ENGINEERING METALLURGY

LEARNING MATERIAL

UNIT-I

IRON AND STEEL MAKING

SYLLABUS: Iron Making: Introduction to iron making- blast furnace, operation of blast furnace, coke oven batteries, types of reduction reactions in blast furnace.

Steel making: production of cast iron- Cupola furnace; production of steel – Bessemer converter, open hearth furnace & electric furnace.

Introduction to Iron making:

According to most historians, the first iron used by man was of meteoritic origin. It does not contain carbon; therefore, it is soft, malleable. It usually contains an admixture of nickel. It was directly applicable to production of tools. Even though there is evidence of iron production in crucibles already in ancient times, reduction of lump ores by charcoal was used for its practical use at the beginning of iron industry.

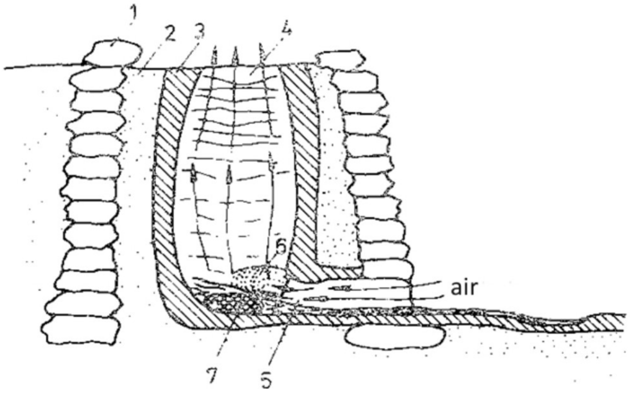


Fig.1 A bloomer furnace

Note: 1- stone lining, 2 - earth or sand, 3 - refractory clay, 4 - furnace chamber, 5 – open slag drain, 6 - space for char, 7 – mass of iron and slag ("bloom")

- Charcoal provided necessary heat and reducing gas. Reached temperature did not exceed 1000 °C.

In the mid-19th century, Henry Bessemer developed a steel-making process that used oxygen to burn off some of the carbon in cast iron. The Basic Oxygen

Steelmaking process was introduced in the 1950s and now accounts for about two-thirds of steel production.

Types of Iron:

- ✓ Pure iron
- ✓ Wrought iron
- ✓ Direct reduced iron
- ✓ Cast Iron

- **Pure iron**, it is around 99.8 % pure with a carbon content of around 0.005 % and manganese content of around 0.005 %. Pure Iron, with a minimum Fe content of 99.85 %, without the addition of alloy elements.
- **Wrought iron** is a form of commercial iron which has very low carbon content (less than 0.10 %), less than 0.25 % of impurities consisting of sulphur, phosphorus, silicon and manganese. Wrought iron is soft, ductile, magnetic, and strong with high elasticity and tensile strength, malleable.
- **Direct reduced iron (DRI)** is produced by the reduction of iron ore (in the form of lumps or pellets) by either non-coking coal or a reducing gas produced by reforming of natural gas. it has a porous, sponge like form Consequently, it has a large surface area relative to its mass
- **Cast Iron** is one of the important alloys of Iron (Fe) and carbon. Percentage of carbon in cast iron varies from 2 to 6.67. The main elements presented in the cast iron: Fe, C, Si, Mn, P, S.

BLAST FURNACE:

- **Principle:** The principle of a blast furnace is to chemically reduce and physically convert iron oxides into liquid iron called "hot metal".
- **Construction:** The blast furnace is a huge, steel stack lined with refractory brick. Where iron ore, coke and limestone are dumped into the top, and preheated air is blown into the bottom as shown in figure 2.
- **Input materials used in blast furnace:** Iron oxides can come to the blast furnace plant in the form of raw ore, pellets or sinter.
    - **Iron ore:** The raw ore is removed from the earth and sized into pieces that range from 0.5 to 1.5 inches. This ore is either Hematite (Fe_2O_3) or Magnetite (Fe_3O_4) and the iron content ranges from 50% to 70%.

- This ore is crushed and ground into a powder, so the waste material called gangue can be removed. The remaining iron rich powder is rolled into balls and fired in a furnace to produce strong, marble-sized pellets that contain 60% to 65% iron.

- **Coke:** The **coke** is produced from a mixture of coals. The coal is crushed and ground into a powder and then charged into an oven.
- **Limestone**: The final raw material in the iron making process is limestone. It acts as a flux, it can be pure high calcium limestone, dolomite limestone containing magnesia or a blend of the two types of limestone. The limestone is melted to become the slag which removes sulfur and other impurities.

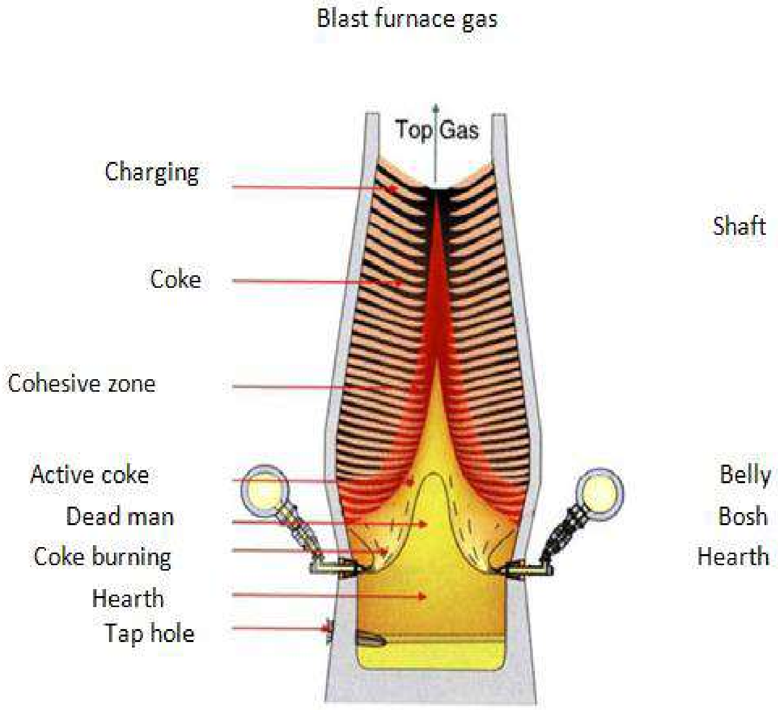


Fig.2 Constructional details of blast furnace

➢ Reduction reactions in Blast furnace:

