow Ta \rightarrow Zr$$

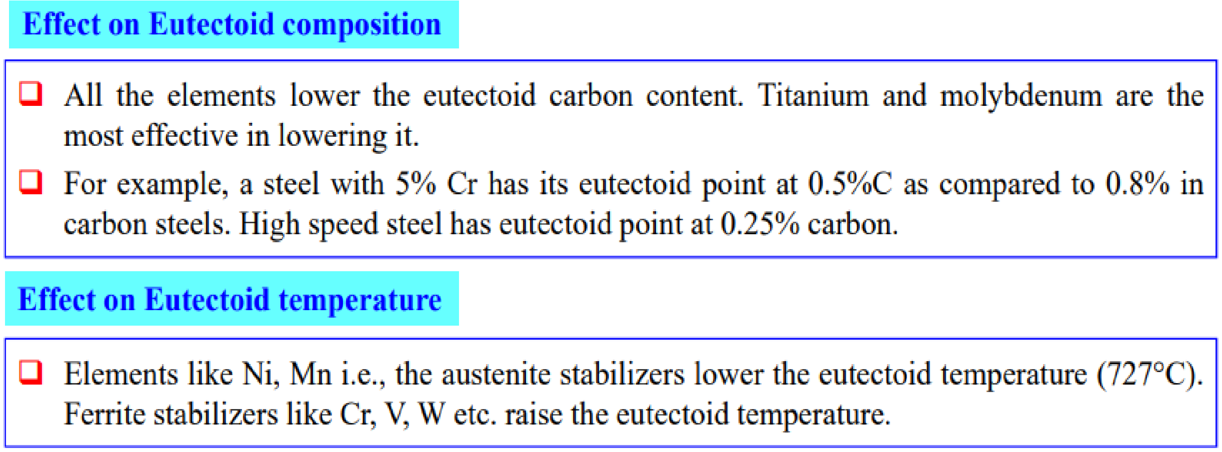
- For example, vanadium is added in steel having chromium and molybdenum with insufficient carbon, then vanadium first removes carbon from chromium carbide, the remaining vanadium then removes carbon from molybdenum carbide and forms its own carbide. The released Cr and Mo dissolve to form solid solution in austenite.

Graphitising elements

- Si, Ni, Cu, Al are common graphitizes. Small amount of these elements in steel can graphitise it and thus, impair the properties of steel unless elements of austenite stabilizers are present to counteract the effect.

Neutral element

- Co is the only element which neither forms carbide, nor causes graphitisation.



Effect on Eutectoid composition

- All the elements lower the eutectoid carbon content. Titanium and molybdenum are the most effective in lowering it.
- For example, a steel with 5% Cr has its eutectoid point at 0.5%C as compared to 0.8% in carbon steels. High speed steel has eutectoid point at 0.25% carbon.

Effect on Eutectoid temperature

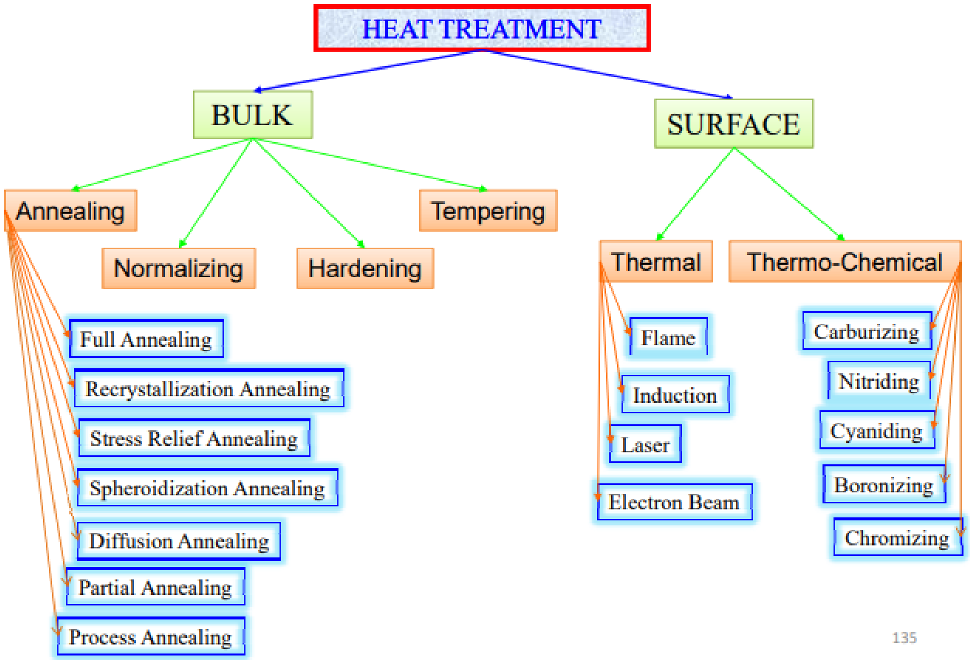
- Elements like Ni, Mn i.e., the austenite stabilizers lower the eutectoid temperature (727°C). Ferrite stabilizers like Cr, V, W etc. raise the eutectoid temperature.

Heat treatment is defined as an operation involving the heating and cooling of a metal or an alloy in the solid-state to obtain certain desirable properties without change composition. The process of heat treatment is carried out to change the grain size, to modify the structure of the material, and to relieve the stresses set up the material after hot or cold working.

- The heat treatment is done to improve the machinability.
- To improve magnetic and electrical properties.
- To increase resistance to wear, heat and corrosion, and much more reason.

Heat treatment consists of heating the metal near or above its critical temperature, held for a particular time at that finally cooling the metal in some medium which may be air, water, brine, or molten salts. The heat treatment process includes annealing, case hardening, tempering, normalizing and quenching, nitriding, cyaniding, etc

Types of Heat Treatment Processes



Following are the **different types of heat treatment processes:**

1. Annealing
2. Normalizing
3. hardening
4. Tempering
5. Nitriding
6. Cyaniding
7. Induction Hardening
8. Flame Hardening

Annealing

Annealing is one of the most important processes of heat treatment. It is one of the most widely used operations in the heat treatment of iron and steel and is defined as the softening process. Heating from 30 – 50°C above the upper critical temperature and cooling it at a very slow rate by seeking it the furnace. The main aim of annealing is to make steel more ductile and malleable and to remove internal stresses. This process makes the steel soft so that it can be easily machined.

Purpose of Annealing

- It softens steel and to improve its machinability.
- To refine grain size and remove gases.
- It removes the internal stresses developed during the previous process.
- To obtain desired ductility, malleability, and toughness.
- It modifies the electrical and magnetic properties.

Procedure for Annealing

Depending on the carbon content, the steel is heated to a temperature of about 50° to 55°C above its critical temperature range. It is held at this temperature for a definite period of time depending on the type of furnace and nature of work. The steel is then allowed to cool inside the furnace constantly.

Application of annealing

It is applied to castings and forgings.

Types of annealing:

1 Complete Annealing:

In this process, steel is heated to 30 to 50 degrees Celcius above the critical temperature of steel and this temperature is maintained for specified period of time, heat preservation for a period of time after slow cooling .The cooling rate may be about 10 degree C per hour.After that, material is allowed to cool down slowly inside the furnace without any forced cooling.Complete annealing is used in worked sheets, forging and casting made from medium and high carbon steels.Low carbon steel has low hardness and is not applicable to machining. After complete annealing process, Fe3C2 precipitated in mesh along the grain boundary, the strength, hardness, plasticity and toughness of steel are significantly reduced.

Purpose of Complete Annealing:

Complete annealing is done to get all the changes in the properties of the metals like
1 Producing equibrilium microstructure.
2 Increase in ductility
3 Reduction in hardness, strength, brittleness and
4 Removal of internal stresses.
The microstructure after annealing contains coarse ferrite and pearlite.

2. Process Annealing:

This process is mainly suited for low carbon steel. In this process material is heated up to a temperature just below the lower critical temperature of steel or above its recrystallisation temperature and then is allowed to cool slowly for some time. Cold worked steel normally have increased hardness and decrease ductility making it difficult to work. Process annealing improves this characteristics by making it more ductile and decreasing its hardness. This is mainly carried out on cold rolled steel like wire drawn steel, etc.

Purpose of Process Annealing:

1 Process annealing is done for recrystallization of metal.
2 During process annealing, new equiaxed, strain-free grains nucleate at high-stress regions in the cold-worked microstructure, and hence hardness and strength decrease whereas ductility increases.
3 The main aim of the process annealing is to restore ductility of cold worked metal.

3. Stress relief annealing:

In stress relief annealing, the metal is heated to a lower temperature about 650 degree and is kept at this temperature for some time in the furnace to remove the internal stress of metal followed by slow cooling.

Large castings or welded structures tend to possess internal stresses mainly caused during their manufacturing and uneven cooling.
No phase transformation takes place during stress relief annealing.

Purpose of stress Relief annealing:

The main aim of the stress relief annealing is to remove the internal stresses produced in the metal due to
i) Plastic deformation.
ii) Non-uniform cooling
iii) Phase transformation

4 Spheroidizing Annealing:

Spheroidizing Annealing process is for high carbon and alloy steel in order to improve their machinability. In spheroidizing annealing, the steel is heated to a temperature below A1 temperature, kept at the temperature for sometime followed by slow cooling. The holding time varies from 15-25 hours. It is mainly used for eutectoid steel and hypereutectic steel such as carbon tool steel, alloy tool steel, bearing steel etc.

This process improves the internal structure of the steel. This can be done by two methods:

i) The material is heated just below the lower critical temperature about 700 degrees and the temperature is maintained for hours and then allowed to cool down.

ii) Heating and cooling the material alternatively between the temperature just above and below the lower critical temperature.

Pupose of Spheroidizing Annnealing:

a) The main aim of spheroidizing annealing is to improve the machinability of steel.
b) This process reduces harness, uniform structure and prepare the material for quenching.
c) In this process cementite is converted into spherical form.

5 Isothermal Annealing:

In isothermal annealing process, the steel is heated above the upper critical temperature. When the steel is heated above upper critical temperature, it converts rapidly into austenite structure. After that, the steel is cooled to a temperature below the lower critical temerature 600 to 700 degree Celcius.The cooling is done by force cooling methods.
This temperature is maintained for a specific time period to produce a homogenous structure in the material.
Isothermal Annealing process is mainly applied to low carbon and alloy steel to improve their machinability.

6 Diffusion Annealing:

This process is known as diffusion annealing as in this process the iron and carbide diffuses with each other. For diffusion higher temperature is required, so the steel is heated above the upper critical temperature. The temperature is nearly about 1000 to 1200 degrees Celcius.
The heat preservation time in this process is nearly 10 to 15 hours.

After diffusion annealing, complete annealing and normalizing are done to refine the tissue.

This process is applied to high-quality steel and segregation of serious alloy steel casting and ingots.

Purpose of Diffusion Annealing:

The main purpose of diffusion annealing is to eliminate dendritic segregation and regional segregation.in the solidification process and to homogenize the composition and organization.

7 .Incomplete Annealing:

In this incomplete annealing process, the steel is heated to about upper critical temperature. The heat treatment process is obtained by slow cooling after thermal insulation.

Purpose of Incomplete Annealing:

This process is mainly used to obtain spherical pearlite tissues for the hypereutectic steel to eliminate the internal stress, reduce the hardness and improve the machinability.

NORMALIZING

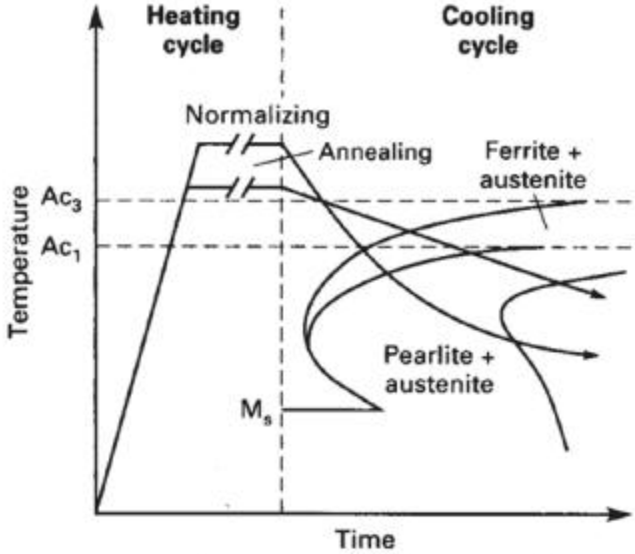
In this heat treatment steel is heated in the austenite region and then cooled in still air. The microstructure of normalized plain carbon steels consists of pro-eutectoid ferrite and fine pearlite.

The aim of the normalizing process is:

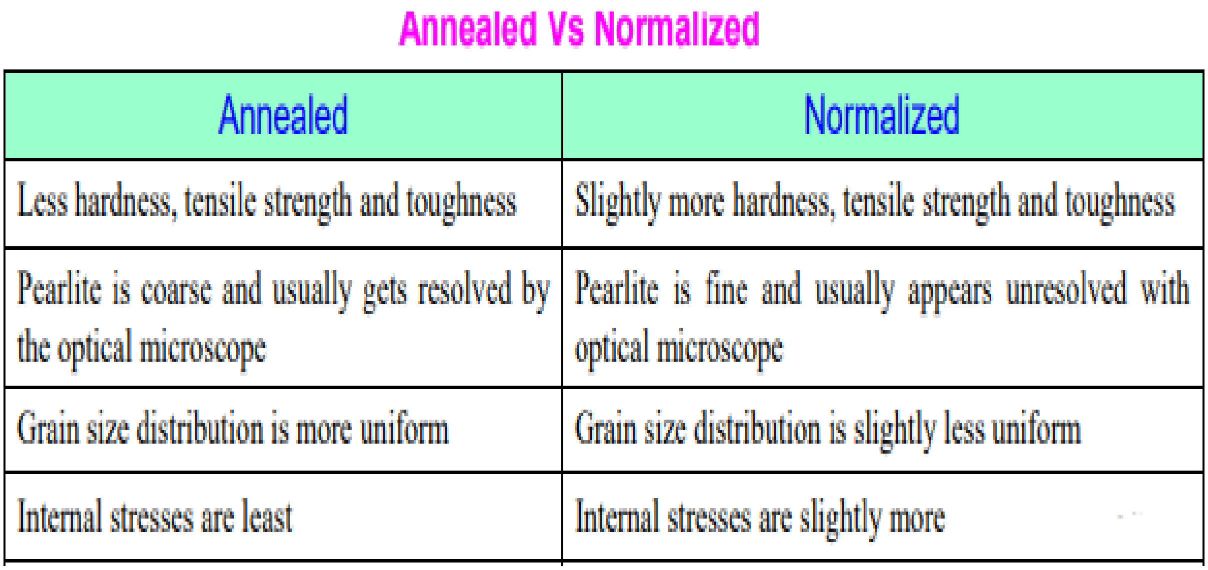
1. To refine the gain structure
2. To increase the strength of the steel
3. To reduce compositional segregation in castings or forgings and provide a more uniform structure.

- Steel is normalized to refine grain size, make its structure more uniform, make it more responsive to hardening, and to improve machinability.
- When steel is heated to a high temperature, the carbon can readily diffuse, resulting in a reasonably uniform composition from one area to the next. The steel is then more homogeneous and will respond to the heat treatment more uniformly.

- Normalizing is an austenitizing heating cycle followed by cooling in still or slightly agitated air. Typically, the temperatures for normalizing are approximately 55°C (100°F) above the upper critical line (that is, above Ac3 for hypoeutectoid steels and above Acm for hypereutectoid steels).
- To be properly classed as a normalizing treatment, the heating portion of the process must produce a homogeneous austenitic phase prior to cooling. Fig compares the time-temperature cycle of normalizing to that of full annealing.



Comparison of normalizing and full annealing heat treatment cycle



Annealed Vs Normalized

Annealed	Normalized
Less hardness, tensile strength and toughness	Slightly more hardness, tensile strength and toughness
Pearlite is coarse and usually gets resolved by the optical microscope	Pearlite is fine and usually appears unresolved with optical microscope
Grain size distribution is more uniform	Grain size distribution is slightly less uniform
Internal stresses are least	Internal stresses are slightly more

Hardening

- The maximum hardness of any steel is associated with a fully martensitic structure. This microstructure can be produced only if the cooling rate applied is higher than the critical cooling rate for the corresponding steel.
- Hardenability is defined as the “susceptibility to hardening by rapid cooling”, or as “the property, in ferrous alloys, that determines the depth and distribution of hardness produced by quenching”. Both of these definitions emphasize hardness. As discussed previously, the source of hardening is the formation and presence of martensite, and therefore a third definition of hardenability, “the capacity of a steel to transform partially or completely from austenite to some percentage of martensite at a given depth when cooled under some given conditions,” more accurately describes the physical process underlying hardening

Hardenability

- Hardenability is one of the most important properties of a steel because it describes the ease with which a given steel can be quenched to form martensite or the depth to which martensite is formed on a given quench.
- It is an important property for welding, since it is inversely proportional to weldability, that is, the ease of welding a material.
- The ability of steel to form martensite on quenching is referred to as the hardenability. Hardenability is a measure of the capacity of a steel to be hardened in depth when quenched from its austenitizing temperature.
- Steels with high hardenability form martensite even on slow cooling.
- High hardenability in a steel means that the steel forms martensite not only at surface but to a large degree throughout the interior.
- For the optimum development of strength, steel must be fully converted to martensite.
- To achieve this, the steel must be quenched at a rate sufficiently rapid to avoid the decomposition of austenite during cooling to such products as ferrite, pearlite and bainite. Hardenability of a steel should not be confused with the hardness of a steel.

Hardness ≠ Hardenability

- The Hardness of a steel is a measure of a sample's resistance to indentation or scratching
- Harden ability refers to its ability to be hardened to a particular depth under a particular set of conditions.

- It is a qualitative measure of the rate at which hardness drops off with distance into the interior of a specimen as a result of diminished martensite content. Hardenability is more related to depth of hardening of a steel upon heat treat. The depth of hardening in a plain carbon steel may be 2-3 mm Vs 50 mm in an alloy steel. A large diameter rod quenched in a particular medium will obviously cool more slowly than a small diameter rod given a similar treatment. Therefore, the small rod is more likely to become fully martensitic

Determination of Hardenability

- Fig. shows the shape and dimensions of a Jominy specimen and the fixture for supporting the specimen in a quenching system.
- The specimen is cooled at one end by a column of water; thus, the entire specimen experiences a range of cooling rates between those associated with water and air cooling.
- After quenching, parallel flats are ground on opposite sides of the specimen, and hardness readings are taken every 1⁄16 in. from the quenched end and plotted as shown in Fig. 4.4. Hardenability differences between different grades of steels can be readily compared if Jominy curves are available.
- For example, Fig. shows hardenability differences between different grades of alloy steels containing 0.5% C. Higher hardness persists to greater distances from the quenched end in the more hardenable steels.

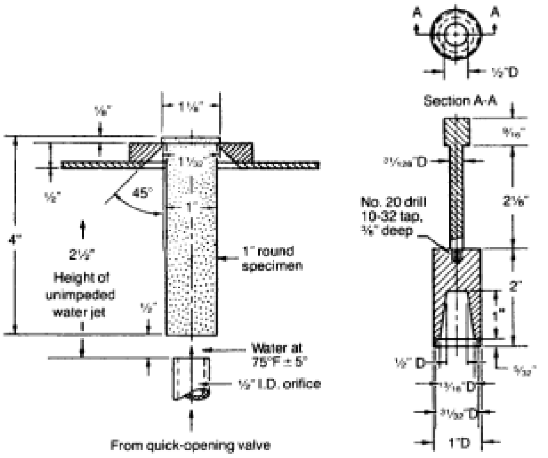


Fig. Jominy-Boegehold specimen for end-quench test for hardenability.

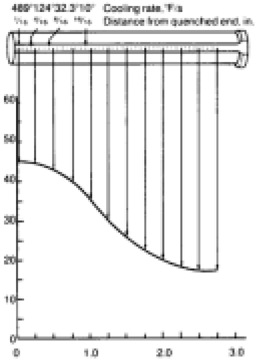


Fig. Method of plotting hardness data from an end-quenched Jominy specimen.

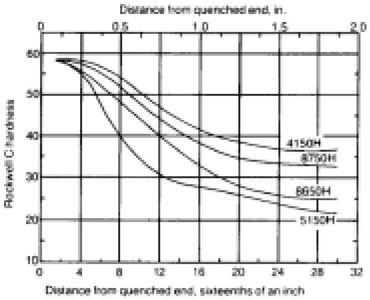
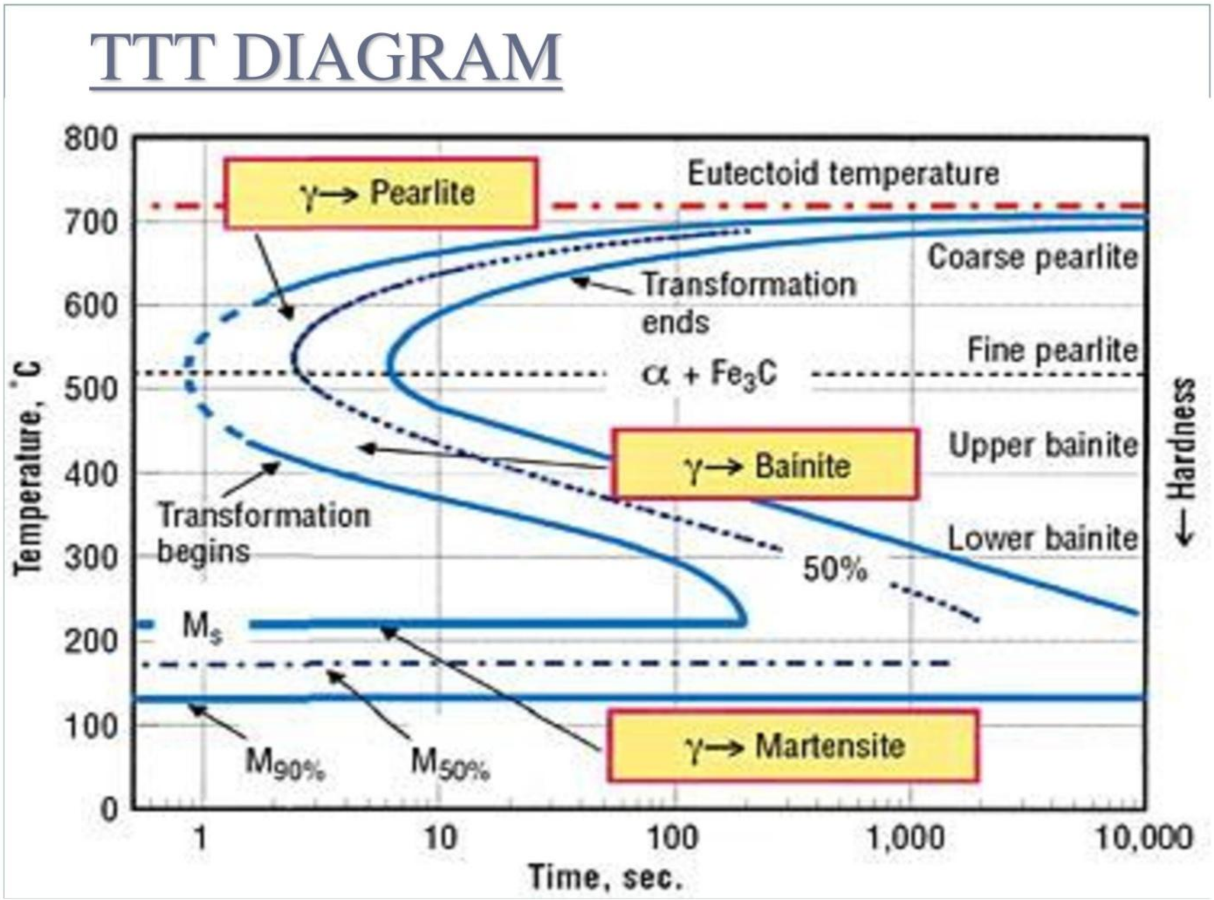


Fig. Results of end-quench tests for four different grades of alloy steels, all containing 0.5% C.