- These reactions occur as follows:

  $3\ Fe_2O_3 + CO \rightarrow CO_2 + 2\ Fe_3O_4$ Begins at 850° F
  $Fe_3O_4 + CO \rightarrow CO_2 + 3\ FeO$ Begins at 1100° F
  $FeO + CO \rightarrow CO_2 + Fe$ or
  $FeO + C \rightarrow CO + Fe$ Begins at 1300° F

- The coke is ignited by this hot blast and immediately reacts to generate heat as follows
  $C + O_2 \rightarrow CO_2 + Heat$
  $CO_2 + C \rightarrow 2CO$
  $CaO + CO_2 \rightarrow CaCO_3$

- The reaction takes place in the presence of excess carbon at a high temperature the carbon dioxide is reduced to carbon monoxide as follows
  $CO_2 + C \rightarrow 2CO$
- The product of this reaction, carbon monoxide, is necessary to reduce the iron ore as seen in the previous iron oxide reactions.
  $CaO + CO_2 \rightarrow CaCO_3$
- This sulfur removing reaction
  $FeS + CaO + C \rightarrow CaS + FeO + CO$

➢ COKE OVEN BATTERIES:

- Coke oven are used to convert coal into coke by carbonizing coal in absence of air for 17-18 hours and there by distilling the volatile matter out of coal.

- Coke is taken as product which is use as fuel and as a reducing agent in smelting iron ore in a blast furnace and coke oven gas as byproduct is treated for recovery of coal chemicals.

- The coke oven temperature is kept as high as 2000 ^{o}C. Crushing and screening of coke is done to obtain suitable size for use in blast furnace.

- The ovens are maintained under positive pressure by maintaining high hydraulic main pressure of 7 mm water column in batteries.

➢ PRODUCTION OF CAST IRON:

I. CUPOLA FURNACE:

- For many years, the cupola was the primary method of melting used in iron foundries.

- Cupola furnace is employed for melting scrap metal or pig iron for production of various cast irons.

- **Construction**: A typical cupola melting furnace consists of a water-cooled vertical cylinder which is lined with refractory material. Gray Cast iron, nodular cast iron, some malleable iron castings and some copper base alloys can be produced by Cupola Furnace. The schematic representation of various zones and construction details of cupola is as shown in figure 3.

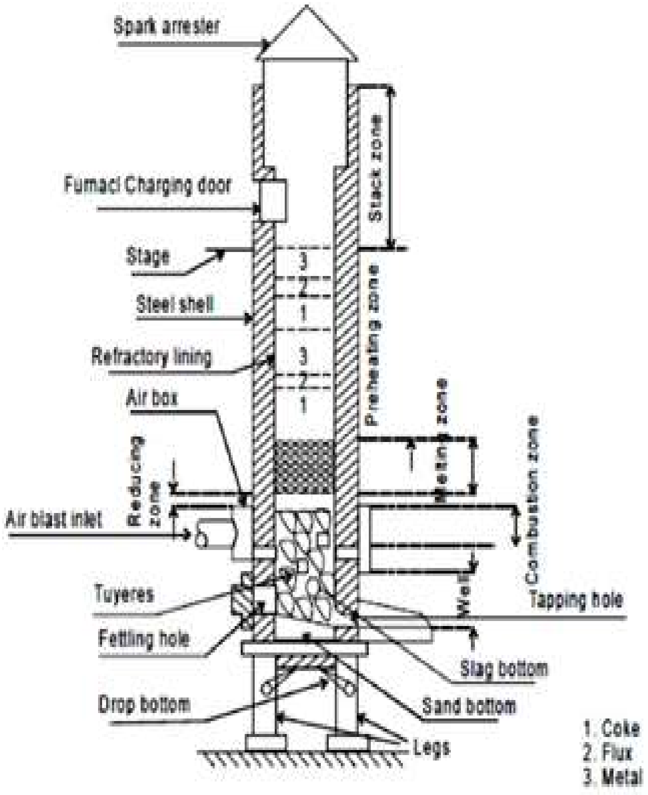


Fig. 3. Schematic representation of Cupola furnace

- The construction of a conventional cupola consists of a vertical steel shell which is lined with a refractory brick. The charge is introduced into the furnace body by means of an opening approximately half way up the vertical stack Zone.
- The charge consists of alternate layers of the metal to be melted, coke fuel and limestone flux. The fuel is burnt in air which is introduced through tuyeres positioned above the hearth.
- The hot gases generated in the lower part of the stack ascend and preheat the descending charge.

❖ Various Zones and reactions of Cupola Furnace:

- **Well:** The space between the bottom of the tuyeres and the sand bed inside the cylindrical shell of the cupola is called as well of the cupola. As the melting occurs, the molten metal is get collected in this portion before tapping out.

- **Combustion zone:** The combustion zone of Cupola is also called as oxidizing zone.

  $C + O2 \rightarrow CO2 + Heat$

  $Si + O2 \rightarrow SiO2 + Heat$

  $2Mn + O2 \rightarrow 2MnO + Heat$

- **Reducing zone:** Reducing zone of Cupola is also known as the protective zone which is located between the upper level of the combustion zone and the upper level of the coke bed. In this zone, CO2 is changed to CO through an endothermic reaction, as a result of which the temperature falls from combustion zone temperature to about 1200°C at the top of this zone.

  $CO2 + C\ (coke) \rightarrow 2CO + Heat$

- **Melting zone:** The lower layer of metal charge above the lower layer of coke bed is termed as melting zone of Cupola. The metal charge starts melting in this zone and trickles down through coke bed and gets collected in the well. Sufficient carbon content picked by the molten metal in this zone is represented by the chemical reaction given as under.

  $3Fe + 2CO \rightarrow Fe_3C + Co_2$

- **Preheating zone**: Preheating zone starts from the upper end of the melting zone and continues up to the bottom level of the charging door. This zone contains a number of alternate layers of coke bed, flux and metal charge. The main objective of this zone is to preheat the charges from room temperature to about 1090°C before entering the metal charge to the melting zone.

- **Stack:** The empty portion of cupola above the preheating zone is called as stack. It provides the passage to hot gases to go to atmosphere from the cupola furnace.

Charging of Cupola Furnace:

- Before the blower is started, the furnace is uniformly pre-heated and the metal and coke charges, lying in alternate layers, are sufficiently heated up.
- The cover plates are positioned suitably and the blower is started. The height of coke charge in the cupola in each layer varies generally from 10 to 15 cms.
- The requirement of flux to the metal charge depends upon the quality of the charged metal and scarp, the composition of the coke and the amount of ash content present in the coke.

Advantages:

- It is simple and economical to operate.
- Cupolas can refine the metal charge, removing impurities out of the slag.
- From a life-cycle perspective, cupolas are more efficient and less harmful to the environment than electric furnaces.
- The continuous rather than batch process suits the demands of a repetition foundry.

Limitations

- Since molten iron and coke are in contact with each other, certain elements like si, Mn are lost and others like sulphur are picked up. This changes the final analysis of molten metal.
- Close temperature control is difficult to maintain.

II. BESSEMER CONVERTER PROCESS:

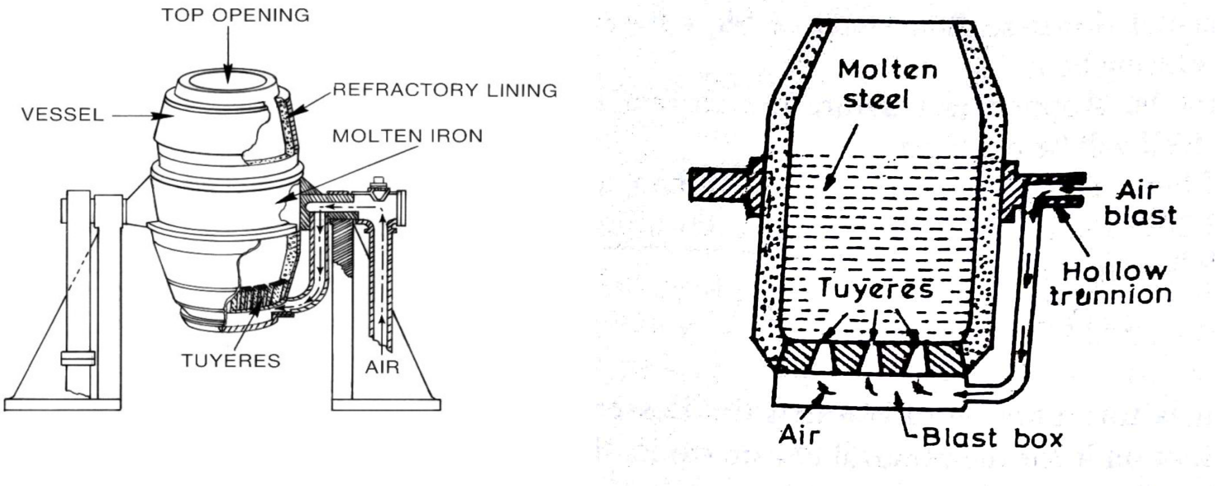
- The Bessemer process was the first inexpensive industrial process for the mass-production of steel from molten pig iron. The process is named after its inventor, Henry Bessemer, who took out a patent on the process in 1855.
- **Principle of Bessemer converter:** The key principle is removal of impurities from the iron by oxidation with air being blown through the molten iron. The oxidation also raises the temperature of the iron mass and keeps it molten.

❖ Working of Bessemer Converter:

- The process is carried on in a large steel container with inside refractory lining (Clay or dolomite).
- The Bessemer process consists of blowing compressed air upward through a refractory lined vessel (converter)
- The pear shaped vessel (i,e converter) has openings (tuyeres) at the bottom through which the air enters.
- Oxidation
  - The oxidation process removes impurities such as silicon, manganese, and carbon as oxides.
  - These oxides either escape as gas or form a solid slag.
  - The refractory lining of the converter also plays a role in the conversion

❖ Construction and operational Details:

- Pear shaped steel vessels lined with refractory material (holing capacity 10 to 25 tons).
- First, converter is set horizontally, a charge of molten pig iron is poured through the mouth and the air blast is turned on.
- Then the converter is rotated into vertical position and in this state, the molten iron is supported by the stream of air coming into from below. After 15-20 minutes, the converter is returned to the horizontal position, the air blast shut off and steel is ready to be poured into ingot moulds.
- The schematic representation of Bessemer converter is as shown in figure 4.