Time-Temperature-Transformation (TTT) Diagrams

- TTT diagrams, also called as Isothermal (temperature constant) Transformation diagrams.
- For every composition of steel we should draw a different TTT diagram
- For the determination of isothermal transformation (or) TTT diagrams, we consider molten salt bath technique combined with metallography and hardness measurements.
- In molten salt bath technique two salt baths and one water bath are used.
- Salt bath I is maintained at austenising temperature (780˚C for eutectoid steel).
- Salt bath II is maintained at specified temperature at which transformation is to be determined (below Ae1), typically 700-250°C for eutectoid steel.
- Bath III which is a cold water bath is maintained at room temperature
- In bath I number of samples are austenite at A1+20-40°C for eutectoid, A3+20-40°C for hypo-eutectoid steel and A +20-40°C for hyper-eutectoid steels for about an hour.
- Determination of TTT diagram for eutectoid steel hypo-eutectoid steel and ACm+20-40°C for hyper-eutectoid steels for about an hour.
- Then samples are removed from bath I and put in bath II and each one is kept for different specified period of time say t1, t2, t3, t4,…...........,tn etc.
- After specified times, the samples are removed and quenched in cold water.
- The microstructure of each sample is studied using metallographic techniques.
- The type, as well as quantity of phases, is determined on each sample.
- Transformation of austenite to ferrite-cementite mixtures occurs after a definite time (say t1) This time during which transformation does not proceed is known as incubation period.
- The magnitude of incubation period provides a qualitative idea about the relative stability of supercooled austenite. Smaller incubation period corresponds to lesser stability of austenite.



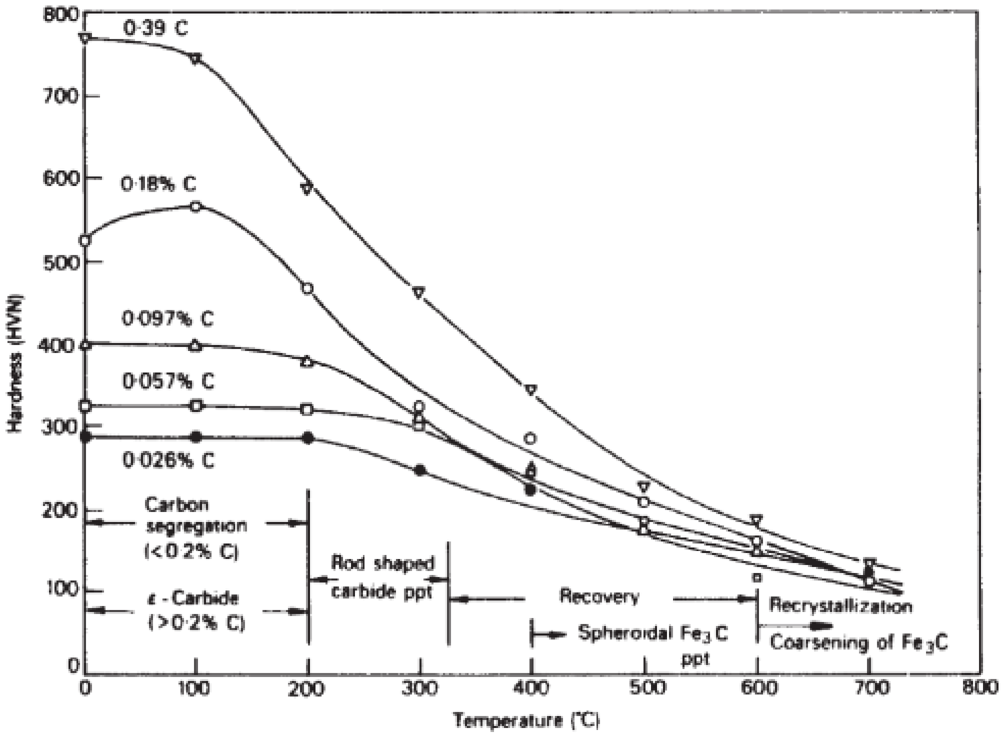
Tempering

- ➢ Martensite in steels can be a very strong and in its “as quenched” condition rather brittle. It is then necessary to modify its mechanical properties by heat treatment in the range 150–700oC. This process is called tempering, in which the microstructure approaches equilibrium under the influence of thermal activation.
- ➢ The general trend during the tempering of martensite therefore begins with the rejection of excess carbon to precipitate carbides but the substitutional solutes do not diffuse during this process. The end result of tempering is a dispersion of coarse carbides in a ferritic matrix which bears little resemblance to the original martensite.
- ➢ It should be borne in mind that in many steels, the martensite reaction does not go to completion on quenching, resulting in varying amounts of retained austenite which might decompose during the tempering process.
- ➢ The effect of tempering temperature on the hardness of steel is shown in Fig

Tempering of Plain Carbon Steels

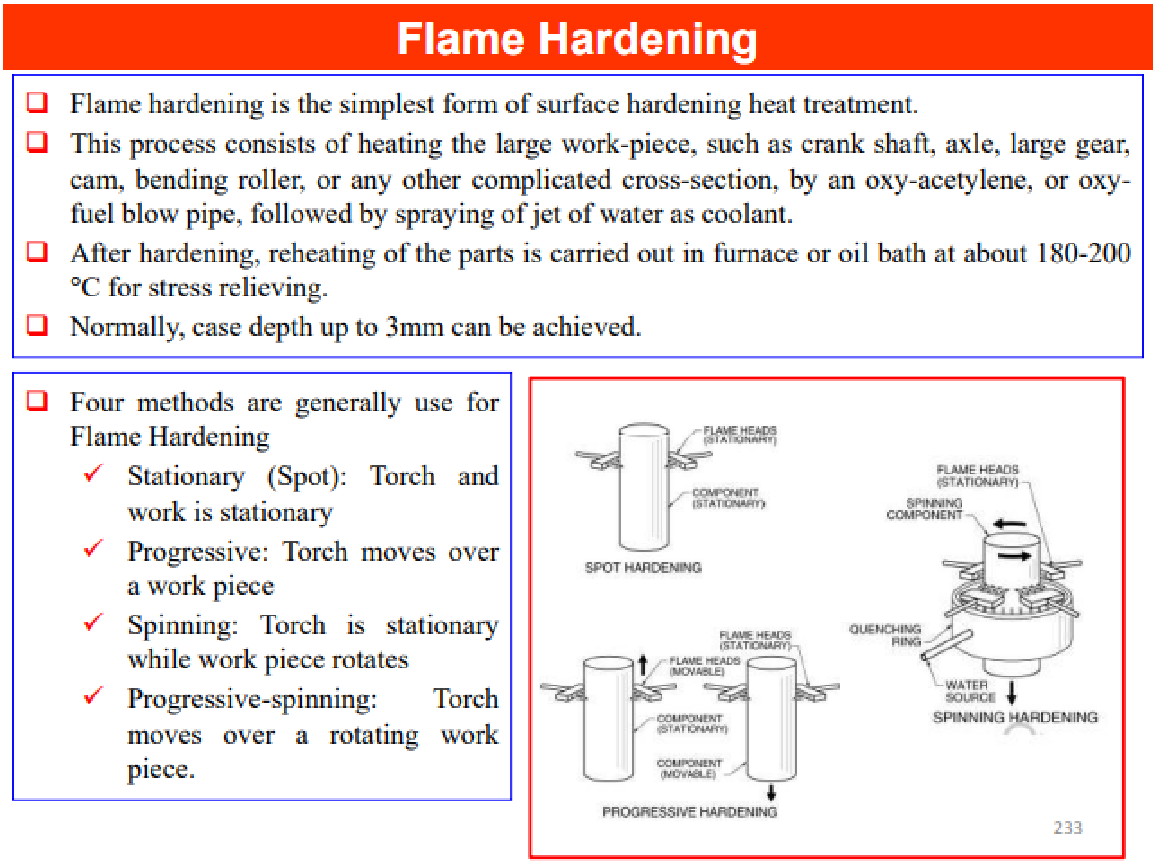
- On reheating as-quenched martensite, the tempering takes place in four distinct but overlapping stages:

- Stage 1, up to 250◦C: precipitation of ε-iron carbide; partial loss of tetragonality in martensite.
- Stage 2, between 200◦C and 300◦C: decomposition of retained austenite.
- Stage 3, between 200◦C and 350◦C: replacement of ε-iron carbide by cementite; martensite loses tetragonality.
- Stage 4, above 350◦C: cementite coarsens and spheroidizes; recrystallization of ferrite



[illegible] Hardness of iron–carbon martensites tempered 1 h at 100–700°C.

Surface - hardening methods



Flame Hardening

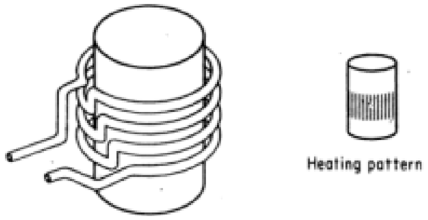
- ❑ Flame hardening is the simplest form of surface hardening heat treatment.
- ❑ This process consists of heating the large work-piece, such as crank shaft, axle, large gear, cam, bending roller, or any other complicated cross-section, by an oxy-acetylene, or oxy-fuel blow pipe, followed by spraying of jet of water as coolant.
- ❑ After hardening, reheating of the parts is carried out in furnace or oil bath at about 180-200 °C for stress relieving.
- ❑ Normally, case depth up to 3mm can be achieved.

- ❑ Four methods are generally use for Flame Hardening
  - ✓ Stationary (Spot): Torch and work is stationary
  - ✓ Progressive: Torch moves over a work piece
  - ✓ Spinning: Torch is stationary while work piece rotates
  - ✓ Progressive-spinning: Torch moves over a rotating work piece.

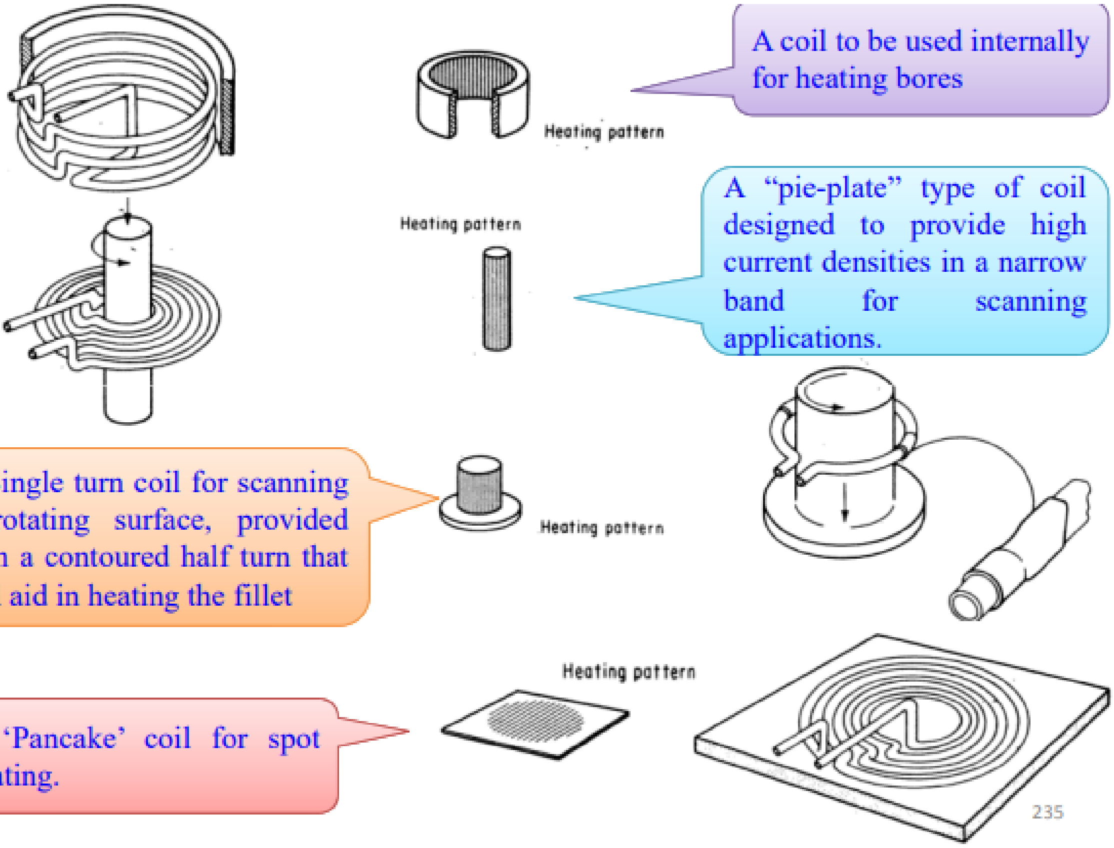
Induction Hardening

- Induction hardening may be used for local surface heat treatment. Generally, it is used to surface harden crank shafts, cam shafts, gears, crank pins and axles. In this process, heating of the component is achieved by electromagnetic induction.
- Here, an alternating current of high frequency passes through an induction coil enclosing the steel part to be heat treated. The induced emf heats the steel. the depth up to which the heat penetrates and rises the temperature above Ac_3 is inversely proportional to the square root of the AC frequency.
- Correspondingly, the hardened depth decreases with increasing frequency in induction hardening, the heating time is usually a few seconds. Immediately after heating water jets are activated to quench the surface . Martensite is produced at the surface, making it hard and wear resistant. The microstructure of the core remains unaltered. Induction hardening is suitable for mass production of articles of uniform cross section

Five basic designs of work coils with the heat patterns developed by each are shown below



A Simple Solenoid for external heating



A coil to be used internally for heating bores

A "pie-plate" type of coil designed to provide high current densities in a narrow band for scanning applications.

A Single turn coil for scanning a rotating surface, provided with a contoured half turn that will aid in heating the fillet

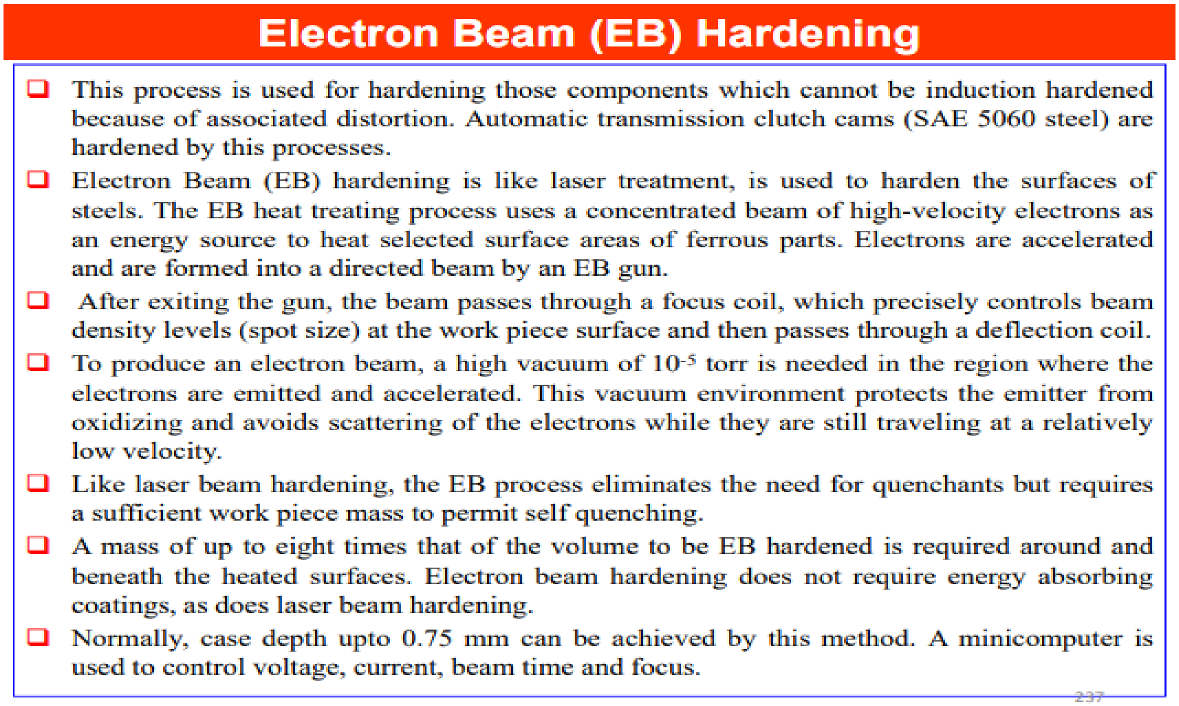
A 'Pancake' coil for spot heating.

Laser Hardening

- Laser hardening treatment is widely used to harden localized areas of steel and cast iron machine components. This process is sometimes referred to as laser transformation hardening to differentiate it from laser surface melting phenomena.
- There is no chemistry change produced by laser transformation hardening, and the process, like induction and flame hardening, provides an effective technique to harden ferrous materials selectively.
- As laser beams are of high intensity, a lens is used to reduce the intensity by producing a defocused spot of size ranging from 0.5 to 25 mm. proper control of energy input is necessary to avoid melting.
- Laser transformation hardening produces thin surface zones that are heated and cooled very rapidly, resulting in very fine Martensitic microstructures, even in steels with relatively low hardenability. High hardness and good wear resistance with less distortion result from this process.
- Laser hardening has the advantage of precise control over the area to be hardened, an ability to harden reentrant surfaces, very high speed of hardening and no separate quenching step (the quench is effected by the mass of the unheated material).
- The relationship between depth of hardening and power is as follows

$$casedepth(mm) = -0.11 + \frac{3.02P}{(D_b V)^{1/2}} \qquad P = laser\ power,\ D_b = Incident\ beam\ diameter \quad V = traverse\ speed\ (mm/s)$$

- The disadvantage is that the hardening is shallower than in induction and flame hardening.



Electron Beam (EB) Hardening

- This process is used for hardening those components which cannot be induction hardened because of associated distortion. Automatic transmission clutch cams (SAE 5060 steel) are hardened by this processes.
- Electron Beam (EB) hardening is like laser treatment, is used to harden the surfaces of steels. The EB heat treating process uses a concentrated beam of high-velocity electrons as an energy source to heat selected surface areas of ferrous parts. Electrons are accelerated and are formed into a directed beam by an EB gun.
- After exiting the gun, the beam passes through a focus coil, which precisely controls beam density levels (spot size) at the work piece surface and then passes through a deflection coil.
- To produce an electron beam, a high vacuum of 10^{-5} torr is needed in the region where the electrons are emitted and accelerated. This vacuum environment protects the emitter from oxidizing and avoids scattering of the electrons while they are still traveling at a relatively low velocity.
- Like laser beam hardening, the EB process eliminates the need for quenchants but requires a sufficient work piece mass to permit self quenching.
- A mass of up to eight times that of the volume to be EB hardened is required around and beneath the heated surfaces. Electron beam hardening does not require energy absorbing coatings, as does laser beam hardening.
- Normally, case depth upto 0.75 mm can be achieved by this method. A minicomputer is used to control voltage, current, beam time and focus.

Thermo Chemical Heat Treatment

- Chemical heat treatment is the process used to achieve different properties in core and steel components. Numerous industrial applications require a hard wear resistant surface called the case, and a relatively soft, tough inside called the core. Example: Gears
- They are two different methods. The first method is known as thermochemical treatment because the surface composition of steel changes by diffusion of carbon and/or nitrogen and sometimes other elements.
- The second method is known has surface hardening, it involves phase transformation by rapid heating and cooling of the outer surface . The aim of both methods are same

Carburizing

- Carburizing is the most widely used method of surface hardening. Here, the surface layers of a low carbon steel (<0.25) is enriched with carbon up to 0.8-1.0%. The source of carbon may be a solid medium, a liquid or a gas.
- In all cases, the carbon enters the steel at the surface and diffuses into the steel as a function of time at an elevated temperature. Carburizing is done at 920-950°C. at this temperature the following reaction takes place

$$\boxed{Fe+2CO\rightarrow Fe_{(c)}+CO_2}$$

- Where $Fe_{(c)}$ represents carbon dissolved in austenite. the rate of diffusion of carbon in austenite, at a given temperature is dependent upon the diffusion coefficient and the carbon concentration gradient.
- The carburizing equation given previously, $Fe+2CO\rightarrow Fe_{(c)}+CO_2$ is reversible and may proceed to the left, removing carbon from the surface layer if the steel is heated in an atmosphere containing carbon dioxide (CO_2). This is called decarburization.
- Decarburization may be prevented by using an endothermic gas atmosphere in the furnace to protect the surface of the steel from oxygen, carbon dioxide and water vapor. An endothermic gas atmosphere is prepared by reacting relatively rich mixtures of air and hydrocarbon gas (usually natural gas) in an externally heated generator in the presence of a nickel catalyst.
- Carburizing can be done by Pack carburizing, Liquid carburizing, Gas carburizing and vacuum carburizing.

Pack Carburizing

- This method of carburizing is also known as solid carburizing.
- In this process, steel components to be heat treated are packed with 80% granular coal and 20% $BaCO_3$ as energizer in heat resistant boxes and heated at 930°C in furnace for a specific time which depends on the case depth required.
- Such a high temperature in furnace helps in absorption of carbon at the outer layer. The following reactions takes place:
  i. Energizer decomposes to give CO gas to the steel surface

$$BaCO_3 \rightarrow BaO + CO_2$$

$$CO_2 + C \rightarrow 2CO$$

  ii. Carbon monoxide reacts with the surface of steel :

$$2CO + Fe \rightarrow Fe(c) + CO_2$$

  iii. Diffusion of carbon into steel

  iv. CO_2 formed in step (ii) reacts with "C" in the coal

$$CO_2 + C \leftrightarrow 2CO$$

- For a given steel at a given temperature, the depth of penetration is dependent on diffusion and can be related to the time t by the equation

$$casedepth = k\sqrt{t} \qquad \text{Where } k \text{ is constant}$$

- Generally, carburizing time varies from 6 hours to 8 hours, and case depth obtained varies from 1 mm to 2 mm.

Liquid Carburizing

- It is also popularly known as salt bath carburizing. In this process, carburizing occurs through molten cyanide (CN) in low carbon steel cast pot type furnace heated by oil or gas. Bath temperature is maintained between 815°C and 900°C.
- The life of pot depends on quality of material, operating temperature and mode of operation, viz. whether it is continuous or intermittent. Continuous and automatic processes give good end results.
- The bath surface is covered with graphite or coal to reduce radiation losses and excessive decomposition of cyanide.
- Different salt mixtures used in this processes are named according to their carbon potential activity. Besides sodium or potassium cyanide, the bath contains (i) Sodium and potassium chloride (ii) Barium chloride which acts as an activator

$$BaCl_2 + 2NaCN \rightarrow Ba(CN)_2 + 2NaCl$$

$$Ba(CN)_2 + Fe \rightarrow Fe(c) + BaCN_2$$

- Some beneficial nitrogen diffusion may also take place through oxidation of CN to CNO. In liquid carburizing, heating time is short and heat transfer is rapid. There is complete uniformity of the carburized layer in the component.
- This process gives a thin and clean hardened layer of ~0.08mm thick.

Gas Carburizing

- This is the most widely used method of carburizing. It is carried out in retort type, sealed quench type, or continuous pusher type furnaces. These furnaces are either gas fired or are heated electrically. Gas carburizing temperature varies from 870°C to 950°C.
- Gas atmosphere for carburizing is produced from liquid (methanol, isopropanol) or gaseous hydrocarbons (propane and methane). An endothermic gas generator is used to supply endothermic gas.
- A mixture of propane or methane with air is cracked in hot retort of an endogas generator to form carrier gas, whose dew point is adjusted at about +4°C by proper gas/air ratio. The approximate composition of this gas is as follows.