(a) **(b)**

Figure 4: (a) Over view of Bessemer Converter
(b) Cross sectional view of Bessemer Converter

❖ **<u>Operation in Bessemer Converter:</u>**

The sequential steps of Bessemer converter consist of charging, blowing and pouring. These steps are shown as in figure 6.

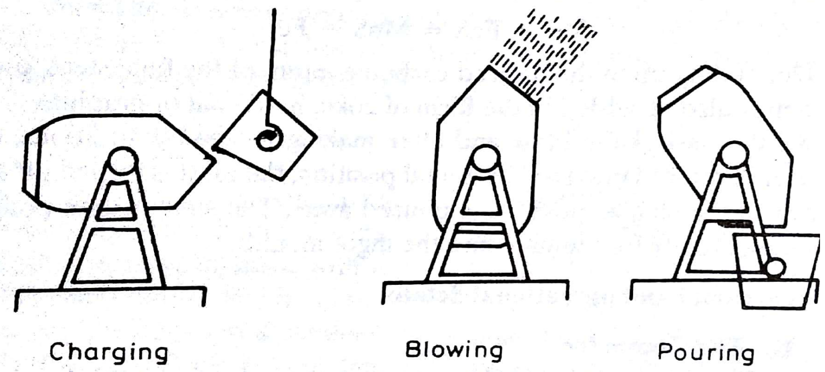


Fig. 5. Various steps in Bessemer converter

III. ELECTRIC ARC FURNACES:

- It is a furnace heating charged materials done by an electric arc. These furnaces exist in all the sizes. Temperatures risen up to 1800 Celsius Charging Material: “Steel scrap (60% to 80%); Pig iron or sponge iron” and limestone, sand.

❖ **Construction of EAF (Electric arc Furnaces):**

- The furnace consists of a steel shell, lined with suitable refractory materials and is mounted on the tilting mechanism. The shell thickness is around 0.005 times the shell diameter.
- Three sections in Furnace:
  - The **shell,** which consists of the sidewalls and lower steel 'bowl'
  - The **hearth**, which consists of the refractory that contains metal and slag
  - The **roof**, which may be refractory-lined or water-cooled, and can be shaped as a section of a sphere. The roof also supports the refractory delta in its center, through which one or more graphite electrodes enter. The schematic diagram is as shown in figure 6.

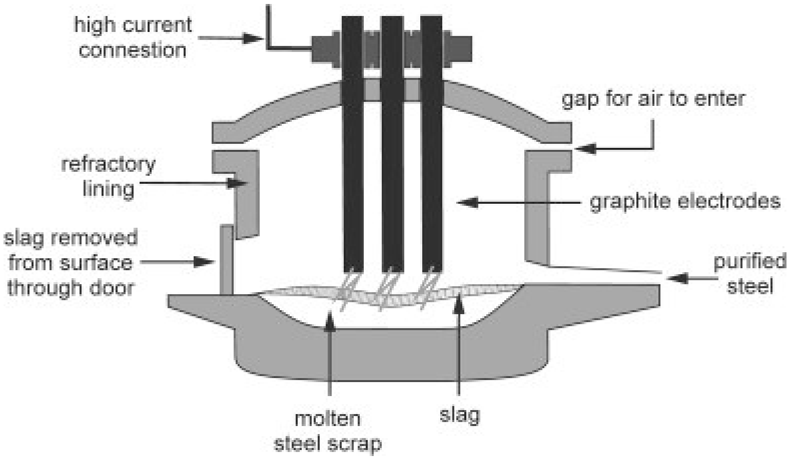


Fig.6. Construction of Electric Arc Furnace

❖ HEAT ENERGY SOURCE OF ELECTRIC ARC FURNACE:

- An electric arc is formed between the electrode and the metallic charge and charge is heated from the arc radiation.
- Two type of Electric arc furnace
    - **Direct Arc Type:** In this type the arc establishes between electrode and the material to be melt.
    - **Indirect Arc Type:** In this the arc is established between electrodes after attaining the enough temperature the electrodes will be dropped down in to material. Material absorbs heat from electrodes and melts.

❖ ADVANTAGES:

- The use of EAFs allows steel to be made from a 100% scrap metal feedstock, commonly known as 'cold ferrous feed' to emphasize the fact that for an EAF, scrap is a regulated feed material.
- The primary benefit of this is the large reduction in specific energy (energy per unit weight) required to produce the steel.
- Another benefit is flexibility: while blast furnaces cannot vary their production by much and are never stopped, EAFs can be

rapidly started and stopped, allowing the steel mill to vary production according to demand.

- Although steelmaking arc furnaces generally use scraps steel as their primary feedstock, if hot metal from a blast furnace or direct-reduced iron is available economically, these can also be used as furnace feed.

IV. OPEN HEARTH FURNACE:

- One difficulty in the manufacture of steel is its high melting point, about 1370° C (about 2500° F), which prevents the use of ordinary fuels and furnaces.
- To overcome this difficulty the open-hearth furnace was developed; this furnace can be operated at a high temperature by regenerative preheating of the fuel gas and air used for combustion in the furnace.

❖ Working principle:

- Under this principle, the direction flow of gases used in heating a furnace is periodically reversed, and the heat left by out-going gases is trapped and used to preheat incoming fuel gases.
- In regenerative preheating, the exhaust gases from the furnace are drawn through one of a series of chambers containing a mass of brickwork and give up most of their heat to the bricks. Then the flow through the furnace is reversed and the fuel and air pass through the heated chambers and are warmed by the bricks. Through this method open-hearth furnaces can reach temperatures as high as 1650°C.
- The name open-hearth probably came from the fact that the steel, while melted on hearth under a roof accessible through furnace doors for visual inspection and sampling.

❖ Construction of open hearth furnace:

- The open-hearth Furnace consists of essentially of a hearth in the shape of large, elongated basin which can hold 60 to 500 tons of steel according to its size.
- In the acid O.H process the working hearth is made of silica sand sintered into place and in the basic O.H process the hearth is made of mixture of calcined magnetite or dolomite and basic slag.
- Along one side is a row of charging doors, whilst on the other side, which contains the tap hole, is the casting pit. The schematic representation of open hearth is as shown in figure 7.

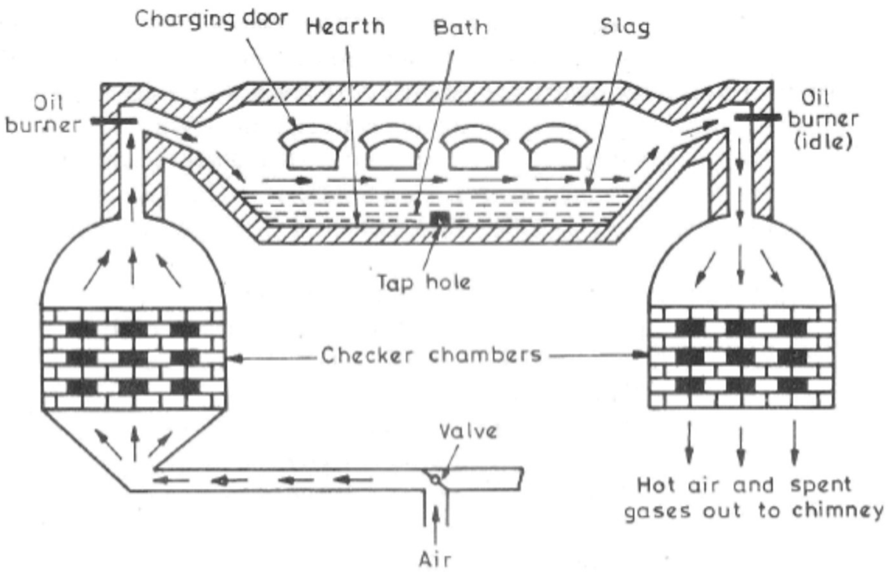


Fig.7: Open hearth furnace

- At each end is a pair of ports (or inlets) for fuel gas and air respectively.
- The gas and air are preheated before their combustion in chambers filled with firebrick laid in checker-board fashion and called checkers.
- Above each end of the hearth is a burner to burn the gaseous fuel; gas and air unite at the burners and burnt forth in along flam that plays over the surface of the metal in the hearth, supplying terrific heat.

➢ **URLs/Hyperlinks for further study:**

- https://onlinecourses.nptel.ac.in/noc18_mm09/preview
- https://nptel.ac.in/courses/113104010/26
- https://www.coursera.org/lecture/ferrous-technology-1/ironmaking-process-9TfCu
- http://www.madehow.com/Volume-2/Iron.html
- https://www.steelconstruction.info/Steel_manufacture

ENGINEERING METALLURGY

UNIT – II

SOLIDIFICATION OF PURE METALS AND ALLOYS

Syllabus: Mechanism of solidification, Nucleation-Homogeneous and Heterogenous Nucleation-Growth -Single crystal -Polycrystalline Materials, crystal growth-Planar growth – dendritic growth – Solidification time - Cooling curves - Non-crystalline solids- Glass Transition Temperature. Crystal Defects: One, Two and Three-dimensional defects.

Solid solutions: Hume Rothary rule substitutional, and interstitial solid solutions, intermediate phases

Solidification Mechanism:-

- Solidification is basically phase transformation from liquid phase to solid phase. The progress of a phase transformation takes place in two stages: **nucleation** and grain growth (Dendritic structure) as shown in Fig-1

- Nucleation involves the appearance of very small particles, or nuclei of the new phase (often consisting of only a few hundred atoms), which are capable of growing.

- During the growth stage these nuclei increase in size, which results in the disappearance of some (or all) of the parent phase.

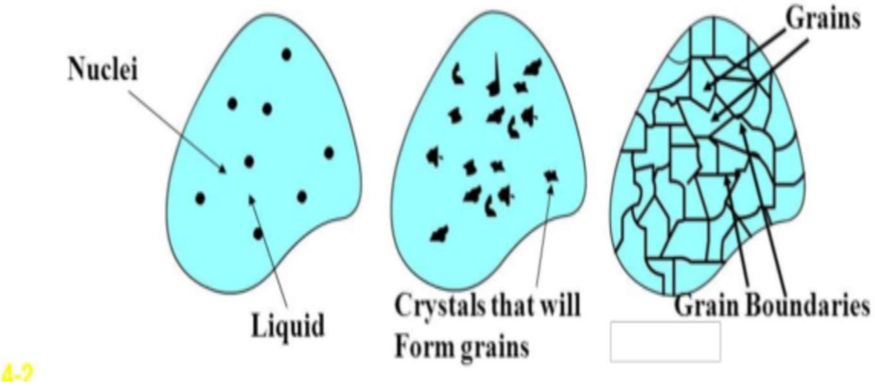


Fig 1: - Solidification mechanism(nucleation, grain growth and formation of grain boundaries)

Nucleation:

- There are two types of nucleation: *homogeneous* and *heterogeneous*.
- The distinction between them is made according to the site at which nucleating events occur.

- For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase.
- whereas for the heterogeneous type, nuclei form preferentially at structural in homogeneities, such as container surfaces, insoluble impurities, grain boundaries, dislocations, and so on.

Homogeneous Nucleation

- Nucleation without preferential nucleation sites is homogeneous nucleation. Homogeneous nucleation occurs spontaneously and randomly, but it requires Superheating or super cooling of the medium.