- Such a gas acts as a 'carrier gas' for the process. Furnace chamber is purged with this gas to gas maintain a slightly positive pressure. This in turn prevents infiltration of air from atmosphere.
- This gas also prevents oxidation of the steel during heating. When the material reaches carburizing temperatures, propane or methane is introduced to maintain a specific carbon potential

Nitrogen	40%
Hydrogen	40%
Carbon monoxide	20%
Carbon dioxide	0.3%
Methane	0.5%
Water vapour	0.8%
Oxygen	In traces

Gas Carburizing

- During gas carburizing, the following reactions take place:
    1. $C_3H_8 \rightarrow 2CH_4 + C$ (cracking of hydrocarbon)
    2. $CH_4 + Fe \rightarrow Fe(C) + 2H_2$
    3. $CH_4 + CO_2 \rightarrow 2CO + 2H_2$
    4. $2CO + Fe \rightarrow Fe(C) + CO_2$
- Carburizing occurs mainly due to conversion of CO to CO_2 through reaction (iv). Hydrogen reacts with CO_2 and increases CO concentration by the reaction

$$H_2 + CO_2 \rightarrow CO + H_2O$$

- Traces of O_2 are also present due to the following reactions:

$$2CO_2 \rightarrow 2CO + O_2$$

$$CO_2 + Fe \rightarrow Fe(c) + O_2$$

- Average concentrations of CO_2 , H_2O, and O_2 are 0.2%, 0.5% and 10^{-14} ppm respectively.
- One of the recent developments in the gas carburizing technique is the use of nitrogen as a carrier gas. Normally, nitrogen gas is used with some minor additives. Carbon potential is controlled by adjusting the level of oxidizing constituents.
- Currently the cost of equipment for this modified process is high. Also, skilled and well trained operators are required for successful operation of this process.

Cyaniding and Carbonitriding

- In cyaniding and carbonitriding processes, the surface layer of steel (with 0.3-0.4%C) is hardened by addition of both carbon and nitrogen.
- In this case that contain both carbon and nitrogen are produced in liquid salt baths (cyaniding) or by use of gas atmospheres (carbonitriding). The temperatures used are generally lower than those used in carburizing, being between 750-900°C.
- Exposure is for a shorter time, and thinner cases are produced, up to 0.010in. For cyaniding and up to 0.030in. For carbonitriding.
- In Cyaniding is done in a liquid bath of NaCN, with the concentration varying between 30 and 97%. Both carbon and nitrogen enter the steel via the following reactions:

$$2NaCN + O_2 \longrightarrow 2NaCNO$$

$$2NaCNO + O_2 \rightarrow Na_2CO_3 + CO + 2N$$

$$2CO \rightarrow CO_2 + C$$

- Carbon and nitrogen so formed in atomic form diffuse into the steel and give thin wear resistant layer of the carbonitride ε-phase.
- The temperature used for cyaniding is lower than that for carburizing and in the range of 800-870°C. the time of cyaniding is 0.5-3 hour to produce a case depth of 0.25 mm or less.
- Cyaniding process is not suitable for hardening those parts which are subjected to shock, fatigue and impact because nitrogen addition has adverse effects on such properties of steels.

Cyaniding and Carbonitriding

- Carbonitriding is a case-hardening process in which a steel is heated in a gaseous atmosphere of such composition that carbon and nitrogen are absorbed simultaneously.
- This process is also known as dry cyaniding or gas cyaniding. It is the gas carburizing process modified by the addition of anhydrous ammonia.
- The decomposition of ammonia provides the nitrogen, which enters the steel along with carbon.
- A typical gas mixture consists of 15% $NH_{3,}$ $CH_{4,}$ and 80% of neutral carrier gas. The temperature used is 750-900°C. With increasing temperature, a greater proportion of carbon enters the steel.
- The presence of nitrogen in the austenite accounts for the major differences between carbonitriding and carburizing.
- Carbon-nitrogen austenite is stable at lower temperatures than plain-carbon austenite and transforms more slowly on cooling. Carbonitriding therefore can be carried out at lower temperatures and permits slower cooling rates than carburizing in the hardening operation
- In this process, surface hardenability, wear resistance and corrosion resistance are better than in the carburizing process. But the time required for heat treatment is longer than that for carburizing.

Nitriding

- In contrast to the processes described before, nitriding is carried out in the ferrite region. Consequently, no phase change occurs after nitriding .
- This part to be nitrided should possess the required core properties prior to nitriding. Pure ammonia decomposes to yield nitrogen which enters the steel:

$$2NH_3 \rightarrow 2[N]_{Fe} + 3H_2$$

- The solubility of nitrogen in ferrite is small. Most of the nitrogen that enters the steel forms hard nitrides (e.g. Fe_3N). A typical nitriding steel contains alloying elements of 1%Al, 1.5%Cr and 0.2%Mo. Al, Cr, and Mo form very hard and wear resistant nitrides.
- The temperature of nitriding is 500-590°C. the time for a case depth of 0.02mm is about 2 hour. In addition with wear resistance, it also increases the resistance of a carbon steel to corrosion in moist atmospheres.
- A common problem encountered in nitriding is the formation of γ' nitride (Fe_4N) on the outer layers of the case , known as the "white layer", as it looks white under the microscope. This layer is very brittle and tends to crack. It must be removed by final grinding operation. Its formation can be minimized by maintaining the correct ratio of NH_3/ H_2 in the gas mixture during the heat treatment.
- There are two ways by which white layer can be totally suppressed
    - ✓ Floe process or double stage nitriding, where a white layer is first produced and then decomposed
    - ✓ Ion nitriding process or Plasma nitriding

UNIT-4
Powder Metallurgy

Powder Metallurgy–Engineering and technology of producing metal powders and making finished / semifinished objects from mixed or alloyed powders with or without the addition of nonmetallic constituents

Basic Processes In Powder Metallurgy:

Powder production, Compaction, Sintering, & Secondary operations

Powder production:
Raw materials: Powder
Powders can be pure elements, pre-alloyed powders.
Methods for making powders –

- Atomization: Produces powders of both ferrous and non-ferrous powders like stainless steel, superalloys, Ti alloy powders.
- Reduction of compounds: Production of iron, Cu, tungsten, molybdenum
- Electrolysis: for making Cu, iron, silver powders.

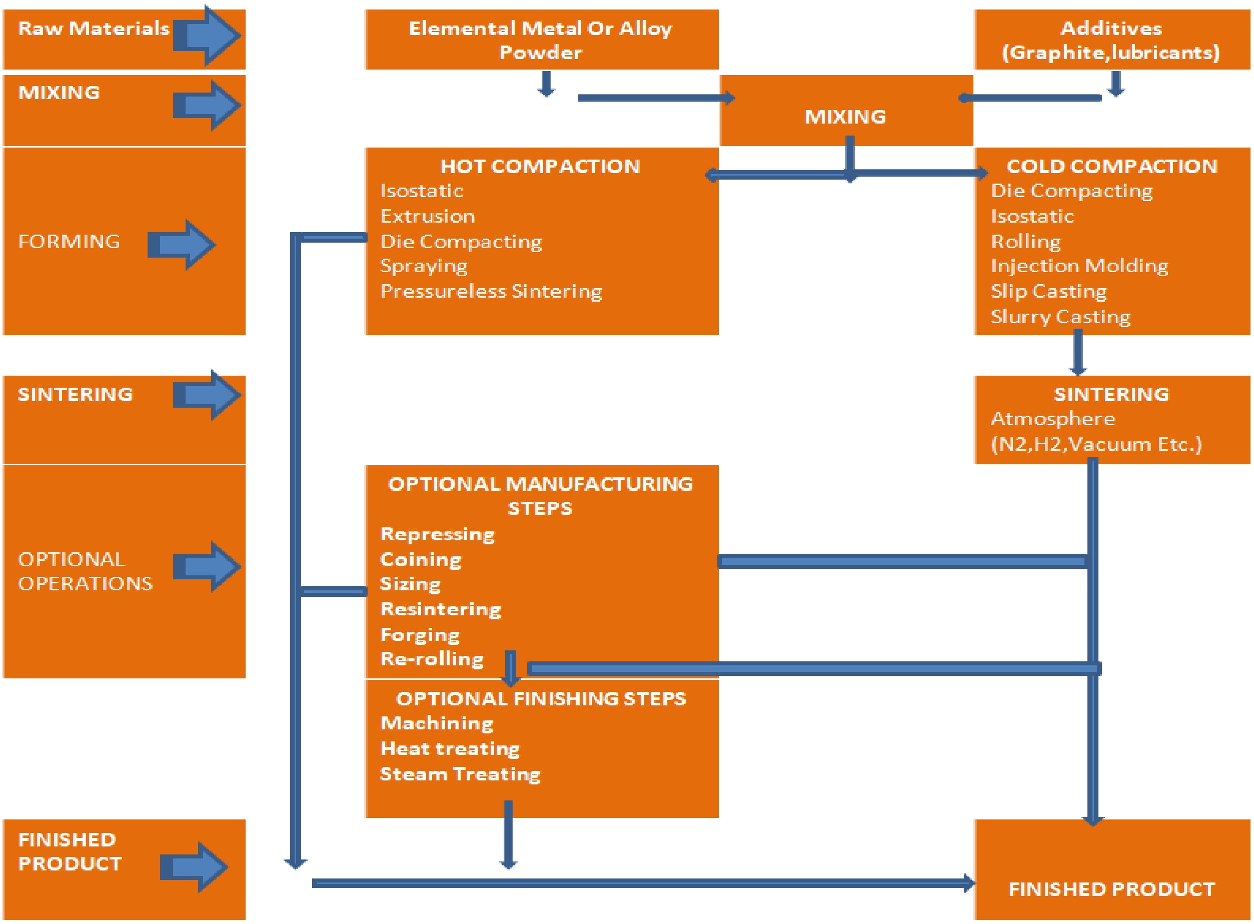
Powders along with additives are mixed using mixers. Lubricants are added prior to mixing to facilitate easy ejection of compact and to minimize wear of tools; Waxes, metallic stearates, graphite etc.
Powder characterization –
size, flow, density, compressibility tests.

Compaction:
compaction is performed using dies machined to close tolerances.Dies are made of cemented carbide, die/tool steel; pressed usinghydraulic or mechanical presses.The basic purpose of compaction is to obtain a green compact with sufficient strength to withstand further handling operations.The green compact is then taken for sintering
Hot extrusion, hot pressing, hot isostaticpressing - consolidation at high temperatures

Sintering:
Performed at controlled atmosphere to bond atoms metallurgically; Bonding occurs by diffusion of atoms; done at 70% of abs. melting point of materials. It serves to consolidate the mechanically bonded powders into a coherent body having desired on service behavior.Densification occurs during the process and improvement in physical and mechanical properties are seen.

Furnaces –mesh belt furnaces (up to 1200C), walking beam, pusher type furnace, batch type furnaces are also used
Protective atmosphere: Nitrogen

Secondary operations:
Operations include repressing, grinding, plating can be done; They are used to ensure close dimensional tolerances, good surface finish, increase density, corrosion resistance etc.



Flow Chart For Making P/M Components

Advantages & Limitations

- Efficient material utilization
- Enables close dimensional tolerances –near net shape possible
- Good surface finish
- Manufacture of complex shapes possible
- Hard materials used to make components that are difficult to machine can be readily made –tungsten wires for incandescent lamps
- Environment friendly, energy efficient
- Suited for moderate to high volume component production
- Powders of uniform chemical composition - reflected in the finished part
- wide variety of materials - miscible, immiscible systems; refractory metals
- Parts with controlled porosity can be made
- High cost of powder material & tooling
- Less strong parts than wrought ones
- Less well known process

Production of powders

- Metal powders - Main constituent of a P/M product; final properties of the finished P/M part depends on size, shape, and surface area of powder particles
- Single powder production method is not sufficient for all applications

Powder production methods: 1. Mechanical methods, 2. Physical methods, 3. Chemical methods

1.Mechanical methods- Cheapest of the powder production methods; These methods involve using mechanical forces such as compressive forces, shear or impact to facilitate particle size reduction of bulk materials;

Eg.:Milling-illing:During milling, impact, attrition, shear and compression forcesare acted upon particles. During impact, striking of one powder particle against another occurs. Attritionrefers to the production of wear debris due to the rubbing action between two particles. Shearrefers to cutting of particles resulting in fracture. The particles are broken into fine particles by squeezing action in compression force type.

Main objective of milling:Particle size reduction (main purpose),Particle size growth, shape change, agglomeration (joining of particles together), solid state alloying, mechanical or solid state mixing, modification of material properties

Mechanism of milling: Changes in the morphology of powder particles during milling results in the following events.

1.Microforging, 2. Fracture, 3. Agglomeration, 4. Deagglomeration

Microforging- Individual particles or group of particles are impacted repeatedly so that they flatten with very less change in mass

Fracture- Individual particles deform and cracks initiate and propagate resulting in fracture

Agglomeration - Mechanical interlocking due to atomic bonding or vandeWaals forces

Deagglomeration- Breaking of agglomerates

The different powder characteristics influenced by milling are shape, size, texture, particle size distribution, crystalline size, chemical composition, hardness, density, flowability, compressibility, sinterability, sintered density

Milling equipment:The equipments are generally classified as crushers & mills

Crushing- for making ceramic materials such as oxides of metals;

Grinding- for reactive metals such as titanium, zirconium, niobium, tantalum

Ball mills:

- This contains cylindrical vessel rotating horizontally along the axis. Length of the cylinder is more or less equal to diameter. The vessel is charged with the grinding media. The grinding media may be made of hardened steel, or tungsten carbide, ceramics like agate, porcelain, alumina, zirconia. During rolling of vessel, the grinding media & powder particles roll from some height. This process grinds the powder materials by impact/collision & attrition.
- Milling can be dry milling or wet milling. In dry milling, about 25 vol% of powder is added along with about 1 wt% of a lubricant such as stearicor oleic acid. For wet milling, 30-40 vol% of powder with 1 wt% of dispersing agent such as water, alcohol or hexane is employed.
- Optimum diameter of the mill for grinding powders is about 250 mm

Vibratory ball mill:

- Finer powder particles need longer periods for grinding
- In this case, vibratory ball mill is better - here high amount of energy is imparted to the particles and milling is accelerated by vibrating the container
- This mill contains an electric motor connected to the shaft of the drum by an elastic coupling. The drum is usually lined with wear resistant material. During operation, 80% of the container is filled with grinding bodies and the starting material. Here vibratory motion is obtained by an eccentric shaft that is mounted on a frame inside the mill. The rotation of eccentric shaft causes the drum of the vibrating mill to oscillate.
- In general, vibration frequency is equal to 1500 to 3000 oscillations/min.The amplitude of oscillations is 2 to 3 mm. The grinding bodies is made of steel or carbide balls, that are 10-20 mm in diameter.The mass of the balls is 8-10 times the charged particles.Final particle size is of the order of 5-100 microns

Attrition mill: In this case, the charge is ground to fine size by the action of a vertical shaft with side arms attached to it. The ball to charge ratio may be 5:1, 10:1, 15:1. This method is more efficient in achieving fine particle size.

Rod mills: Horizontal rods are used instead of balls to grind. Granularityof the discharge material is 40-10 mm. The mill speed varies from 12 to 30 rpm.

Planetary mill:High energy mill widely used for producing metal, alloy, and composite powders.

Fluid energy grinding or Jet milling:

The basic principle of fluid energy mill is to induce particles to collide against each other at high velocity, causing them to fracture into fine particles

•Multiple collisions enhance the reduction process and therefore, multiple jet arrangements are normally incorporated in the mill design. The fluid used is either air about 0.7 MPa or stream at 2 MPa. In the case of volatile materials, protective atmosphere of nitrogen and carbon-di-oxide is used.

•The pressurized fluid is introduced into the grinding zone through specially designed nozzles which convert the applied pressure to kinetic energy. Also materials to be powdered are introduced simultaneously into the turbulent zone.

•The velocity of fluid coming out from the nozzles is directly proportional to the square root of the absolute temperature of the fluid entering the nozzle. Hence it is preferable to raise the temperature of fluid to the maximum possible level without affecting the feed material.

•If further powdering is required, large size particles are separated from the rest centrifugal forces and re-circulated into the turbulent zone for size reduction. Fine particles are taken to the exit by viscous drag of the exhaust gases to be carried away for collection.

•This Jet millingprocess can create powders of average particle size less than 5 µm

Machining:Mg, Be, Ag, solder, dental alloy are specifically made by machining; Turning and chips thus formed during machining are subsequently crushed or ground into powders

Shotting: Fine stream of molten metal is poured through a vibratory screen into air or protective gas medium. When the molten metals falls through screen, it disintegrates and solidifies as spherical particles. These particles get oxidized. The particles thus obtained depends on pore size of screen, temperature, gas used, frequency of vibration. Metal produced by the method are Cu, Brass, Al, Zn, Sn, Pb, Ni. (this method is like making Boondhi)

Graining: Same as shottingexcept that the falling material through sieve is collected in water; Powders of cadmium, Bismuth, antimony are produced.

2. Physical methods

Electrolytic deposition

•In this method, the processing conditions are so chosen that metals of high purity are precipitated from aqueous solution on the cathode of an electrolytic cell. This method is mainly used for producing copper, iron powders. This method is also used for producing zinc, tin, nickel, cadmium, antimony, silver,lead, beryllium powders.

•Copper powder Solution containing copper sulphateand sulphuricacid; crude copper as anode

•Reaction: at anode: Cu --> Cu++ e-; at cathode: Cu++ e-->Cu

•Iron powder- Anode is low carbon steel; cathode is stainless steel. The iron powder deposits are subsequently pulverized by milling in hammermill. The milled powders are annealed in hydrogen atmosphere to make them soft

•Mg powder-Electrodeposition from a purified magnesium sulphateelectrolyte using insoluble lead anodes and stainless steel cathodes

•Powders of thorium, tantalum, vanadium - fused salt electrolysis is carried out at a temperature below melting point of the metal. Here deposition will occur in the form of small crystals with dendriticshape

Atomization

This uses high pressure fluid jets to break up a molten metal stream into very fine droplets, which then solidify into fine particles

High quality powders of Al, brass, iron, stainless steel, tool steel, superalloysare produced commercially

Types:

water atomization, gas atomization, soluble gas or vacuum atomization, centrifugal atomization, rotating disk atomization, ultrarapidsolidification process, ultrasonic atomization

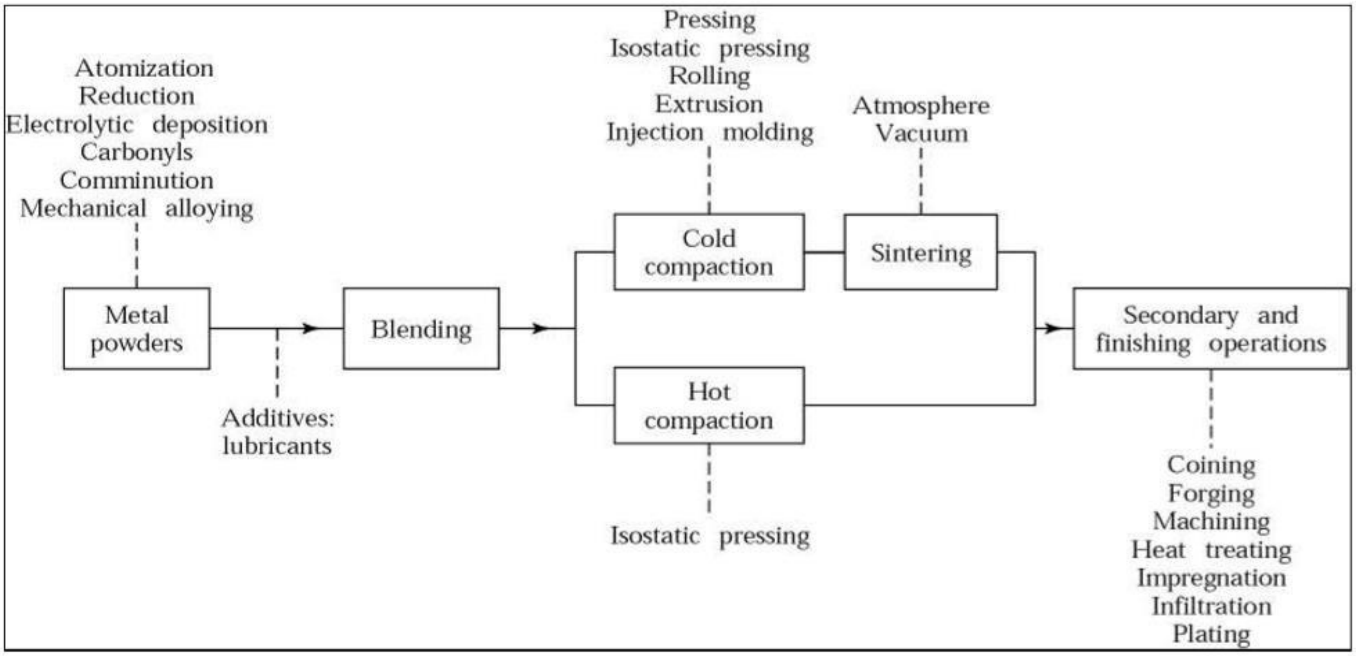
Mechanism of atomization:

In conventional (gas or water) atomization, a liquid metal is produced by pouring molten metal through a tundishwith a nozzle at its base. The stream of liquid is then broken into droplets by the impingement of high pressure gas or water. This disintegration of liquid stream is shown in fig. This has five stages

i)Formation of wavy surface of the liquid due to small disturbances
ii) Wave fragmentation and ligament formation
iii)Disintegration of ligament into fine droplets
iv)Further breakdown of fragments into fine particles
v)Collision and coalescence of particles

•The interaction between jets and liquid metal stream begins with the creation of small disturbances at liquid surfaces, which grow into shearing forces that fragment the liquid into ligaments. The broken ligaments are further madeto fine particles because of high energy in impacting jet.
•Lower surface tension of molten metal, high cooling rate - formation of irregular surface : like in water atomization
•High surface tension, low cooling rates - spherical shape formation : like in inert gas atomization
•The liquid metal stream velocity, $v = A [2g (Pi–Pg)\rho]0.5$
where Pi–injection pressure of the liquid, Pg –pressure of atomizing medium, ρ–density of the liquid

Making powder & subsequent processing



Powder treatment & Handling

In powder conditioning, the powders prepared by various methodsare subjected to a variety of treatments to improve or modify their physical, chemical characteristics

Powder treatments

Powders manufactured for P/M applications can be classified into–elemental powders, and pre-alloyed powders
Elemental powders- powdersof single metallic element; eg.: iron for magnetic applications
Pre-alloyed powders- more than one element; made by alloying elemental powders during manufacturing process itself; IN this case, all the particles have same nominal composition and each particle is equivalent to small ingot
Majority of powders undergo heat treatmentsprior to compaction like,
i) Drying to remove moisture, ii) grinding/crushing to obtain fine sizes, iii) particle size classification to obtain the desired particle size distribution, iv) annealing, v) mixing and blending of powders, vi) lubricant addition for powder compaction, vii) powder coating

a)Cleaning of Powders:

•Refers to the removal of contaminants, solid or gaseous, from the powder particles
•Solid contaminants- come from several sources like nozzles or crucible linings. They interfere during compaction and sintering preventing propermechanical bonding
•Most of these contaminants are non-reactive, but they act as sites for crack nucleation and reduce the dynamic properties of the sintered part; Non-metallic solid impurities can be removed from superalloypowders by particle separators, electrostatic

separation techniques

- Gaseous impurities like hydrogen and oxygen get into powders during processing, storage or handling if proper care is not taken. Finer the powders, contamination will be more because of large powder surface area.
- These gaseous impurities can form undesirable oxides during processing at relatively high temperatureor gets trapped inside the material as pores, reducing the in situ performance of the P/M part; Degassing techniques like cold, hotstatic or dynamic degassing methods are used to remove adsorbed gases from the powders
- Lubricants added to the powders for better compaction has to be removed for desirable final P/M part

b) Grinding:

Similar to the mechanical methods seen earlier; Milling is widely used for reducing the aggregates of powder; Milling time, speed, type canbe selected for getting required degree of grinding

c) Powder classification & screening:

Powder size and shape, size distribution varied within specified range is required for better behavior of P/M parts; In this method, the desired particle size distributions with particle sizes within specific limits can be obtained; These variation depends on lot also.

d) Blending & mixing:Blending–

Process in which powders of the same nominal composition but having different particle sizes are intermingled. This is done to (i) obtain a uniform distribution of particle sizes, i.e. powders consisting of different particle sizes are often blended to reduce porosity, (ii) for intermingling of lubricant with powders to modify metal to powder interaction during compaction

Mixing–Process of combining powders of different chemistries such as elemental powder mixes (Cu-Sn) or metal-nonmetal powders. This may be done in dry or wet condition. Liquid medium like alcohol, acetone, benzene or distilled water are used as milling medium in wet milling. Ball mills or rod mills are employed for mixing hard metals such as carbides

Mixing methods

The various types of mixing methods are, (i) convective mixing: transfer of one group of particles from one location to another, (ii) diffusive mixing: movement of particles on to newly formed surface, (iii) shear mixing: deformation & formation of planes within the powders

Depending on the extent of mixing, mixing can be classified as (i) perfectly mixed or uniform mixing, (ii) random mixed, & (iii) totally un-mixed. The mixing should be stopped when random mixture is achieved. Overmixingleads to reduced flow characteristics of the mix

Heat Treatment Of Powders

Heat treatment is generally carried out before mixing or blending the metal powders. Some of the important objectives are,

i)Improving the purity of powder:Reduction of surface oxides from powders by annealing in hydrogen or other reducing atmosphere. Dissolved gases like hydrogen and oxygen, other impurities are removed by annealing of powders. Lowering impurities like carbon results in lower hardness of thepowder and hence lower compaction pressures & lower die wear during compaction. For eg., atomized powders having a combined carbon and oxygen content as high as 1% can be reduced after annealing to about 0.01% carbon and 0.2% oxygen. Heat treatment is done at protective atmosphere like hydrogen, vacuum.

ii)Improving the powder softness:Aim is to reduce the work hardening effect of powders that has be crushed to obtain fine powders; while many powders are made by milling, crushing or grinding of bulk materials. Powder particles are annealed under reducing atmosphere like hydrogen. The annealing temperature is kept low to avoid fusion of the particles.

iii)Modification of powder characteristics: The apparent density of the powders can be modified to a higher or lower value by changing the temperature of treatment.