Heterogeneous nucleation

- Heterogeneous nucleation forms at preferential sites such as phase boundaries, surfaces (of container, bottles, etc.) or impurities like dust. At such preferential sites, the effective surface energy is lower, thus diminishes the free energy barrier and facilitating nucleation.

- Heterogeneous nucleation occurs much more often than homogeneous nucleation.

Solidification of Pure Metals & Alloys: The solidification of pure metal and alloy can be explained by cooling curves as shown in Fig2:

- Pure metal solidifies at constant temperature.
- Alloy solidifies at a temperature range.

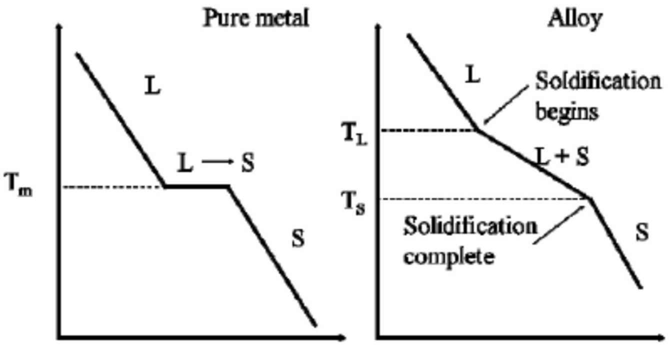


Fig 2: - Colling curves of Pure metal & Alloy

Single crystal: A single crystal or monocrystalline solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries.

Ex: Whiskers

Polycrystal: **Polycrystalline** or multi crystalline **materials**, or polycrystals are solids that are composed of many crystallites of varying size and orientation.

Ex: Most inorganic solids are **polycrystalline**, including all common metals, many ceramics, rocks and ice.

Amorphous: An amorphous material does not have a definite geometric or crystalline shape. An amorphous solid is any noncrystalline solid in which the atoms and molecules are not organized in a definite lattice pattern.

Ex: Glass, plastic, and gel.

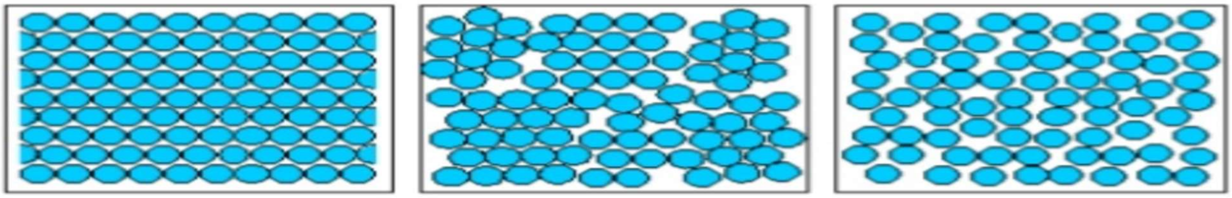
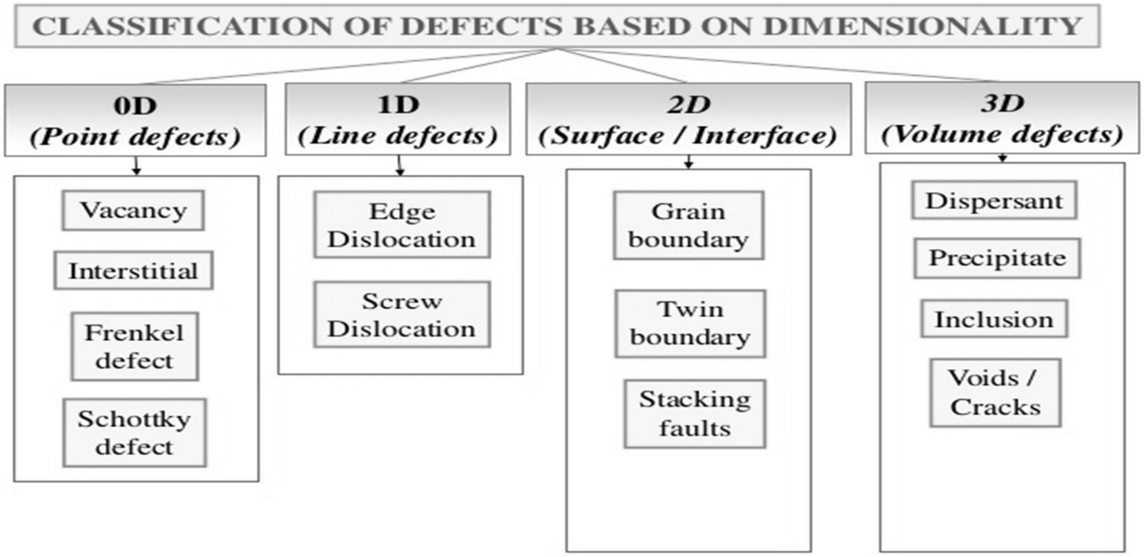


Fig 3: (a) Single crystal (b) Poly crystal (c) Amorphous

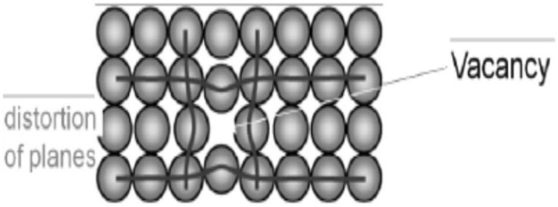
Defects in Solids:

- 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.
- Crystal imperfections can be classified on the basis of their dimension as

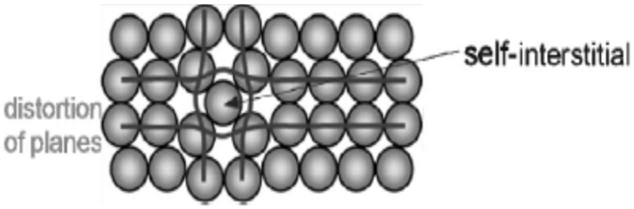


Point Defects in Metals: It is a zero dimension defect, associated with one or two atomic positions.