Toxicity Of Powders

- Toxicity leads to undesirable health effects like eye, skin irritation, vomiting, respiratory problems, blood poisoning etc.
- powder like lead, nickel are highly toxic & Al, iron are less toxic
- Precautions: Use of protective gloves, respiratory masks, protective clothing etc.; use of well ventilated storage, workplace; careful handling, disposal of wastes
- flammability & reactivity data is required
- Health effects: Inhalation –disturbs the respiratory track; remedial measures include moving the person to fresh air. Artificial breathing is requiredif patient not breathing properly.

Skin, eyes –Brushing, washing skin and eyes with water and soap. Clean eyeswith fresh water for 15 mts.

Compaction of Metal Powders

•Compaction is an important step in powder processing as it enables the forming of loose metal powders into required shapes with sufficient strength to withstand till sintering is completed.

•In general, compaction is done without the application of heat.Loose powders are converted into required shape with sufficient strength to withstand ejection from the tools and subsequent sintering process. IN cases like cemented carbide, hot compaction is done followed by sintering. One can not call this as compaction strictly, as sintering is also involved in this.

Powder Compaction Methods

Powder compaction techniques can be classified as,

1. Methods without application of pressure–i) loose powder sintering in mould, ii) vibratory compaction, iii) slip casting, iv) slurry casting, v) injection moulding
2. Methods with applied pressure–i) cold die compaction (single action pressing, double action pressing, floating die pressing), ii) isostaticpressing, iii) powder rolling, iv) powder extrusion, v) explosive compaction

Pressurelesscompaction techniques

-Used for the production of simple and low density parts such as filters, other parts that are porous in nature; these techniques involve no external force and depend upon gravity for powder packing

I) Loose powder sintering:-Also known as loose powder shaping, gravity sintering, pressurelesssintering. In this method, the metal powder is vibrated mechanically into the mould, which is the negative impression of the product and heated to sintering temperature.This is the simplest method and involve low cost equipment. Themain reasons for not using this method for part production are, difficulty of part removal from the mould after sintering, & considerable shrinkage during sintering.

-Applications:Amount of porosity ranges from 40 vol% to as high as 90 vol%; Highly porous filter materials made of bronze, stainless steel, and monel, porous nickel membrane for use as electrodes in alkaline storage batteries andfuel cells are typical examples.

II) Slip casting:-Used for compacting metal and ceramic powders to make large & complex shapes for limited production runs

-A slip is a suspensionof metal or ceramic powder (finer than 5 μm) in water or other soluble liquid which is pored into a mould, dried and further sintered.

-Slip is usually made of, 1) a dispersion agentto stabilize the powder against colloidal forces, 2) a solventto control the slip viscosity and facilitate casting, 3) a binderfor giving green strength to the cast shape, 4) plasticizerto modify the properties of the binder

-For successful slip casting, formation of appropriate and a consistent slip is important. This is achieved by proper control of particle size, size distribution, order of component addition, their mixing time, addition of proper deflocculant-to prevent the settling and aggregation of powders and maintains the desirable viscosity of the slip.

-Mostly water is used as suspending medium, but absolute alcoholor other organic liquids may also be employed. Additives like alginates –ammonium and sodium salts of alginic acids, serve three fold functions of deflocculant, suspension agent & binding agent to improve green strength of the compact.

-The slip to be cast is obtained in a form of suspension of powder in a suspending medium. The slip should have low viscosity & low rate of setting so thatit can be readily poured. The slip cast should be readily removable from the mould. Low shrinkage and high strength after drying is expected.

-To obtain these properties, 5 µm powder particles should be used. In the case of fine molybdenum powders, a slip can be prepared by suspending the powder in 5% aqueous polyvinyl alcohol with a minimum viscosity, at a pH value of 7.

- For coarser, spherical stainless steel powder, a mixer of 80.7%metal powder, 19% water, 0.3% of sodium alginate as deflocculanthaving a pH value of 10 can be used.
- Steps in slip casting:i) Preparing assembled plaster mould, ii) filling the mould, iii) absorption of water from the slip into the porous mould, iv) removal of part from the mould, v) trimming of finished parts from the mould
- Sometimes mould release agents like oil, graphite can be used.
- Hollow and multiple parts can be produced
- Advantages of slip casting:Products that can not be produced by pressing operation can be made, no expensive equipment is required, works best with finest powder particles
- Disadvantage:slow process, limited commercial applications
- Applications:tubes, boats, crucibles, cones, turbine blades, rocket guidancefins; Also products with excellent surface finish like basins, water closets.

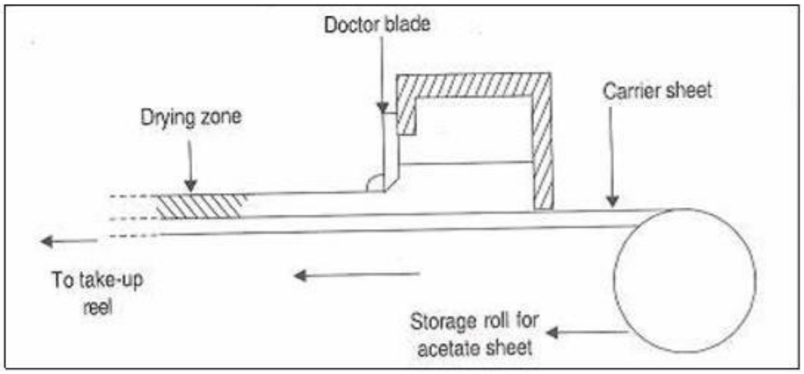
III) Slurry casting: This process is similar to slip casting except that a slurry of metal powders with suitable liquids, various additives, and binders is poured into a mould and dried. The solvent is removed either by absorption into the POP or by evaporation. Very high porous sheet for use as electrodes in fuel cells and nickelcadmium rechargeable batteries are produced by this method.

IV) Tape casting (doctor blade casting):-This is a variation of slurry casting process and is used to produce thin flat sheets.

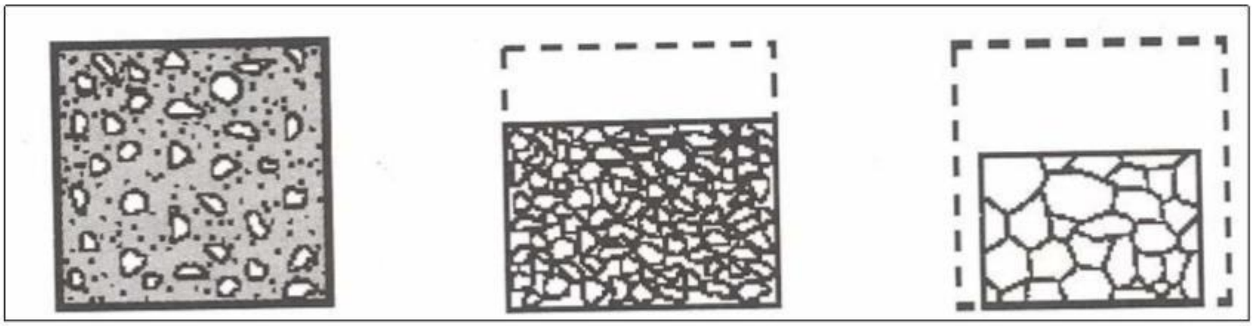
-This process involves preparing a dispersion of metal or ceramicpowder in a suitable solvent with the addition of dispersion agent (to improve the dispersion of the particles). Then a binder is added and fed to a reservoir. Whole mixture is fed on to a moving carrier film from the bottom of the reservoir.

-This slurry layer is deposited on the film by the shearing action of a blade. The slurry should be free of air bubbles, otherwise result in porosity. During sintering, the binder is burnt off first and densification of material occurs.

-In present days, endless stainless steel belt is used instead of carrier tape. This process can be used for making very thin tapes between 50 to 1000 µm thickness. This method is used for making electronic substrates, dielectrics for capacitors and piezoelectric actuators.



Schematic of tape casting



Slip Green tape Sintered tape

Stages in tape casting

V) Vibratory compaction:-

Vibratory compaction uses vibration energy to compact the powder mass. During this process, smaller voids can be filled with particles of still smaller size and this sequence is carried out till a high packing density of powder is achieved even before consolidation. Mechanical vibration facilitates the formation of nearly closed packed powder by settling particles in the voids present in the powder agglomerate. During vibration, small pneumatic pressure is usually superimposed on the powder mass.
-Brittle powders can be compacted by this method as they developcrack if done by pressure compaction
-This method is generally used when, 1) powders have irregular shape, 2) use of plasticizers for forming is not desirable, 3) sintered density is required to be very close theoretical density
-Important variables in vibratory compaction:
1. inertia of system:larger the system, more the energy required for packing
2. friction force between particles:more friction results in need of more KE for compaction
3. particle size distribution:more frequency required if more large particles are present. Vibration cycle is important and not period of vibration.

Pressure compaction techniques

•These techniques involve application of external pressure to compact the loose powder particles; Pressure applied can be unidirectional, bidirectional or hydrostatic in nature.

•Die compaction:

In this process, loose powder is shaped in a die using a mechanical or hydraulic press giving rise to densification. The mechanisms of densification depend on the material and structural characteristics of powder particles.

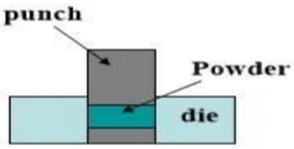
•Unidirectional and bidirectional compaction involves same number of stages and are described in this figure. They are, i) charging the powder mix, ii) applying load using a punch (uni-) or double punch (bi-) to compact powders, iii) removal of load by retracting the punch, iv) ejection of green compact. The table gives compaction pressure ranges for metals and ceramics.

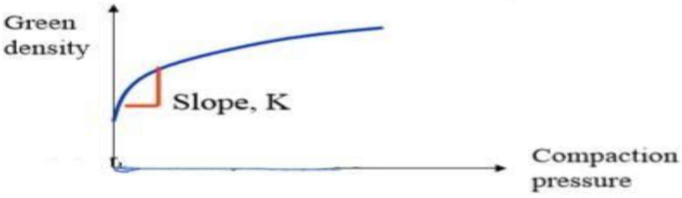
Effect of powder characteristics

For a good compaction, 1) irregular shaped particles are preferred as they give better interlocking and hence high green strength, 2) apparent density of powders decides the die fill during compaction. Hence powder size, shape & density affect the apparent density, 3) flow rate affects the die fill time, and once again powder size, shape & density affect the flow rate.

Powder behavior during compaction

- Compaction involves, 1) flow of powder particles past one another interacting with each other and with die-punch, 2) deformation of particles. In the case of homogeneous compaction, two stages are observed. **First stage** => rapid densification occurs when pressure is applied due to particle movement and rearrangement resulting in improved packing; **Second stage** => increase in applied pressure leads to elastic and plastic deformation resulting in locking and cold welding of particles. In the second stage, large increments in pressures are seen to effect a small increase in density.





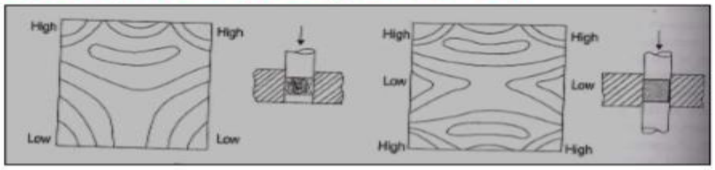
- The green compact produced can be considered as a two-phase aggregate consisting of powder particles and porosity each having own shape and size.

- Compaction can be done at low and high temperatures. Room temperature compaction employs pressures in the range of 100-700 MPa and produce density in the range of 60-90% of the theoretical density. At higher temperatures, pressures are kept low within the limits for preventing die damage.

- In **single die compaction**, powders close to the punch and die walls experience much better force than in center. This results in green density variation across the sample length. Longer the sample more the density difference. This non-uniformity can result in non-uniformity in properties of sintered part.

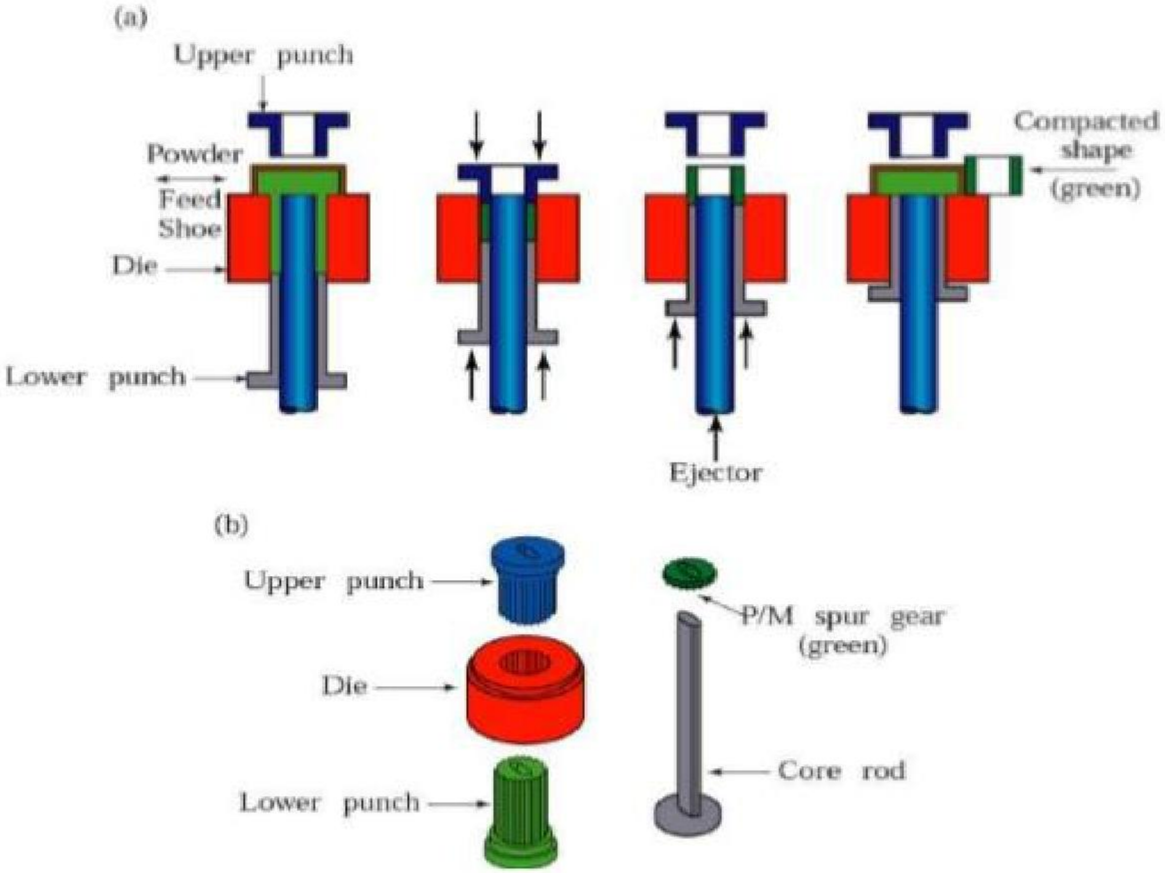
- This density variation and hence final property variation can be greatly reduced by having **double ended die compaction**. In this case, powder experiences more uniform pressure from both top and bottom, resulting in minimization of density variation. But this variation will still be considerable if the components have high aspect ratio (length to diameter ratio). This means that long rods and tubes cannot be produced by die compaction. In this case, isostatic pressing can be used.

Single ended compaction



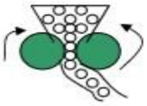
Double ended compaction

Schematic of powder compaction



Powder rolling

This process involves feeding of powders between rolls to produce a coherent and brittle green strip. This green strip is then sintered & re-rolled to obtain a dense, finished product.

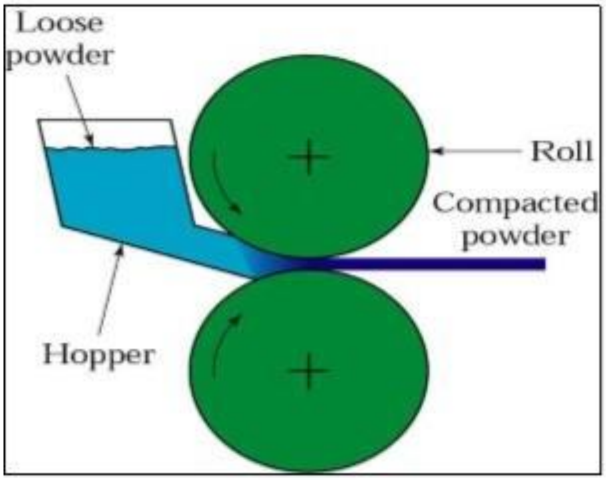


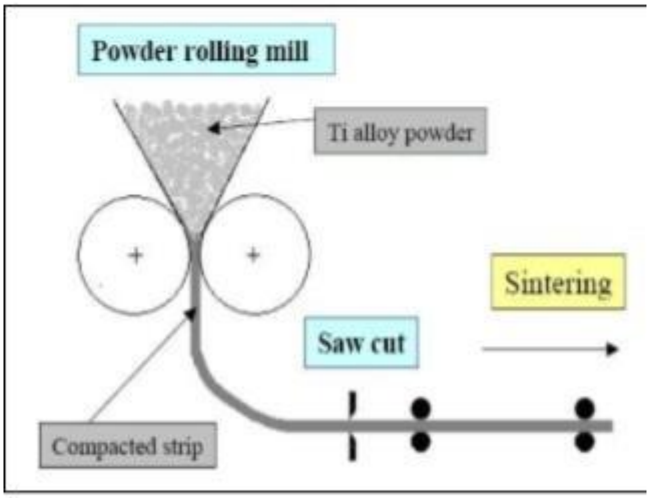
Steps: 1) preparation of green strip, 2) sintering, 3) densification of sintered strip, 4) final cold rolling and annealing

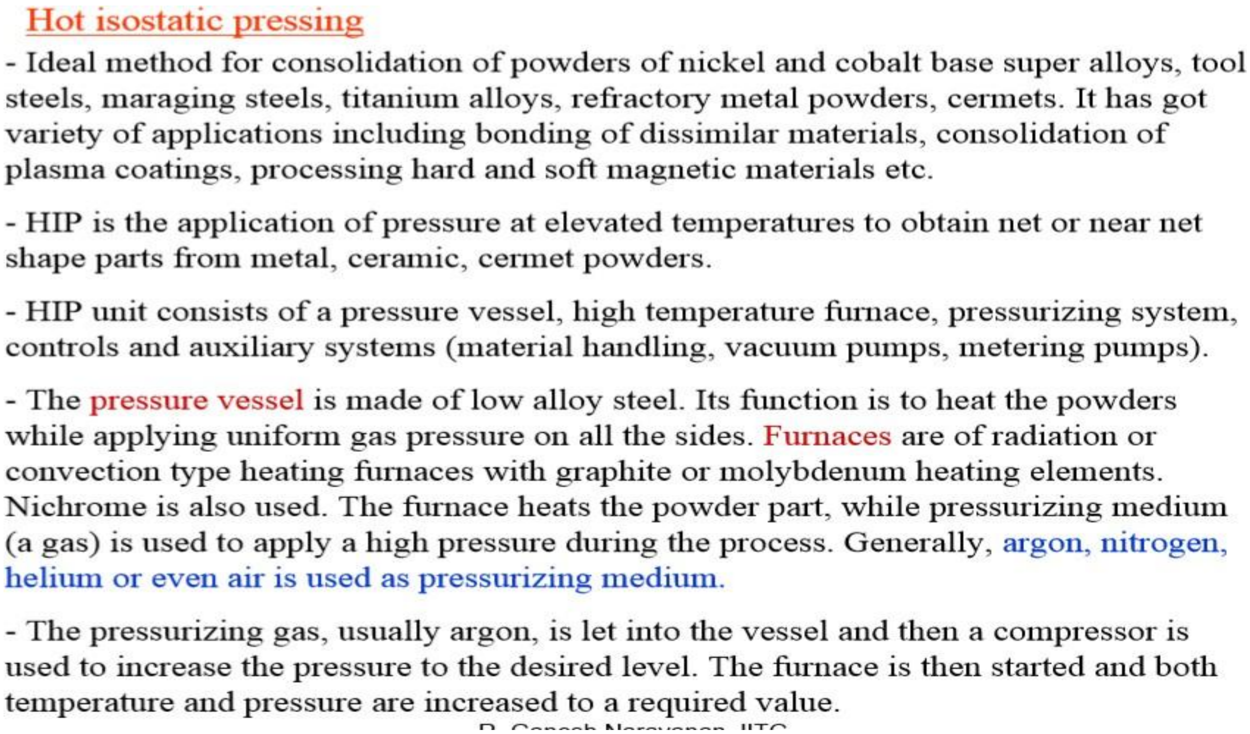
Parameters affecting powder rolling are roll gap, roll diameter, roll speed, powder characteristics; **Roll gap** => large roll gap leads to decrease in green density; very small roll gap leads to edge cracking; **roll diameter** => increase in density and strength with increase in roll dia. for a given strip thickness; **roll speed** => Kept low, 0.3-0.5 m/s; **Powder** => irregular powder with rough surfaces provide better strip density

In densification stage, either **repeated cold rolling followed by annealing** or **hot rolling of strip** can be followed

Applications: nickel strips for coinage, nickel-iron strips for controlled expansion properties, Cu-Ni-Sn alloys for electronic applications, porous nickel strip for alkaline batteries and fuel cell applications.







Hot isostatic pressing

- Ideal method for consolidation of powders of nickel and cobalt base super alloys, tool steels, maraging steels, titanium alloys, refractory metal powders, cermets. It has got variety of applications including bonding of dissimilar materials, consolidation of plasma coatings, processing hard and soft magnetic materials etc.

- HIP is the application of pressure at elevated temperatures to obtain net or near net shape parts from metal, ceramic, cermet powders.

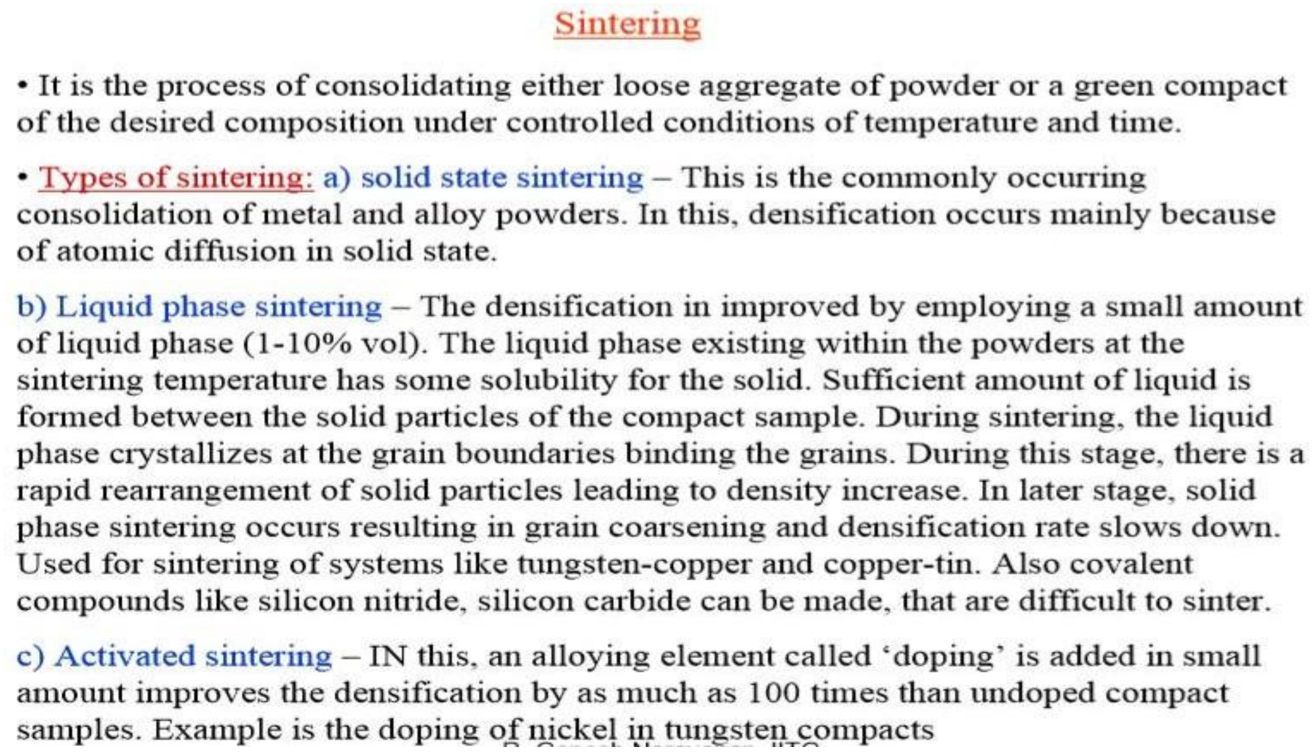
- HIP unit consists of a pressure vessel, high temperature furnace, pressurizing system, controls and auxiliary systems (material handling, vacuum pumps, metering pumps).

- The pressure vessel is made of low alloy steel. Its function is to heat the powders while applying uniform gas pressure on all the sides. Furnaces are of radiation or convection type heating furnaces with graphite or molybdenum heating elements. Nichrome is also used. The furnace heats the powder part, while pressurizing medium (a gas) is used to apply a high pressure during the process. Generally, argon, nitrogen, helium or even air is used as pressurizing medium.

- The pressurizing gas, usually argon, is let into the vessel and then a compressor is used to increase the pressure to the desired level. The furnace is then started and both temperature and pressure are increased to a required value.

-HIP presses are available in diameters up to 2m with pressures ranges from 40 to 300 MPawith temperature range from 500 to 2200 °C. The processing time can last up to 4 hours depending on the material and size of the part.
-during HIP, the pores are closed by flow of matter by diffusionand creep, but also bonded across the interface to form a continuous material.

-Commonly used heating elements:Kanthalheating element –up to 1200 °C; Molybdenum heating element –1200 to 1700 °C; Graphite heating element –2000 to 2600 °C



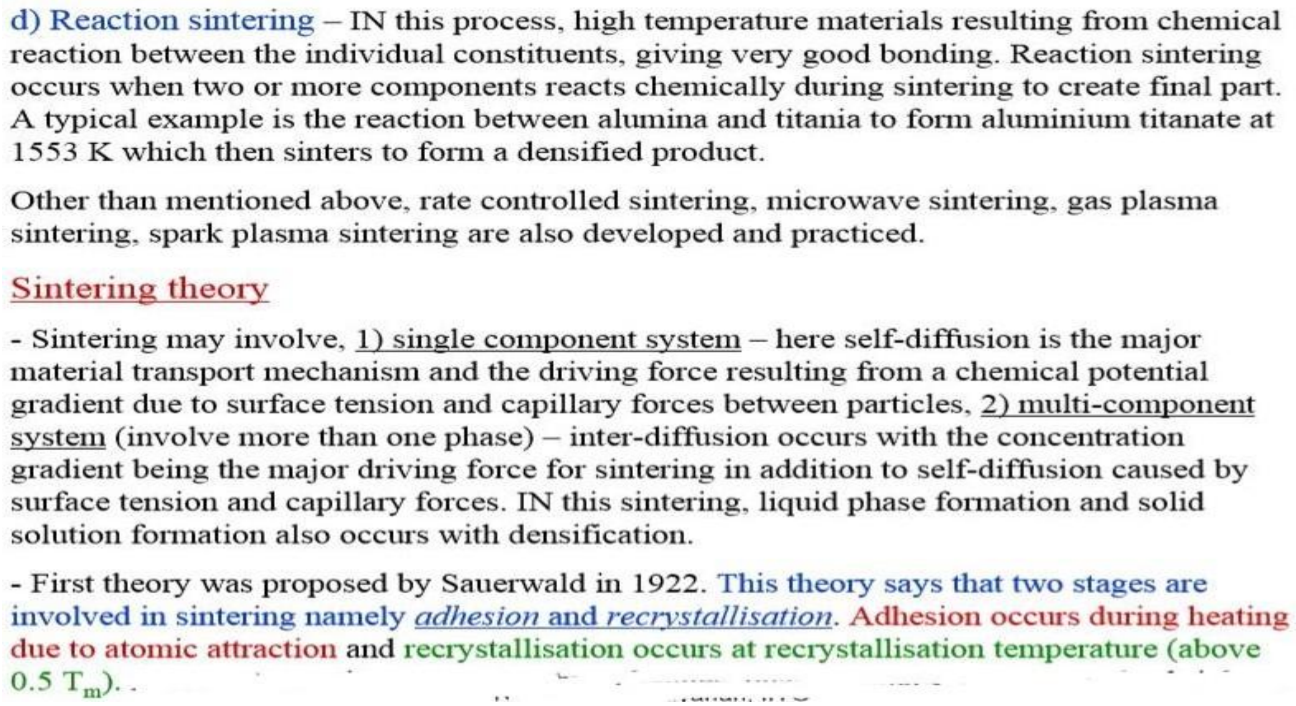
Sintering

• It is the process of consolidating either loose aggregate of powder or a green compact of the desired composition under controlled conditions of temperature and time.

• Types of sintering: a) solid state sintering – This is the commonly occurring consolidation of metal and alloy powders. In this, densification occurs mainly because of atomic diffusion in solid state.

b) Liquid phase sintering – The densification in improved by employing a small amount of liquid phase (1-10% vol). The liquid phase existing within the powders at the sintering temperature has some solubility for the solid. Sufficient amount of liquid is formed between the solid particles of the compact sample. During sintering, the liquid phase crystallizes at the grain boundaries binding the grains. During this stage, there is a rapid rearrangement of solid particles leading to density increase. In later stage, solid phase sintering occurs resulting in grain coarsening and densification rate slows down. Used for sintering of systems like tungsten-copper and copper-tin. Also covalent compounds like silicon nitride, silicon carbide can be made, that are difficult to sinter.

c) Activated sintering – IN this, an alloying element called 'doping' is added in small amount improves the densification by as much as 100 times than undoped compact samples. Example is the doping of nickel in tungsten compacts



d) Reaction sintering – IN this process, high temperature materials resulting from chemical reaction between the individual constituents, giving very good bonding. Reaction sintering occurs when two or more components reacts chemically during sintering to create final part. A typical example is the reaction between alumina and titania to form aluminium titanate at 1553 K which then sinters to form a densified product.

Other than mentioned above, rate controlled sintering, microwave sintering, gas plasma sintering, spark plasma sintering are also developed and practiced.

Sintering theory

- Sintering may involve, 1) single component system – here self-diffusion is the major material transport mechanism and the driving force resulting from a chemical potential gradient due to surface tension and capillary forces between particles, 2) multi-component system (involve more than one phase) – inter-diffusion occurs with the concentration gradient being the major driving force for sintering in addition to self-diffusion caused by surface tension and capillary forces. IN this sintering, liquid phase formation and solid solution formation also occurs with densification.

- First theory was proposed by Sauerwald in 1922. This theory says that two stages are involved in sintering namely *adhesion and recrystallisation*. Adhesion occurs during heating due to atomic attraction and recrystallisation occurs at recrystallisation temperature (above 0.5 T_m). .

Solid state sintering process

Condition for sintering: 1) densification occurs during sintering and solid state sintering is carried out at temperatures where material transport due to diffusion is appreciable. Surface diffusion is not sufficient, atomic diffusion is required.

2) This occurs by replacing high energy solid-vapour interfaces (with free energy γ_{SV}) with the low energy solid-solid interface (particle-particle) of free energy $\gamma_{SS.}$ This reduction in surface energy causes densification.

3) Initially free energy of solid-solid interface must be lower than free energy of solid-vapour interface. The process of sintering will stop if the overall change in free energy of the system (dE) becomes zero, i.e., $dE = \gamma_{SS}\, dA_{SS} + \gamma_{SV}\, dA_{SV} \leq 0$

Where dA_{SS} & dA_{SV} are the interfacial area of solid-solid and solid-vapour interfaces.

4) Initially, the surface area of compact represent the free surface area, since no grain boundaries have developed and hence $A_{SV} = A_{SV0}$ & $A_{SS} = 0$. As sintering proceeds, A_{SV} decreases and A_{SS} increases. The sintering process will stop when $dE = 0$,

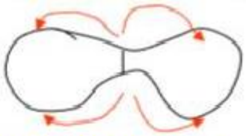
i.e., $\gamma_{SS}\, dA_{SS} + \gamma_{SV}\, dA_{SV} = 0 \Rightarrow \gamma_{SS} / \gamma_{SV} = -\, dA_{SV} / dA_{SS}$

5) Densification stops when $-\, dA_{SV} / dA_{SS}$ is close to zero. To achieve densification without grain growth, the solid-solid interface must be maximized.

Mechanism in solid state sintering

As discussed earlier, material or atom transport forms the basic mechanism for sintering process. A number of mechanisms have been proposed for sintering operation. These are,

1. Evaporation condensation, 2. diffusion (can be volume diffusion, grain boundary diffusion, surface diffusion), 3. viscous flow, 4. plastic flow



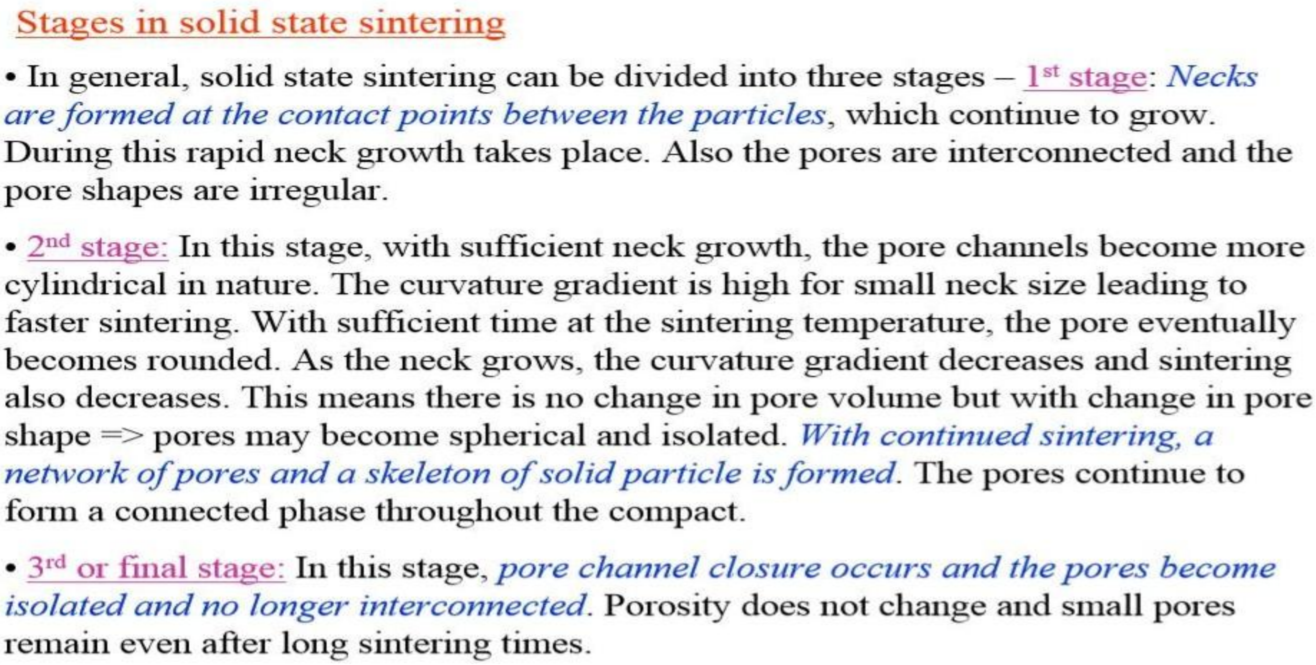
1. Evaporation and condensation mechanism

The basic principle of the mechanism is that the equilibrium vapor pressure over a concave surface (like neck) is lower compared to a convex surface (like particle surface). This creates the vapor pressure gradient between the neck region and particle surface. Hence mass transport occurs because of vapor pressure gradient from neck (concave surface) to particle surface (convex surface). The driving force of this is based on Gibbs-Thomson equation, $\mu - \mu_0 = RT \ln(p/p_0) = (-\gamma)(\Omega)/r$ where μ and μ_0 are chemical potentials of initial and final surfaces, R is universal gas constant, T is temperature in K, p and p_0 are partial pressures over the curved and flat surface respectively, γ is the surface free energy, Ω is the atomic volume

Driving force for sintering

- The main driving force is excess surface free energy in solid state sintering. The surface energy can be reduced by transporting material from different areas by various material transport mechanisms so as to eliminate pores.
- material transport during solid state sintering occurs mainly by surface transport, grain boundary transportation. This surface

transport can be through adhesion, surface diffusion. Many models available to describe sintering process –like viscous flow, plastic flow, grain boundary and volume diffusion models. These models will be briefly described here.

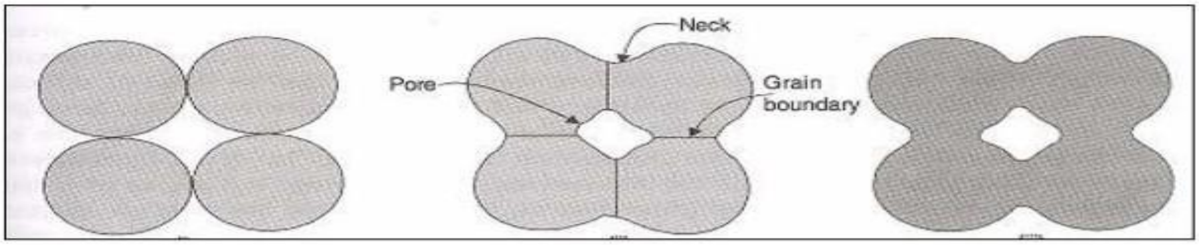


Stages in solid state sintering

- In general, solid state sintering can be divided into three stages – 1st stage: *Necks are formed at the contact points between the particles*, which continue to grow. During this rapid neck growth takes place. Also the pores are interconnected and the pore shapes are irregular.

- 2nd stage: In this stage, with sufficient neck growth, the pore channels become more cylindrical in nature. The curvature gradient is high for small neck size leading to faster sintering. With sufficient time at the sintering temperature, the pore eventually becomes rounded. As the neck grows, the curvature gradient decreases and sintering also decreases. This means there is no change in pore volume but with change in pore shape => pores may become spherical and isolated. *With continued sintering, a network of pores and a skeleton of solid particle is formed*. The pores continue to form a connected phase throughout the compact.

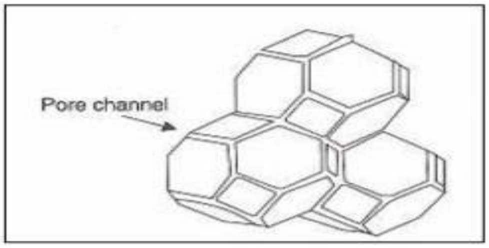
- 3rd or final stage: In this stage, *pore channel closure occurs and the pores become isolated and no longer interconnected*. Porosity does not change and small pores remain even after long sintering times.



Particles in contact

Formation of necks, grain boundaries, pores

Final sintered geometry



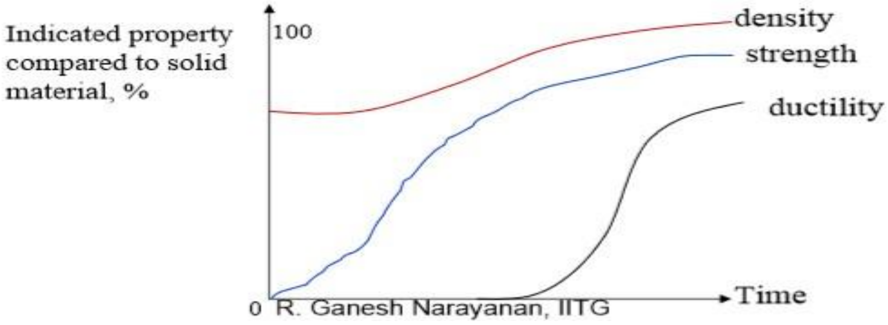
Pore channel formation

Property changes during sintering

- Densification is proportional to the shrinkage or the amount of pores removed in the case of single component system

- IN multicomponent system, expansion rather than shrinkage will result in densification and hence densification can not be treated as equal to the amount of porosity removed.

- densification results in mechanical property change like hardness, strength, toughness, physical properties like electrical, thermal conductivity, magnetic properties etc. Also change in composition is expected due to the formation of solid solution.



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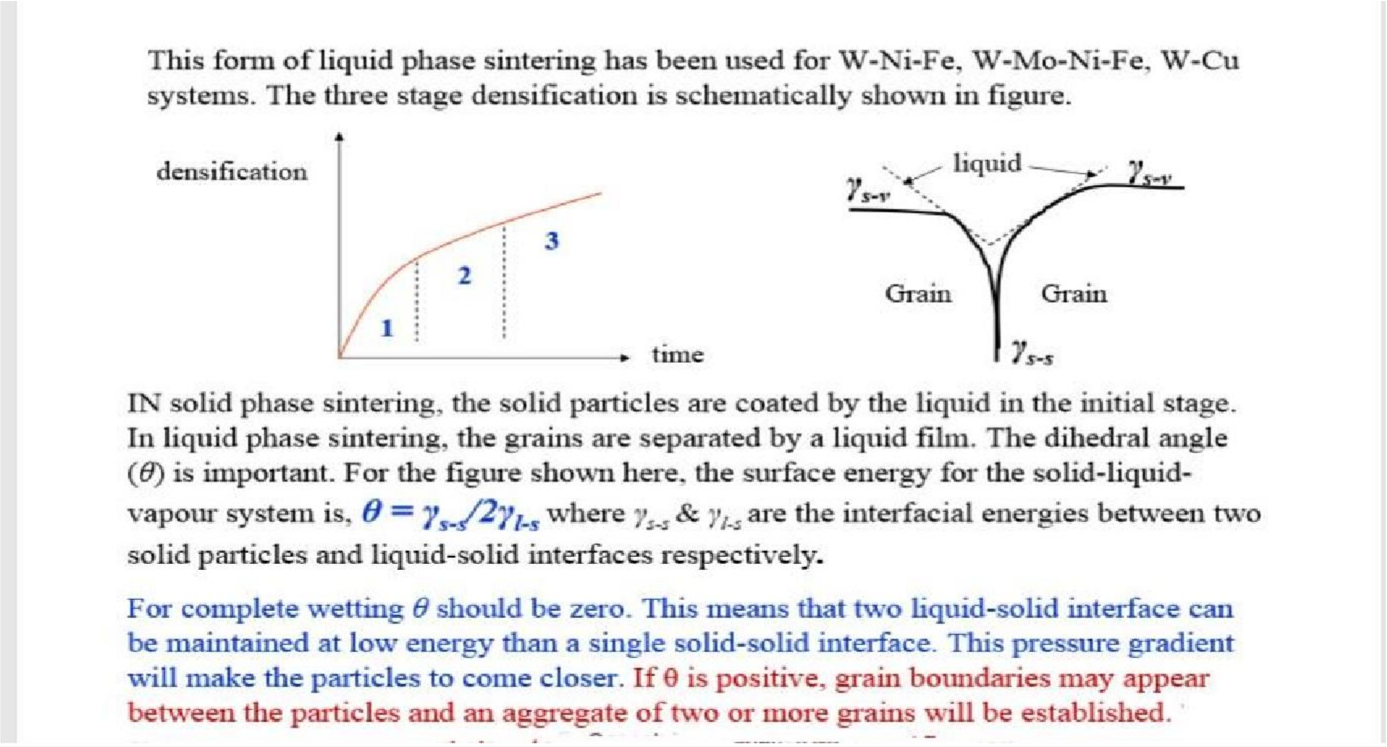
Mechanism during liquid phase sintering

In the sintering of multi-component systems, the material transport mechanisms involve self diffusion and interdiffusion of components to one another through vacancy movement. **Sintering of such systems may also involve liquid phase formation, if the powder aggregate consists of a low melting component whose melting point is below the sintering temperature**

Liquid phase sintering: In this, the liquid phase formed during sintering aids in densification of the compacts. **Liquid phase sintering employs a small amount of a second constituent having relatively low melting point. This liquid phase helps to bind the solid particles together and also aids in densification of the compact.** This process is widely used for ceramics – porcelain, refractories.

Three main considerations are necessary for this process to occurs, 1. presence of appreciable amount of liquid phase, 2. appreciable solubility of solid in liquid, 3. complete wetting of the solid by liquid.