(a) 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 possible to create such a material that is free of these defects, vacant atomic sites in a structure.

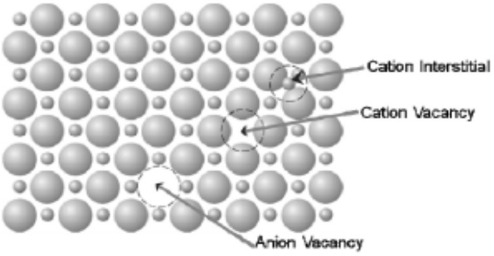


(b) Self-Interstitials- when an atom occupies an interstitial site where no atom would ordinarily appear, causing an interstitialcy.

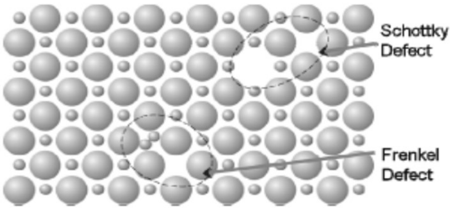


- Interstitials exist for cations**,** interstitials are not normally observed for anions because anions are large relative to the interstitial sites.

(c) Frenkel Defect: To maintain the charge neutrality, a action 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.



d) Schottky Defect: A cation vacancy–anion vacancy pair known as a **Schottky defect.** To maintain the charge neutrality, remove one 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 the regions surrounding the impurity atom.
- All these factors tend to increase the potential energy of the crystal called ***‘enthalpy’***.
- The work done for the creation of such a point defect is called the ‘***enthalpy of formation***’ of the point imperfection.

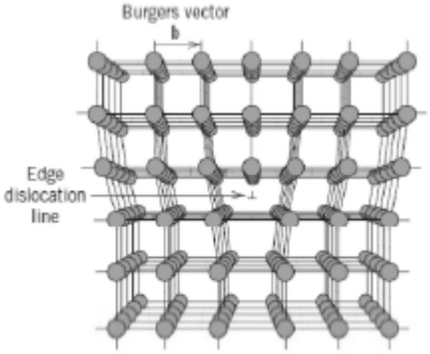
<u>Line Imperfections:</u> A *dislocation* is a linear or one-dimensional defect around which some of the atoms are misaligned.

- 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,

(a) Edge dislocation

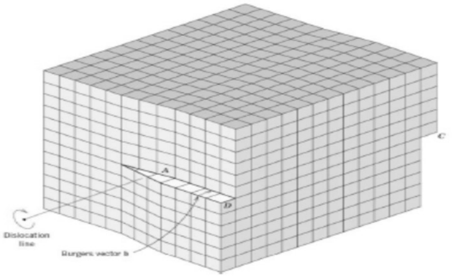
- It is a linear defect that centers around the line that is defined along the end of the extra half-plane of atoms.
- The distorted configuration extends all along the edge into the crystal.
- Thus as the region of maximum distortion is centered around the edge of the incomplete plane, this distortion represents a line imperfection and is called an edge dislocation.



(b) Screw dislocation:-

- In this dislocation, the atoms are displaced in two separate planes perpendicular toe ach 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.

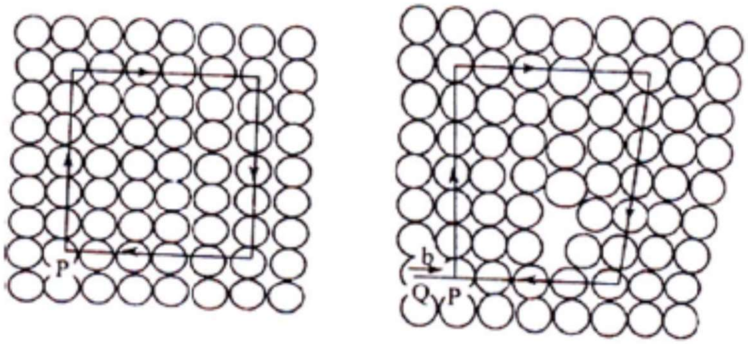


(c) Mixed dislocations –

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

Burgers vector

- The magnitude and direction of the lattice distortion associated with a dislocation is expressed in 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 in each direction around the dislocation.



Surface imperfections

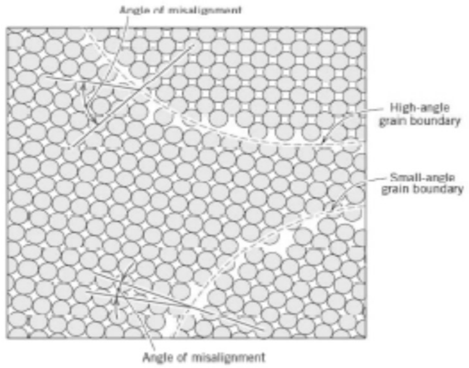
- Surface imperfections arise from a change in the stacking of atomic planes on or across a boundary.
- The change may be one of the orientations or of the stacking sequence of atomic planes.
- In geometric concept, surface imperfections are two- dimensional. They are of two types : external and internal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

(a) 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).

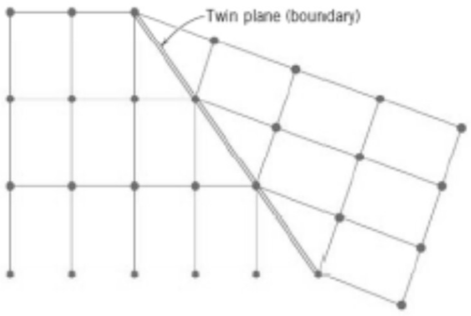
(b) Grain Boundaries

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



(c) 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 properties:

- 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.