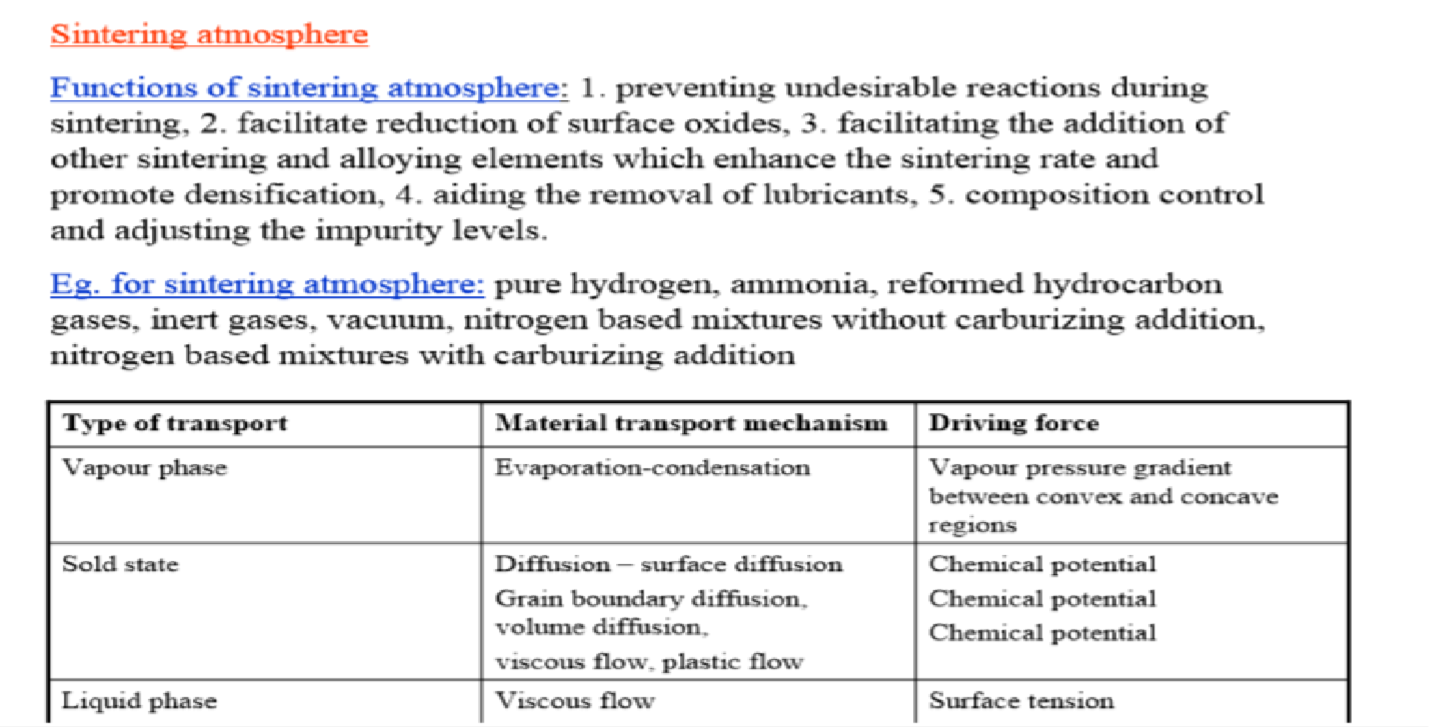
Three main stages are observed in liquid phase sintering, 1. initial particle rearrangement occurs once the liquid phase is formed. The solid particles flow under the influence of surface tension forces, 2. solution & reprecipitation process: in this stage, smaller particles dissolve from areas where they are in contact. This causes the particle centers to come closer causing densification. The dissolved material is carried away from the contact area and reprecipitate on larger particles, 3. solid state sintering



This form of liquid phase sintering has been used for W-Ni-Fe, W-Mo-Ni-Fe, W-Cu systems. The three stage densification is schematically shown in figure.

IN solid phase sintering, the solid particles are coated by the liquid in the initial stage. In liquid phase sintering, the grains are separated by a liquid film. The dihedral angle (θ) is important. For the figure shown here, the surface energy for the solid-liquid-vapour system is, $\theta = \gamma_{s-s}/2\gamma_{l-s}$ where γ_{s-s} & γ_{l-s} are the interfacial energies between two solid particles and liquid-solid interfaces respectively.

For complete wetting θ should be zero. This means that two liquid-solid interface can be maintained at low energy than a single solid-solid interface. This pressure gradient will make the particles to come closer. If θ is positive, grain boundaries may appear between the particles and an aggregate of two or more grains will be established.



Sintering atmosphere

Functions of sintering atmosphere: 1. preventing undesirable reactions during sintering, 2. facilitate reduction of surface oxides, 3. facilitating the addition of other sintering and alloying elements which enhance the sintering rate and promote densification, 4. aiding the removal of lubricants, 5. composition control and adjusting the impurity levels.

Eg. for sintering atmosphere: pure hydrogen, ammonia, reformed hydrocarbon gases, inert gases, vacuum, nitrogen based mixtures without carburizing addition, nitrogen based mixtures with carburizing addition

Type of transport	Material transport mechanism	Driving force
Vapour phase	Evaporation-condensation	Vapour pressure gradient between convex and concave regions
Sold state	Diffusion – surface diffusion Grain boundary diffusion, volume diffusion, viscous flow, plastic flow	Chemical potential Chemical potential Chemical potential
Liquid phase	Viscous flow	Surface tension

Selected Application Of Powder Metallurgy

P/M porous filters: porous filters made by P/M route can be classified into four types based on their applications like filtration, flow control, distribution, porosity. Filtration is the separation process involving the removal of gas, liquid or solid from another gas or liquid. Flow control involves regulation of fluidflow in a system with controlled pressure drop. Distribution involves providing a uniform flow over a wide area.

Production of porous metal filters:Typical filter shapes that can be produced from the powder include discs, cups, bushings, sheets, tubes. The major advantages of porous filters include high temperature resistance, good mechanical strength, corrosion, long service life.

Made by Gravity sintering:-Bronze filters are produced by this method. This sintering, as discussed earlier, involves pouring of graded powders in to a mould prior to sintering operation. Then sintering is performed and metallurgical bonding is achieved by diffusion.

-Bronze filtersare made by gravity sintering using either atomized spherical bronze powder or from spherical Cu powder coated with Snlayer. The powders are sintered in graphite or stainless steel moulds at temperatures near the solidustemperature of the bronze composition. Porosities of the range 40 to 50 % can be formed

-Porous nickel filtersare made in the same fashion. Hollow, cylindrical stainless steel filterswith thin wall thickness can be fabricated by cold extrusion ofthe plasticized mixture. These products are available in corrosion resistant alloys like stainless steel, Ti, Ni, and nickel base alloys. Desired porosity is obtained by using specific particles size and shape. Compaction and sintering is performed under controlled atmosphere to obtain good green compact part.
Made by powder rolling:porous strips of Ni, Ti, Cu, bronze and Ti alloys are prepared by powder rolling. Strips having thickness from 0.25 to 3 mm andlength of several meters can be successfully made by this technique.
Made by die compaction & sintering:porous filter parts can also be made by die compaction, but with only low compaction pressures. Once achieving the green compact, the parts are heated to the desired temperature under protective atmosphere to promote bonding between atoms. Porous parts from bronze, nickel,stainless steel, titanium powders can be produced by this method.
Made by powder spraying:spraying of metal powders on a substrate under controlled conditions can be used to produce porous material. It is also possible to co-spray the material along with a second material and removing the latter toobtain the porous part

IMPORTANT PROPERTIES:

1.ceramic`s are in-organic, non-metallic materials that are pass and /or used at high temperatures

2. They have been subjected to heat treatment

3. They are generally hard & brittle materials that with stand compression very well

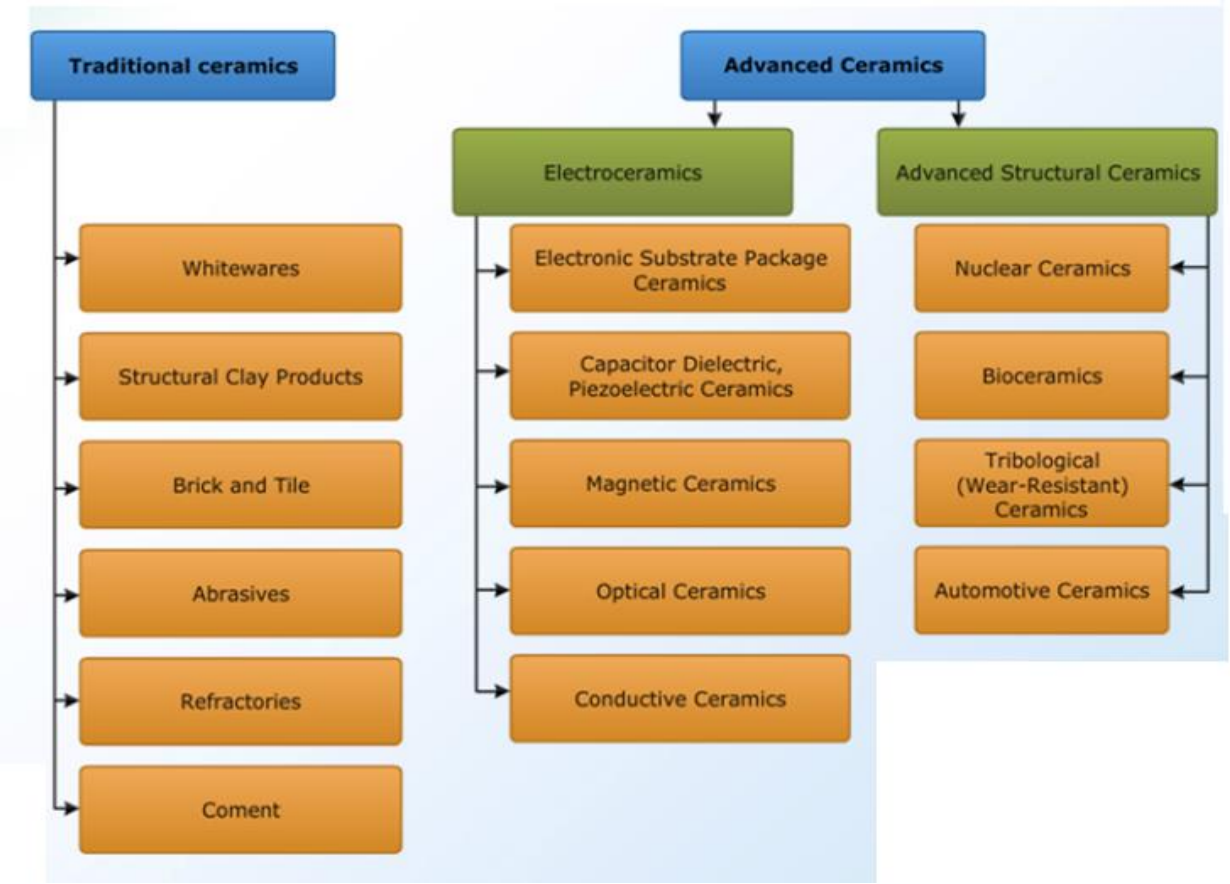
4. They are abrasive resistance, heat resistance &can curtain large compressive loads even at high temperature

5.many ceramic`s are chemically inert even at high temperatures as shown by good oxidation and reduction resistance at these temperature

6. The nature of chemical bond in ceramics generally ionic in character and the coins play on important role in the determination of the properties of the material

EX: anions, carbides, borides, nitrides, oxides.

TYPES OF CERAMIC`S: **1.**Classification of ceramics based on function



EXAMPLES OF CERAMIC MATERIALS:

1. All types of glass product including fibers etc..
2. Cements, line, plaster
3. Abrasives & some types of cutting of tools
4. Bricks, tiles, drain, pipes etc..
5. Refractories for high temperature use
6. Electrical insulators, Ferro magnetic, semi conductors

STRUCTURAL CLASSFICATION:

1. **CRYSTALLINE CERAMICS:**

   These are single phase like MGO to multi phase from MGO to AL2O3 binary system.

2. **NON-CRYSTALLINE CERAMICS**: natural & synthetic in-organic glasses.
3. **GLASS-BONDED CERAMICS**: fire clay products-crystalline phase are held in glass mat
4. **CEMENTS:** crystalline (or) non-crystalline phases.

ADVANTAGES OF CERAMIC MATERIALS:

1. The ceramics are hard, strong & dense.
2. They have high resistance to the action of chemically and to the weathering
3. Passes a high compression strength compressed with tension
4. They offer excellent di-electric properties
5. They are good thermal insulators
6. Good sanitation
7. Better economy

APPLICATIONS:

1. **WHITE WARES:** tools, sanitary wares, high frequency applications, chemical industries etc
2. **NEWER CERAMICS:** borides, carbides, nitrides, single oxides, mixed oxides, silicates, insulators, semi conductors, fuel elements, fuel containers, control rods etc..

3. ADVANCED CERAMICS: these are in I.C engines, turbines, cutting tools, energy conversation, strong & generation

PROPERTIES OF CERAMIC MATERIALS:

MECHANICAL PROPERTIES:

1. Compressive strength is high
2. It is brittle
3. These passes ionic & covalent bond
4. More force required
5. Rigidity high at temperature

ELECTRICAL PROPERTIES:

Di-electric constant:

It is the ratio of capacitance of a di-electric compared to the capacitance of air under the same conditions

Di-electric strength:

It is the ability of a material to with stand electrical break down volume & surfaces resistivity

Thermal properties:

1. Thermal conductivity
2. Thermal capacity
3. Thermal-shock-resistance

STRUCTURE OF CRYSTALLINE CERAMICS:

Most ceramic phases, like metals, have crystalline structure. Ceramic crystals are formed by either a pure ionic bond, a pure covalent (or) by bonds that passes the ionic as well as covalent characteristics.

Ionic bonds give ceramic materials of relatively high stability and high melting point

Covalent crystal:

1. Passes high hardness

2. High melting point & low electrical conductivity at room temperature

CRYSTAL STRUCTURES IN CRYSTAL CERAMICS:

1. Rock salt structure
2. zinc blend structure
3. worzite structure
4. spinel structure
5. fluorite structure
6. ilemenite structure
7. Cesium chloride structure

ADVANCED CERAMICS:

1. **Glass ceramics**:
   The compositions in which nucleation and crystallization have been commercially produced are MgO; Al_2O_3- SiO_2; LiO_2-AL_2O_3-SIO_2; LiO-MgO-SiO

Characteristics:

1. Very low co-efficient of thermal expansion

2. High mechanical strength and thermal conductivity

APPLICATOINS: over ware, table ware & as insulators

2. Die- electric ceramics:

Non linear electric ceramics are suitable in the miniaturation of electric part which have had to the development of increasingly sophisticated electrical circuits and also used in capacitors

2. **Electronic ceramics:**
   There are two types of electronic ceramics that are ferrite, Ferro-electric ceramics
   Ferrite are mixed metal-oxide ceramics
   - Ferro-electric ceramics are can convert electrical signal into mechanical energy

CERMETS:

- Cermets are ceramic & metal compositions
- It contains Al_2O_3 & Cr varying proportions.
- The most common cermets is the cemented carbide which is composed of extremely hard particles of a refractory carbide such as tungsten carbide (or) titanium
- These components are utilized extensively as cutting for hardened steels
- These are manufactured from the powders of ceramics metals by power metallurgy

APPLICATIONS:

1. These are used in jet engines, brake shoe, linings & oxidation resistant parts

2. Used as spinning tools for hot forging dies and other similar ten high temperatures applications

3. These also suitable for cutting of metals at high spends with medium to light chip loads

GLASSES:

1. Glass is a transparent silica product which may be amorphous (or) crystalline. Depending upon the heat treatment

2. Glass is in-organic product of faction in one (or) more oxides of silicon, boron, calcium, mg, Na etc … cooled to rigid material without crystallization

3. Glasses mostly consist of in-organic oxides such as SiO2 & B2O 3 are known as glass formers

many other oxides such as Al2O3, CaO, Na2o MgO etc…are added to glass forming oxides to obtain derived combination of properties such as refractories index, electrical conductivity etc…

STRUCTURE OF GLASS:

Unlike most other ceramic material glass is non-crystalline to manufacture it is a mixture of silica and other oxides is melted and then cooled to a rigid condition.

Glass does not change from liquid to solid at a fixed temperature but remains in the crystalline state and it is considered as a super cooled liquid

Fig: Amorphous non-crystalline structure of glass

GLASS PRODUCTION & PROCESSING STEPS:

1. Melting & refining ~ melting point = 1500 c
2. Forming & shaping
3. Heat treatment
4. Finishing

PROPERTIES OF GLASS:-

1**. Viscosity**: - which determines the suitability of glass for drawing into tubes, rods, for blowing & rolling

2. Chemical stability:-

Which determines the suitability of glass for making chemical wears & optical glasses

3.Optical properties:-this determine the stability of glass for use in optical system

4. **Mechanical properties**:-tensile strength & wear resistance.

5. **Electrical properties: -** good conductivity di-electric and determine the stability of glass for manufacturing the incandescent lamps, radio, valves, x-ray tubes etc

APPLICATIONS OF GLASS:-

1 in doors, windows, furnitures etc..

2. Laboratory equipment & chemical glass wear

3. X-ray tubes, glass tubes, fiber glass insulation, optical glasses

TYPES OF GLASSES:-

1. Soda lime (or) crown glass
2.flint glass
3.pyrex (or) heat resistant glass.

1) SODA LIME (OR) CROWN GLASS:-

1. It is the cheapest quality of glass

2. available in clean & clear state

3. Easily fusible at comparatively low temperatures.

COMPOSITION BY WEIGHT:-

Sand – 75 parts
lime - 12.5 parts

Soda – 12.5 parts

Alumina - 1 part

Waste glass 50 – 100 parts

Applications: - window glass, plate glass, bottles, glass etc…

2. FLINT GLASS:-

- it provide better lastre than sodium glass
- in this load provides brilliance & high polish

COMPOSITION BY WEIGHT: -

sand 100 parts
red lead 70 parts
potash 32 parts
waste glass 10 parts

Applications:- table wears, optical glasses, electrical resistance materials

3. PYREX (OR) HEAT RESISTANT GLASS:-

Which are used extensively for cooking utensils and laboratory wares, are borosilicate glasses.

COMPOSITION BY WEIGHT: -

Silica – 80 parts
borox oxide -14 parts
sodium oxide - 4 parts
alumina 2 parts with trasses of potassium oxide, calcium oxide, mg oxide..

HIGH SILICA GLASS: -

- These are containing 96% silica.
- These are used where high temperature resistance is required
- These are used regularly at temperatures up to about 900 c
- High silica glasses are have a very low thermal expansion co-efficient which accounts for this high resistance to thermal shock.

SPECIAL TYPES OF GLASS:-

Annealing glass, sheet glass, plate glass, fluted glass, ground glass, wired glass, safety glass, bullet-proof glass, insulating glass, foam glass, glass blocks, soluble glass, ultra violet glass, structural glass, glass fiber (or) glass war.

ABRASIVES:-

1.An abrasive is commonly made of ceramic material

2. An abrasive is hard, mechanically resistance i.e material used for grinding (or) cutting

3. An abrasive an wear away softer material

4. An abrasive may be natural (diamond) (or) synthetic

5. Synthatic abrasives are prefer because greater uniform of hardness & structure can be obtained and other desired properties can be introduced.

CLASSFICATION OF ABRASIVES:-

1. Hard Abrasives 2. Siliceous Abrasives

3. Soft Abrasives 4. Artificial Abrasives

1**. HARD ABRASIVES:-**

- These are diamond, corundum, emery and garnet
- (i) Diamond is a crystalline form of carbon found in nature diamond is the hardest material known and it out lasts other abrasive by factors of 10-100 more.

Uses: wire drawing dies, drills for drilling hard locks, dressing for grounding wheels, polishing (or) carbide metals glasses, ceramics etc

EMERY:-

1. It is a natural abrasive
2. Emery papers are used polishing metal

SILICEOUS ABRASIVES:-

These abrasives are quartz, flint, chart, quartzite, sand stone and plumice which are all compassed chiefly of silica.

Sand Stone:-

1. It is a natural abrasive
2. .it is used for sharpening wood working tools

Quartz:

1. It is a natural abrasive
2. It is used for sand paper for wood & fine grinding

ARTIFICIAL ABRASIVE: -

SiC:-

1. It is a synthetic, artificial (or) manufactured abrasive

2. To manufacture sic sand. Cock & sea dust are mixed at high temperature electrical arc (4500c) is passed through a mixture for a long time .the center of the mixture is converted into sic which is then crushed

$$SiO_2+2c\text{-----}SiC+CO_2$$

Applications: -

1. Sic better known by one of its trade name carborcndum
2. For making grinding wheels
3. for refraction material
4. .as heating, element in the electrically heated industrial furnaces
5. as pipe
6. 6.it is used as a pumps for pumping sand

Al_2O_3 (ALUMINIUM OXIDE):-

1. It is obtained by heating AL salts

2. A wide variation of properties is possible depending upon the treatment

3. It has a color, lighter then sic

4.it is not quite so hard as sic , but is tough and more resistance to impact

USES: -

1.for polishing cast iron, non-ferrous metals and high nature finishing of stainless steel.

2. Floor sanding machine

NANO TECHNOLOGY:-

- nano technology is the technology that controlles matter at a smaller scale can bring miniraiturisation of things

Which is a luxury for the present generation but nesting for the future generation?

- It is the only technology which is found to be multi disciplinary that the scientific communities of various disciplinary throughout the world are involved in developing a new kind of material era..

Various studies of a nano particle, revels, that at nano scale, the properties of traditional materials change and the behavior of surface starts to dominate the behavior of bulk material

- Nano materials are crystalline materials having grain size on the order of many atoms
- nano materials normally have grain size very from microns to millimeter
- A micron is a millionth of meter (10^6). A nano meter is very smaller then even microns with is a billionth of meter (10-9)
- nano materials can be in-organic, organic as well as bio-organic materials
- Anano-crystalline materials have grain of the order of 1-100mm

MAJOR FIELDS OF NANO TECHNOLOGY:-

- One of the important fields of development in the biotechnological field.
- In this field the manipulation of genes tissue engineering, drug system etc…of nano sale levels
- This technology is used in computers, cell phones, bio-medical robots, batteries, sensors. Solar cells etc.Will produce fruit feel results & in the future.

AREAS OF COMMERTIAL APPLICATION OF NANO TECHNOLOGY IN FEATURES: -

even through the real fruits of nano technology will reach the people after 10-18 years period of time these include tissue engineering, genetic engineering, cancer research, medical imaging system, carbon nano tubes, sensors, lubricants, films, paints, explosives, textiles etc..

`APPLICATIONS OF NANO MATERIALS:-

1.**Tougher & harder cutting tools** :-

Nano materials cutting tools made of nano crystalline, tic, tantalum, carbide are extremely tough with very high wear-resistance. Such cutting tools can operate at higher temperatures with higher speed reducing the production time.

Also miniaturized cutting tools such as micro drill and cutters with enhanced edge, endurance and wear resistance. can Successfully careful in micro electronic system

- **Mechanical ceramics**:- sic, silicon nitride, have been applied in automatic applications such as high strength springs ,ball bearings ,due to their excellent physical chemical & mechanical properties

COMPOSITE MATERIALS:-

Composite materials are produced by combining two dis-similar materials into a new material that may be better suited for a particular application than either of the original material alone.

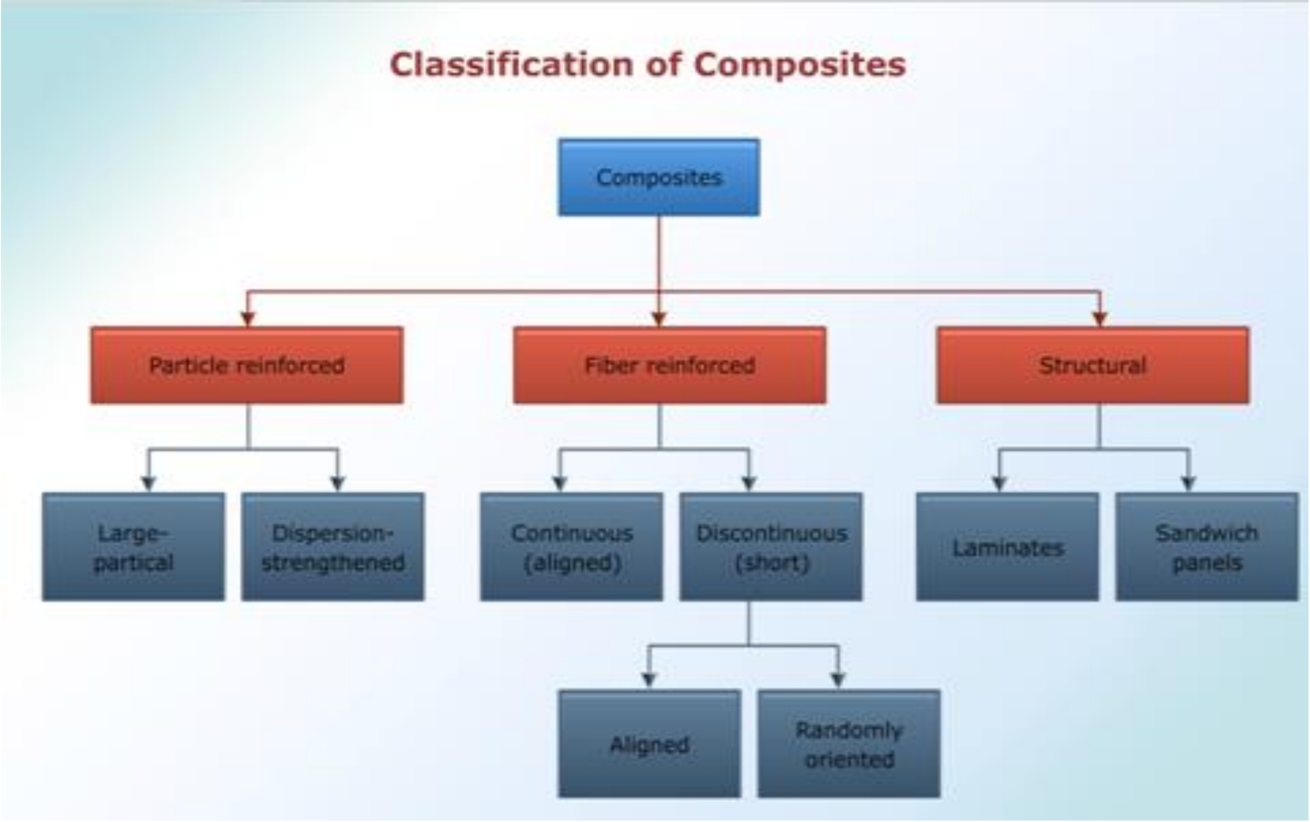
Ex: - Fiber glass, Reinferced plastics commonly used in house hold goods and in many industrial applications.

Their plastic alone is relatively weak& has low elastic modulus i.e., it bends and stretch easily. The glass fiber provides strength and stiffness; their modulus of elasticity may be sometimes more than that of plastics. Since glass fiber can with stand much higher tensile strength before yielding occurs. They take most of load when composite is stressed.

Metals, Ceramics, Glasses, Polymers and cement can be combined in composite materials to produce unique characteristics such as stiffness, toughness and high temperature strength.

Many composite materials are composed of just two phases one is termed as matrix which is continuous and the other phase often called the dispersed phase

Classification of composite materials:-



Manufacturing of composites

1. **Open Mold Processes**- some of the original FRP manual procedures for laying resins and fibers onto forms

2. Closed Mold Processes- much the same as those used in plastic molding

3. Filament Winding- continuous filaments are dipped in liquid resin and wrapped around a rotating mandrel, producing a rigid, hollow, cylindrical shape

- A polymer matrix composite (PMC) is a composite material consisting of a polymer imbedded with a reinforcing phase such as fibers or powders
- FRP composites can be designed with very high strength-to-weight and modulus-to-weight ratios
- These features make them attractive in aircraft, cars, trucks, boats, and sports equipment

Particle Reinforced Composite:-

The dispersed phase of particle reinforced composite is equi axed (Particle dimensions are approx same in all directions)

Large particle Composite:-

Fillers are added to some polymeric materials produces large particle composite. The fillers modified or improve the properties of materials and replace some of the polymers volume with less expensive fillers materials

Ex:-

1. Concrete is an example of large particle compsites.It is composed of cement and sanded gravels. The particles have a verity of geometry but they should be approximately the same dimensions in all in all directions (equi axed).

2. Particles should be small and evenly distributed thought matrix for effective reinforced. More over the volume fraction of the two phases influence the behavior.

3. Mechanical properties are enhanced with increasing the particulate content.

4. Large particles composites are utilized with 3 material types i.e., Metals ,Ceramics and polymers.

Example of ceramic metals composites are cermet, cementite carbide which are composed of extremely hard particles of a refractory carbide ceramics. Such as wc,Tic etc.... embedded in a matrix of metals such as **Cu** or **Ni** is the common cermet.These composites are widely used as a cutting tools.

Dispersed strengthen Composite:-

This type of composite contains small particulates with increses the strength of the composite by blocking the movement of dislocation.

Ex:-Sintered Aluminium Powder (SAP)

SAP has an Al matrix which contains op to 14% Al2O3.This composite is produced with powder metallurgy process where the powder are mixed compacted at high pressure and sintered together.

Sintering involves heating a material until the particles of the material fuse together only the particles are generally bonded together the whole doesn't melt.

Application:- Ag-cdo used as a electrical contact material

Pb-pbo used in battery plates

Ba-bao used in nuclear reactors & aerospace components

The high temp strength of Ni alloy may be enhanced significantly by the addition of about 3% volume of Thoria (Tho2) as finely dispersed particles. This material is known as Thoria dispersed Nickel.

Fiber Reinforced Composite:-

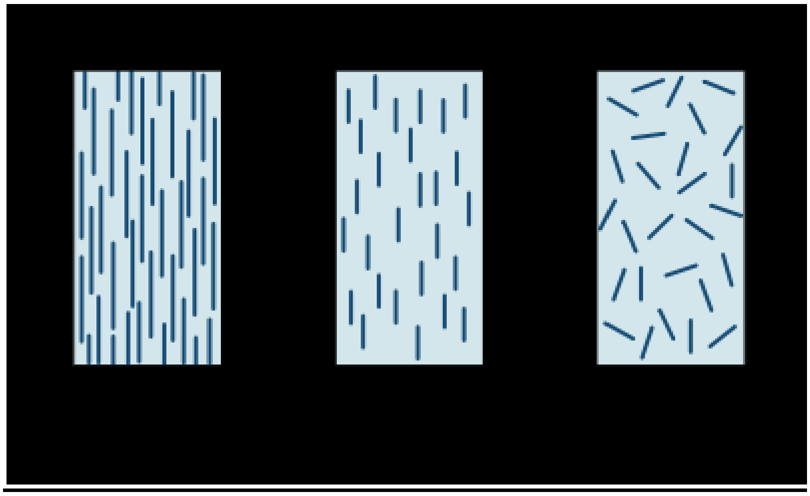


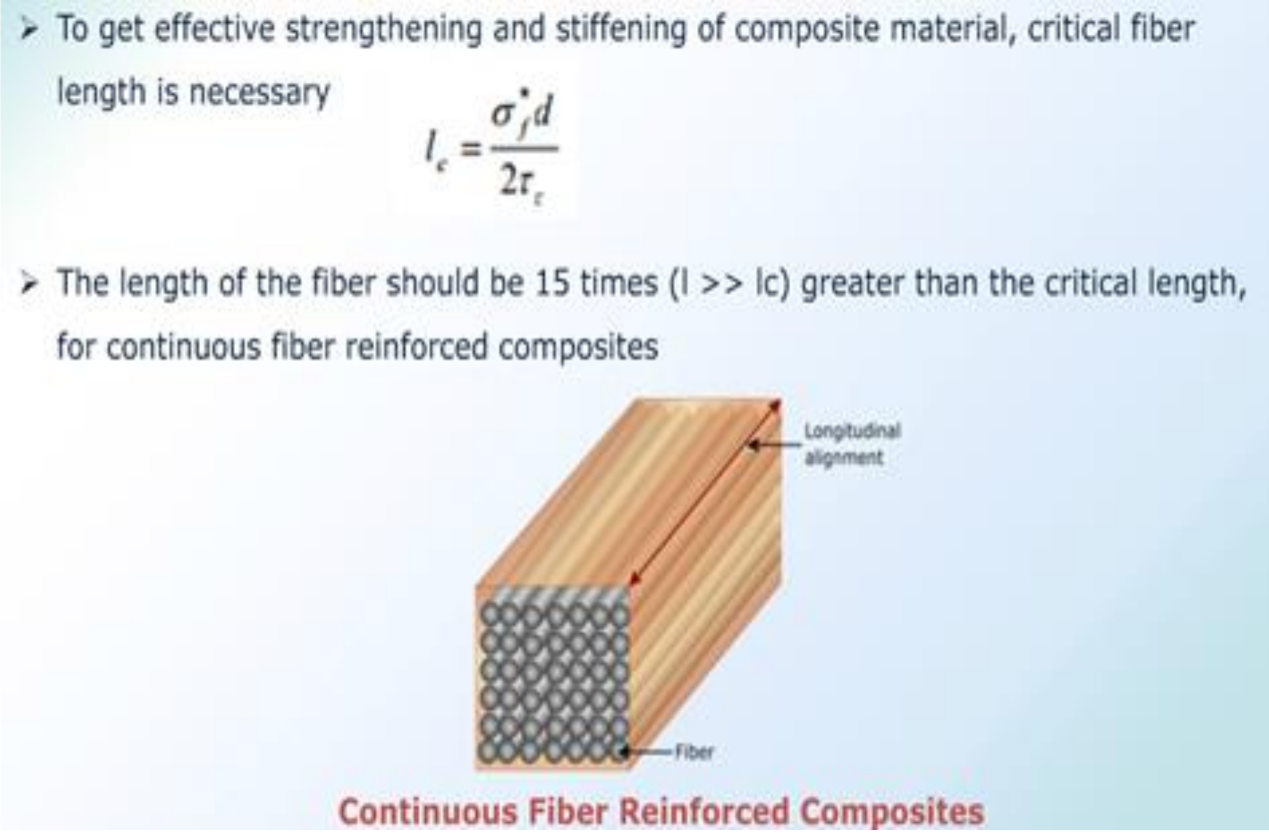
Fig: fiber Reinforced Composite

These are strong fibers embedded in a strong matrix produce products with high strength to weight ratio.

The matrix material transmits the load to the fibers, which absorbs the stress.

2. Fiber reinforced composite with exceptionally high specific strength and moduli have been produced that utilize low density fillers and matrix materials.

3.Some critical length is necessary for effective strengthening and stiffing the composite meterial.The critical lengths(lc) depends upon the fiber diameter(d) and its ultimate tensile change of fiber(sigma f) and matrix bond strength(Tc).



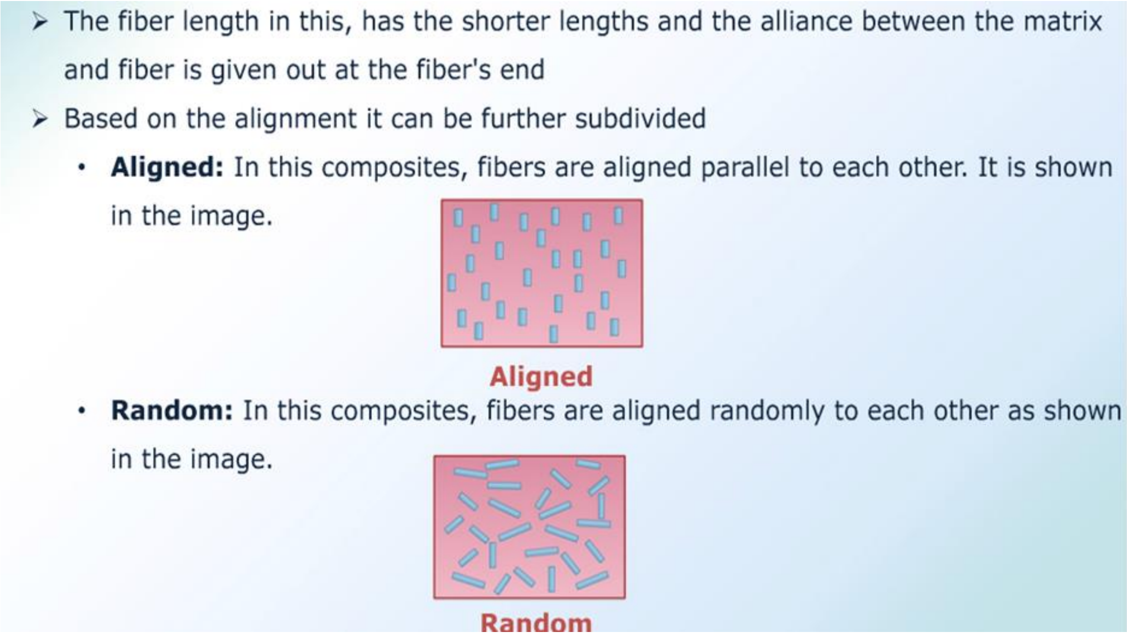
- To get effective strengthening and stiffening of composite material, critical fiber length is necessary

$$l_c = \frac{\sigma^{*}_{f} d}{2\tau_c}$$

- The length of the fiber should be 15 times (l >> lc) greater than the critical length, for continuous fiber reinforced composites

Continuous Fiber Reinforced Composites

2. DISCONTINOUS FRP:



- The fiber length in this, has the shorter lengths and the alliance between the matrix and fiber is given out at the fiber's end
- Based on the alignment it can be further subdivided
  - **Aligned:** In this composites, fibers are aligned parallel to each other. It is shown in the image.

Aligned

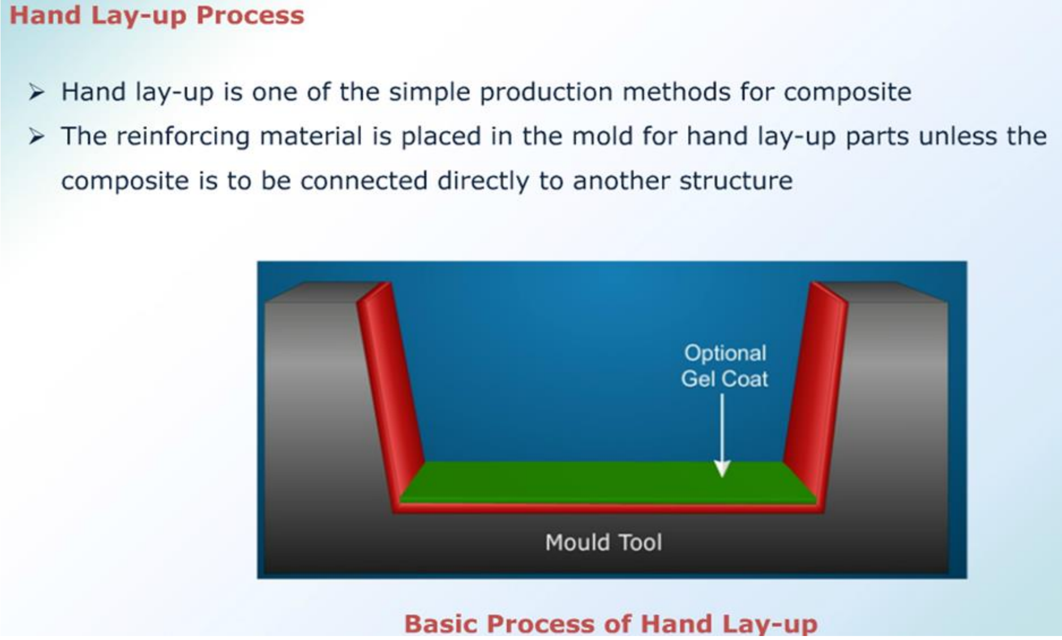
  - **Random:** In this composites, fibers are aligned randomly to each other as shown in the image.

Random

Fabrication of FRP: Fabrication processes of composites are

- Hand layup process
- Filament winding process
- Pultrusion process

Hand layup process

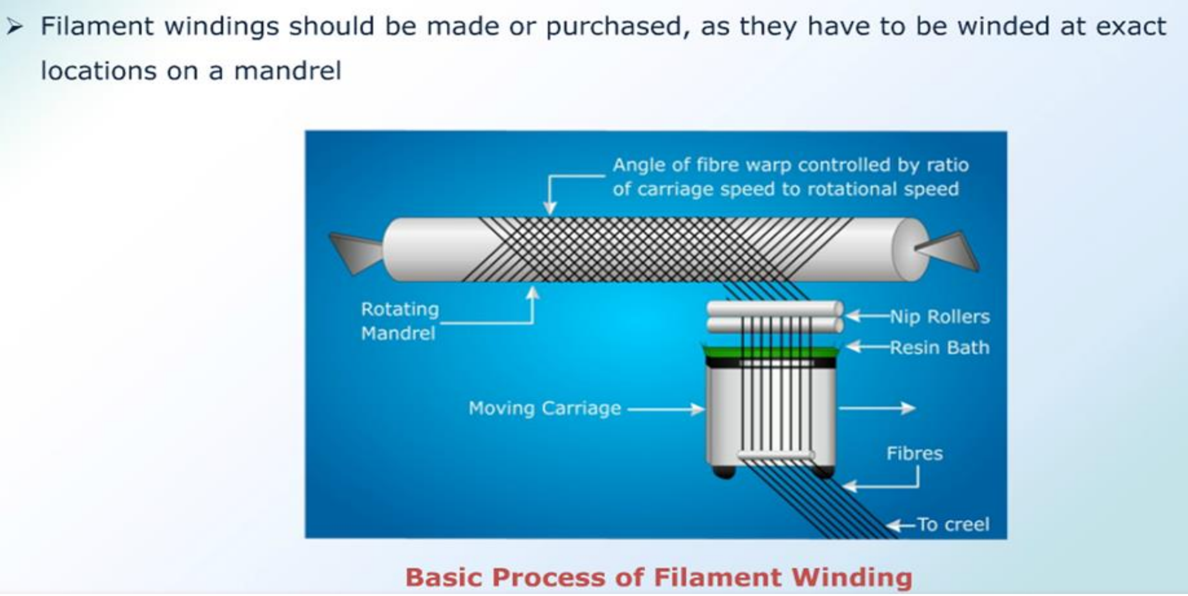


Hand Lay-up Process

- Hand lay-up is one of the simple production methods for composite
- The reinforcing material is placed in the mold for hand lay-up parts unless the composite is to be connected directly to another structure

Basic Process of Hand Lay-up

Filament Winding



- Filament windings should be made or purchased, as they have to be winded at exact locations on a mandrel

Basic Process of Filament Winding

Pultrusion

– Continuous fibers pulled through resin tank, then performing die & oven to cure

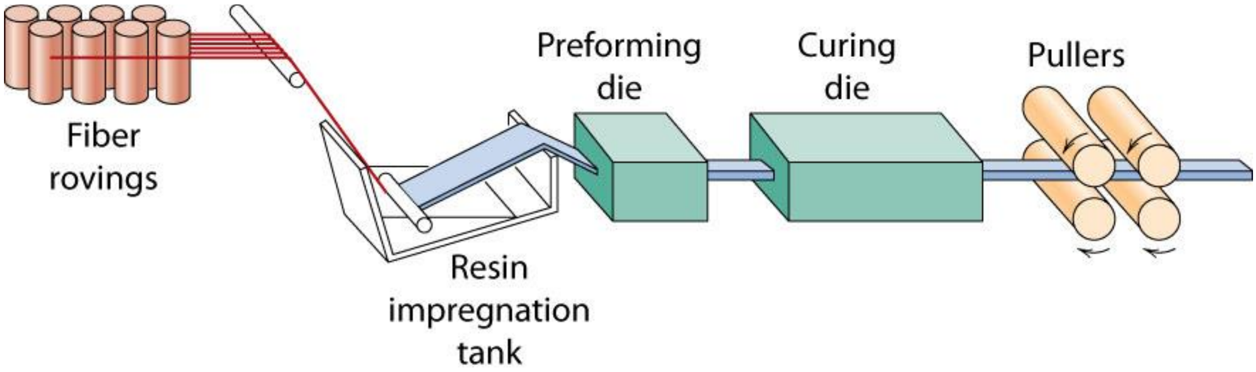
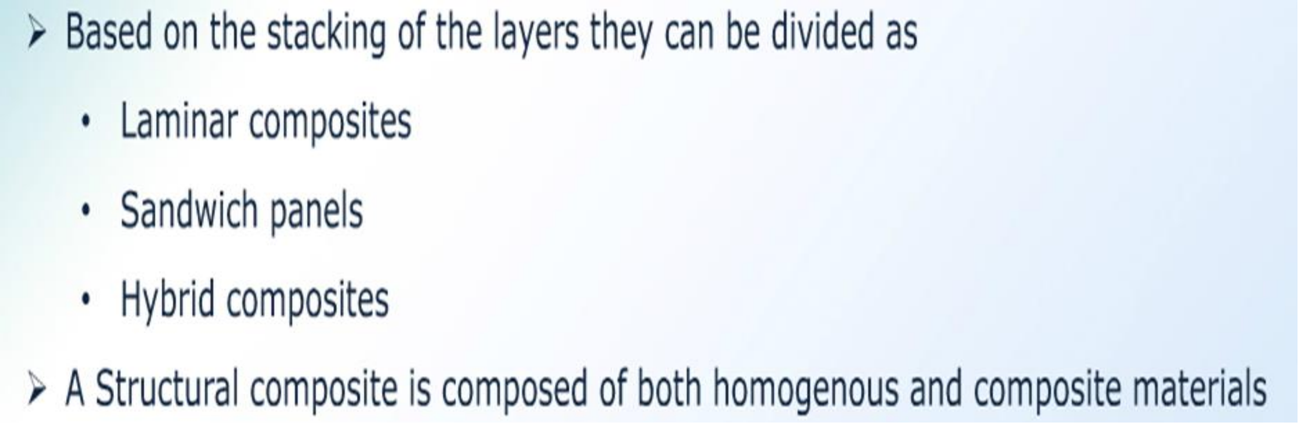
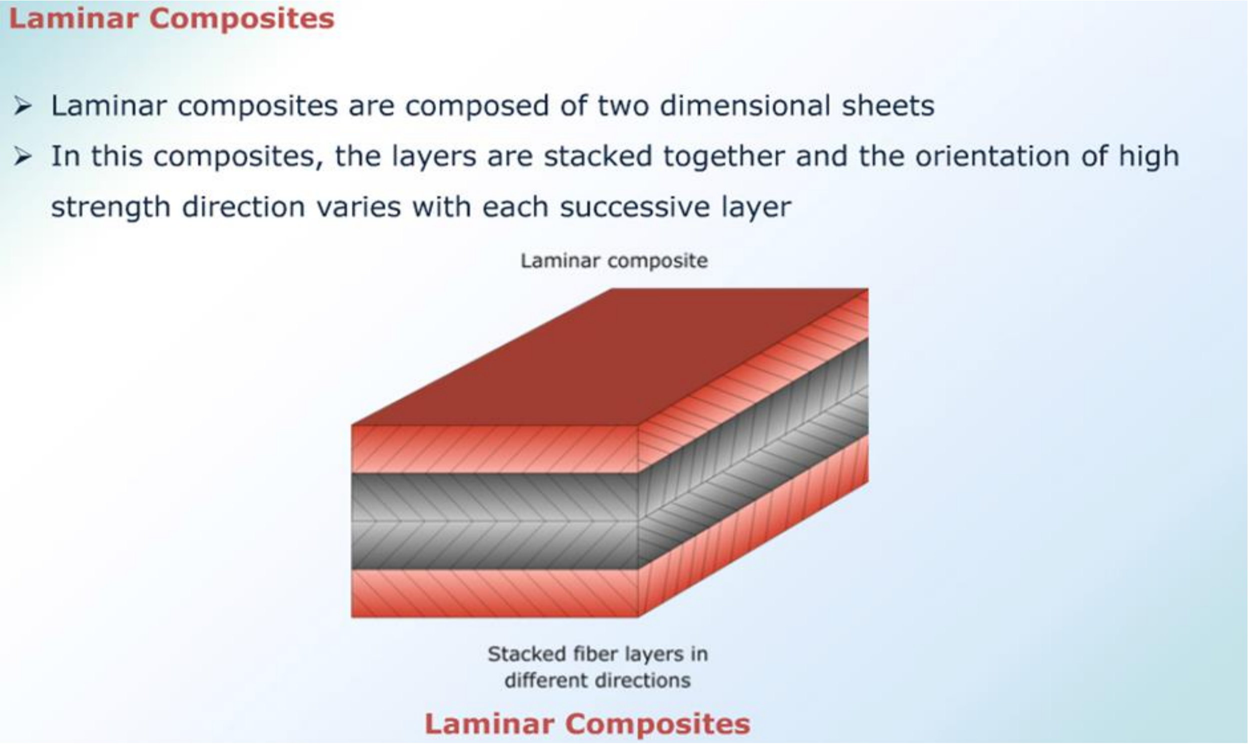


Fig: Pultrusion process



- Based on the stacking of the layers they can be divided as
  - Laminar composites
  - Sandwich panels
  - Hybrid composites
- A Structural composite is composed of both homogenous and composite materials

Laminar Composites

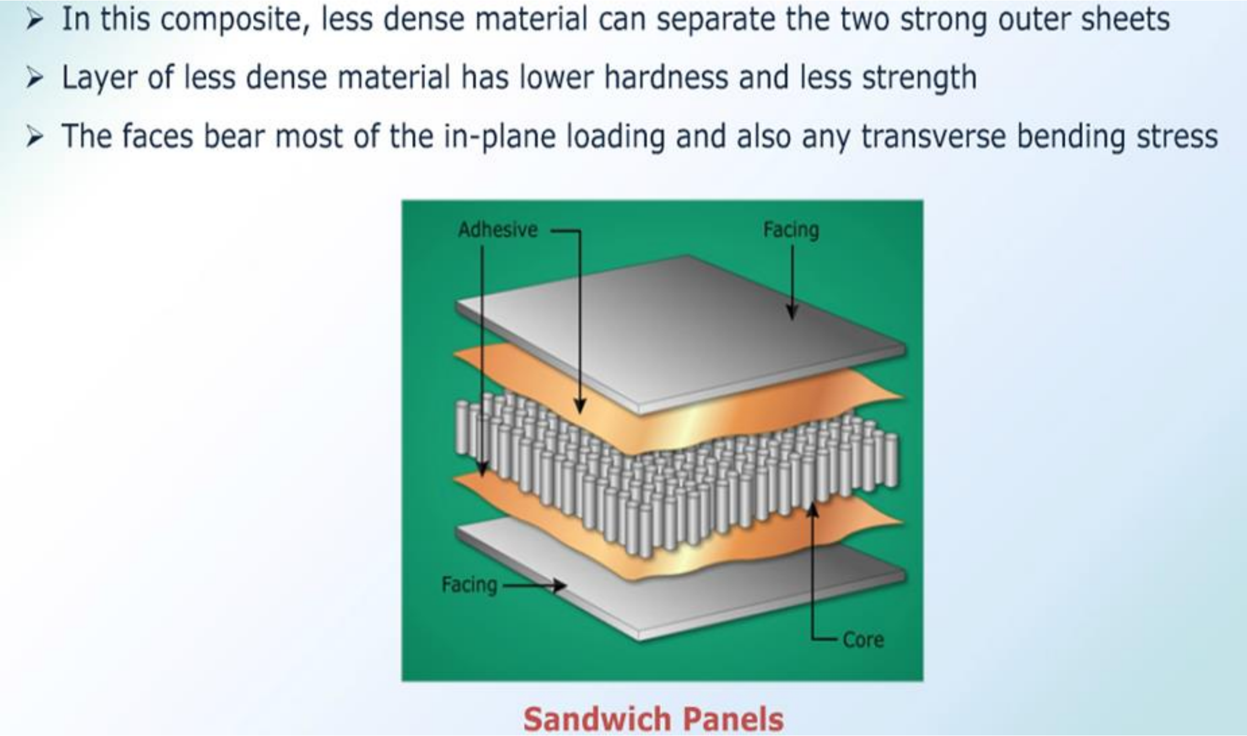


Laminar Composites

- Laminar composites are composed of two dimensional sheets
- In this composites, the layers are stacked together and the orientation of high strength direction varies with each successive layer

Laminar Composites

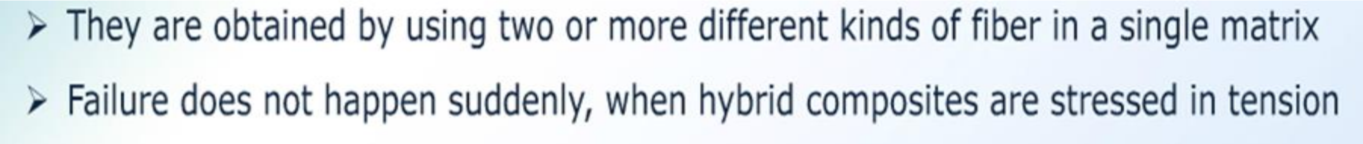
Sandwich panels



- In this composite, less dense material can separate the two strong outer sheets
- Layer of less dense material has lower hardness and less strength
- The faces bear most of the in-plane loading and also any transverse bending stress

Sandwich Panels

Hybrid composites



- They are obtained by using two or more different kinds of fiber in a single matrix
- Failure does not happen suddenly, when hybrid composites are stressed in tension

Types of composites

Cermets/Ceramal

The Cermet is an abbreviation for the "'ceramic" and "metal." A Cermets is a composite material composed of ceramic (Cer) and metallic (Met) materials. A Cermet is ideally designed to have the optimal properties of both a ceramic, such as high temperature resistance and hardness, and those of a metal, such as the ability to undergo plastic deformation. The metal is used as a binder for an oxide, boride, carbide, or alumina. Generally, the metallic elements used are nickel, molybdenum, and cobalt. Depending on the physical structure of the material, cermets can also be metal matrix composites, but cermets are usually less than 20% metal by volume.

It is used in the manufacture of resistors (especially potentiometers), capacitors, and other Electronic components which may experience high temperatures.

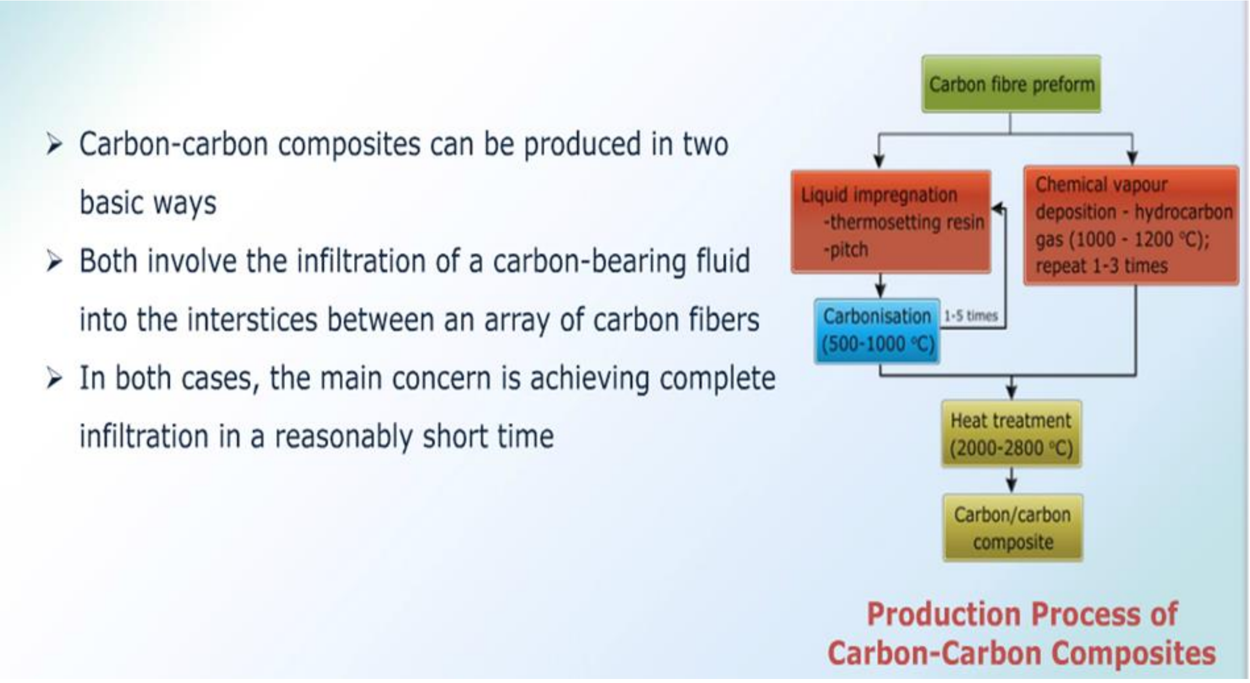
Some types of cermet are also being considered for use as spacecraft shielding as they resist the high velocity impacts of micrometeoroids and orbital debris much more effectively than more traditional spacecraft materials such as aluminum and other metals.

One application of these materials is their use in vacuum tube coatings, which are key to solar hot water systems. Cermets are also used in dentistry as a material for fillings and prostheses. Also it used in machining on cutting tools.

Cermets are one of the premier groups of particle strengthened composites and usually comprises ceramic grains of borides, carbides or oxides. The grains are dispersed in a refractory ductile metal matrix, which accounts for 20 to 85% of the total volume. The bonding between ceramic and metal constituents is the result of a small measure of mutual solutions.

Metal oxide systems show poor bonding and require additional bonding agents. Cermet Structures are usually produced using power metallurgy techniques. Their potential properties are several and varied depending on the relative volumes and compositions and of the metal and ceramic constituents. Impregnation of a porous ceramic structure with a metallic matrix binder is another method used to produce cermets. Cermets may be employed as coating in a power form. The power is sprayed through a gas flame and fused to a base material. A wide variety of cermets have been produced on a small scale, but only a few have appreciable value commercially.

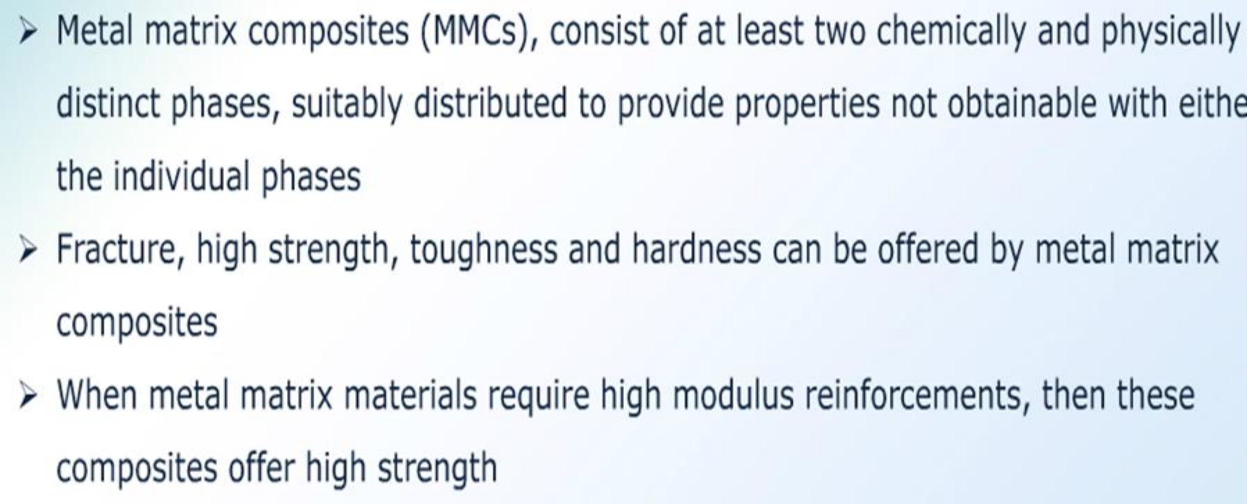
Carbon-carbon composites



- Carbon-carbon composites can be produced in two basic ways
- Both involve the infiltration of a carbon-bearing fluid into the interstices between an array of carbon fibers
- In both cases, the main concern is achieving complete infiltration in a reasonably short time

Production Process of Carbon-Carbon Composites

Metal matrix composites (MMCs):



- Metal matrix composites (MMCs), consist of at least two chemically and physically distinct phases, suitably distributed to provide properties not obtainable with eithe the individual phases
- Fracture, high strength, toughness and hardness can be offered by metal matrix composites
- When metal matrix materials require high modulus reinforcements, then these composites offer high strength

Introduction

Although it is undoubtedly true that the high strength of composites is largely due to the fiber reinforcement, the importance of matrix material cannot be underestimated as it provides support for the fibers and assists the fibers in carrying the loads. It also provides stability to the composite material. Resin matrix system acts as a binding agent in a structural component in which the fibers are embedded. When too much resin is used, the part is classified as resin rich. On the other hand if there is too little resin, the part is called resin starved. A resin rich part is more susceptible to cracking due to lack of fiber support, whereas a resin starved part is weaker because of void areas and the fact that fibers are not held together and they are not well supported.

Matrix Selection

Thermodynamically stable dispersions are essential for the use of metal matrix composites for high temperature applications. This can be done by using an alloy dispersion system in which **solid state diffusivity**, **interfacial energies** and **elemental solubility** are minimized, in turn reducing coarsening and interfacial reactions. Aluminium and magnesium alloys are regarded as widely used matrices due to low density and high thermal conductivity. Composites with low matrix alloying additions result in attractive combinations of ductility, toughness and strength. In discontinuous reinforced metal matrix composites minor alloying elements, used in wrought alloys as grain refiners, are not required. These additions should be avoided since coarse inter-metallic compounds get formed during consolidation, thus, reducing the tensile ductility of the composite.

Role of matrix materials

The choice of a matrix alloy for an MMC is dictated by several considerations. Of particular importance is whether the composite is to be continuously or discontinuously reinforced. The use of continuous fibers as reinforcements may result in transfer of most of the load to the reinforcing filaments and hence composite strength will be governed primarily by the fiber strength. The primary roles of the matrix alloy then are to provide efficient transfer of load to the fibers and to blunt cracks in the event that fiber failure occurs and so the matrix alloy for continuously reinforced composites may be chosen more for toughness than for strength. On this basis, lower strength, more ductile, and tougher matrix alloys may be utilized in continuously reinforced composites. For discontinuously reinforced composites, the matrix may govern composite strength. Then, the choice of matrix will be influenced by consideration of the required composite strength and higher strength matrix alloys may be required.

Additional considerations in the choice of the matrix include potential reinforcement/matrix reactions, either during processing or in service, which might result in degraded composite performance; thermal stresses due to thermal expansion mismatch between the reinforcements and the matrix; and the influence of matrix fatigue behavior on the cyclic response of the composite. Indeed, the behavior of composites under cyclic loading conditions is an area requiring special consideration. In composites intended for use at elevated temperatures, an additional consideration is the difference in melting temperatures between the matrix and the reinforcements. A large melting temperature difference may result in matrix creep while the reinforcements remain elastic, even at temperatures approaching the matrix melting point. However, creep in both the matrix and reinforcement must be considered when there is a small melting point difference in the composite.

Functions of a Matrix

In a composite material, the matrix material serves the following functions:

- Holds the fibers together.
- Protects the fibers from environment.
- Distributes the loads evenly between fibers so that all fibers are subjected to the same amount of strain.
- Enhances transverse properties of a laminate.
- Improves impact and fracture resistance of a component.

Helps to avoid propagation of crack growth through the fibers by providing alternate failure path along the interface between the fibers and the matrix.

- Carry interlaminar shear.

The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, selection of a matrix has a major influence on the interlaminar shear as well as in-plane shear properties of the composite material.

The interlaminar shear strength is an important design consideration for structures under bending loads, whereas the in-plane shear strength is important under torsion loads. The matrix provides lateral support against the possibility of fiber buckling under compression loading, thus influencing to some extent the compressive strength of the composite material. The interaction between fibers and matrix is also important in designing **damage tolerant structures**. Finally, the processability and defects in a composite material depend strongly on the physical and thermal characteristics, such as viscosity, melting point, and curing temperature of the matrix.

Desired Properties of a Matrix

The needs or desired properties of the matrix which are important for a composite structure are as follows:

- Reduced moisture absorption.
- Low shrinkage.
- Low coefficient of thermal expansion.
- Good flow characteristics so that it penetrates the fiber bundles completely and eliminates voids during the compacting/curing process.
- Reasonable strength, modulus and elongation (elongation should be greater than fibre).
- Must be elastic to transfer load to fibers.
- Strength at elevated temperature (depending on application).
- Low temperature capability (depending on application).
- Excellent chemical resistance (depending on application).
- Should be easily process able into the final composite shape.
- **Dimensional stability** (maintains its shape).

As stated above, the matrix causes the stress to be distributed more evenly between all fibers by causing the fibers to suffer the same strain. The stress is transmitted by shear process, which requires good bonding between fiber and matrix and also high shear strength and modulus for the matrix itself. One of the important properties of cured matrix system is its glass transition temperature (T) at which the matrix begins to soften and exhibits a decrease in mechanical properties. The glass transition temperature is not only an important parameter for dimensional stability of a composite part under influence of heat, but it also has effect on most of the physical properties of the matrix system at ambient temperature.

As the load is primarily carried by the fibers, the overall elongation of a composite material is governed by the elongation to failure of the fibers that is usually 1-1.5%. A significant property of the matrix is that it should not crack.

The function of the matrix in a composite material will vary depending on how the composite is stressed. For example, in case of compressive loading, the matrix prevents the fibers from **buckling** and is, therefore, a very critical part of the composite since without it; the reinforcement could carry no load. On the contrary, a bundle of fibers could sustain high tensile loads in the direction of the filaments without a matrix. Some of the physical properties of the matrix which influence the behavior of composites are:

- **Shrinkage** during cure,
- Modulus of elasticity,
- Ultimate elongation,
- Strength (tensile, compressive and shear), and
- **Fracture toughness**.

Factors considered for Selection of Matrix

In selecting matrix material, following factors may be taken into consideration:

- The matrix must have a mechanical strength commensurate with that of the reinforcement i.e. both should be compatible. Thus, if a high strength fiber is used as the reinforcement, there is no point using a low strength matrix, which will not transmit stresses efficiently to the reinforcement.
- The matrix must stand up to the service conditions, viz., temperature, humidity, exposure to ultra-violet environment, exposure to chemical atmosphere, abrasion by dust particles, etc.
- The matrix must be easy to use in the selected fabrication process.
- Smoke requirements.
- Life expectancy.
- The resultant composite should be cost effective.

The fibers are saturated with a liquid resin before it cures to a solid. The solid resin is then said to be the matrix for the fibers.

Advantages and Limitations of Composites Materials

Advantages of Composites

The advantages exhibited by composite materials, which are of significant use in aerospace industry are as follows:

- High resistance to fatigue and corrosion **degradation**.
- High 'strength or stiffness to weight' ratio. As enumerated above, weight savings are significant ranging from 25-45% of the weight of conventional metallic designs.
- Due to greater **reliability**, there are fewer inspections and structural repairs.
- Directional **tailoring capabilities** to meet the design requirements. The fibre pattern can be laid in a manner that will tailor the structure to efficiently sustain the applied loads.
- Fiber to fiber redundant load path.
- Improved dent resistance is normally achieved. Composite panels do not sustain damage as easily as thin gage sheet metals.
- It is easier to achieve smooth **aerodynamic profiles** for drag reduction. Complex double-curvature parts with a smooth surface finish can be made in one manufacturing operation.
- Composites offer improved **torsion stiffness**. This implies high whirling speeds, reduced number of intermediate bearings and supporting structural elements. The overall part count and manufacturing & assembly costs are thus reduced.
- High resistance to impact damage.
- Thermoplastics have rapid process cycles, making them attractive for high volume commercial applications that traditionally have been the domain of sheet metals. Moreover, thermoplastics can also be reformed.
- Like metals, thermoplastics have indefinite shelf life.
- Composites are **dimensionally stable** i.e. they have low thermal conductivity and low coefficient of thermal expansion. Composite materials can be tailored to comply with a broad range of thermal expansion design requirements and to minimize thermal stresses.
- Manufacture and assembly are simplified because of part integration (joint/fastener reduction) thereby reducing cost.
- The improved **weather ability** of composites in a marine environment as well as their corrosion resistance and durability reduce the down time for maintenance.

- Close tolerances can be achieved without machining.
- Material is reduced because composite parts and structures are frequently built to shape rather than machined to the required configuration, as is common with metals.
- Excellent heat sink properties of composites, especially Carbon-Carbon, combined with their lightweight have extended their use for aircraft brakes.
- Improved friction and wear properties.
- The ability to tailor the basic material properties of a Laminate has allowed new approaches to the design of **aero elastic flight structures**.

The above advantages translate not only into airplane, but also into common implements and equipment such as a graphite racquet that has inherent damping, and causes less fatigue and pain to the user.

Limitations of Composites

Some of the associated disadvantages of advanced composites are as follows:

- High cost of raw materials and fabrication.
- Composites are more brittle than wrought metals and thus are more easily damaged.
- Transverse properties may be weak.
- Matrix is weak, therefore, low toughness.
- Reuse and disposal may be difficult.
- Difficult to attach.
- Repair introduces new problems, for the following reasons:
  - Materials require refrigerated transport and storage and have limited shelf life.
  - Hot curing is necessary in many cases requiring special tooling.
  - Hot or cold curing takes time.
  - Analysis is difficult.
  - Matrix is subject to environmental degradation.

However, proper design and material selection can circumvent many of the above disadvantages.

New technology has provided a variety of reinforcing fibers and matrices those can be combined to form composites having a wide range of exceptional properties. Since the advanced composites are capable of providing structural efficiency at lower weights as compared to equivalent metallic structures, they have emerged as the primary materials for future use.

In aircraft application, advanced fiber reinforced composites are now being used in many structural applications, viz. floor beams, engine cowlings, flight control surfaces, landing gear doors, wing-to-body fairings, etc., and also major load carrying structures including the vertical and horizontal stabilizer main torque boxes.

Composites are also being considered for use in improvements to civil infrastructures, viz., earthquake proof highway supports, power generating wind mills, long span bridges, etc.

Comparison with Metals

Requirements governing the choice of materials apply to both metals and reinforced plastics. It is, therefore, imperative to briefly compare main characteristics of the two.

- Composites offer significant weight saving over existing metals. Composites can provide structures that are 25-45% lighter than the conventional aluminium structures designed to meet the same functional requirements. This is due to the lower density of the composites.

  Depending on material form, composite densities range from 1260 to 1820 kg/in^3 (0.045 to 0.065 lb/in^3) as compared to 2800 kg/in^3 (0.10 lb/in^3) for aluminium. Some applications may require thicker composite sections to meet strength/stiffness requirements, however, weight savings will still result.
- Unidirectional fibre composites have specific tensile strength (ratio of material strength to density) about 4 to 6 times greater than that of steel and aluminium.
- Unidirectional composites have specific -modulus (ratio of the material stiffness to density) about 3 to 5 times greater than that of steel and aluminium.
- **Fatigue endurance limit** of composites may approach 60% of their **ultimate tensile strength**. For steel and aluminium, this value is considerably lower.
- Fiber composites are more versatile than metals, and can be tailored to meet performance needs and complex design requirements such as **aero-elastic loading** on the wings and the vertical & the horizontal stabilizers of aircraft.
- Fiber reinforced composites can be designed with excellent structural **damping features**. As such, they are less noisy and provide lower vibration transmission than metals.
- High corrosion resistance of fiber composites contributes to reduce life- cycle cost.

- Composites offer lower manufacturing cost principally by reducing significantly the number of detailed parts and expensive technical joints required to form large metal Structural components. In other words, composite parts can eliminate joints/fasteners thereby providing parts simplification and integrated design.
- Long term service experience of composite material environment and **durability behavior** is limited in comparison with metals.