Constitution of Alloys

Phase:

- Anything which is homogenous and physically distinct.
- It can also be defined as anything which is physically distinct, chemically homogeneous, and mechanically separable.
- Any structure which is visible as physically distinct under microscope is called phase.
- For pure elements phase means the states of the materials:

  Solid state –solid phase Liquid state –liquid phase Gaseous state-gaseous phase.
- In solid states three types of phases are possible to form: Pure Metal, Compound and Solid Solution

Pure Metal:

- Sharp melting and freezing point under equilibrium condition.
- Cooling curve (Temp vs Time) of a pure metal shows a horizontal line at its melting or freezing point.

Alloy:

- It a combination of two or more elements from which at least one is metal, the substance formed will must showing properties of metals.
- Alloys are made by mixing the constituents in liquid state. Here one will be the host metal and other is alloying elements.

  Example of alloys: plain carbon steels, alloy steels etc.
- Classification of alloy on basis of no of elements present:

  Binary alloy system-990 system possible

  Ternary alloy system-14000 system possible
- Alloys can also classify as

  1. Homogeneous alloy (consist of single phase)
  2. Heterogeneous alloy or mixture (consists of multiple or mixture of phases)

Alloy system	
Homogeneous (Single phase)	Heterogeneous alloy or mixture
1-solid solution Solid solution are two types : **a-interstitial solid solution** **b-substitution solid solution** i-Order solid solution (form a regular pattern of arrangements) ii-Disorder solid solution (ex- nikel and copper form monel alloy)	Any combination of solid phases; may be combination of Pure metals , solid solution, intermediate alloy
2-intermediate alloy phase (compound)	

Solid solution:

- It can be defined as a solution in solid state, which consists of two kinds of atoms combined in one type of space lattice.

  Example: Austenite, ferrite, delta iron, martensite
- Solution may be solid, liquid or gaseous; Example – sugar or salt in water.
- Solution may consist of two parts one is major part called solvent and minor called solute.
- On the basis of dissolution capacity or amount of solute present in solution there possible condition of solution are there:
  1- Unsaturated 2- Saturated 3- Supersaturated.
- Solubility of solute is a function of temperature with pressure constant.
- Solid solution is of two types: Substitutional and Interstitial as shown in Fig 4

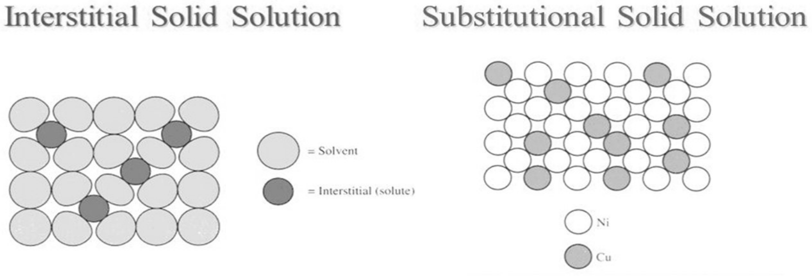


Fig 4 : Types of Solid Solution

Substitutional Solid Solution:

- In this type of solution, the atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent.

Several factors are now known, largely through the work of *Hume-Rothery*, that control the range of solubility in alloy systems

Empirical rules for the formation of substitutional solid solution (Hume-Rothery's Rule)

- **Crystal structure factor:** For complete solid solubility, the two elements should have the same type of crystal structure i.e., both elements should have either F.C.C. or B.C.C. or H.C.P. structure.

- **Relative size factor:** As the size (atomic radii) difference between two elements increases, the solid solubility becomes more restricted. For extensive solid solubility the difference in atomic radii of two elements should be less than about 15 percent. If the relative size factor is more than 15 percent, solid solubility is limited. For example, both silver and lead have F.C.C. structure and the relative size factor is about 20 percent. Therefore, the solubility of lead in solid silver is about 1.5 percent and the solubility of silver in solid lead is about 0.1 percent. Copper and nickel are completely soluble in each other in all proportions. They have the same type of crystal structure (F.C.C.) and differ in atomic radii by about 2 percent.

- **Chemical affinity factor:** Solid solubility is favored when the two metals have lesser chemical affinity. If the chemical affinity of the two metals is greater than greater is the tendency towards compound formation. Generally, if the two metals are separated in the periodic table widely then they possess greater chemical affinity and are very likely to form some type of compound instead of solid solution.

- **Relative valence factor**: It is found that a metal of lower valence tends to dissolve more of a metal of higher valence than vice versa. For example, in aluminum-nickel alloy system, nickel (lower valance) dissolves 5 percent aluminum but aluminum (higher valence) dissolves only 0.04 percent nickel.

Interstitial Solid Solution:

- The second species added goes into the voids of the parent lattice
  E.g. Octahedral and tetrahedral voids in CCP, HCP (& BCC) crystals
  E.g. of solvents: Fe, Mo, Cr etc.
  E.g. of solute: C ($r = 0.77$ Å), N ($r = 0.71$ Å), O ($r = 0.66$ Å), H ($r = 0.46$ Å)
- If the solute atom has a diameter < 0.59 then extensive solubility is expected *(may or may not happen!)*
- Solubility for interstitial atoms is more in transition elements (Fe, Ti, V, Zr, Ni, W, U, Mn, Cr) → due to electronic structure *(incomplete inner shell)*
- C is especially insoluble in most non-transition elements

Compound or Intermediate Alloy Phase:

- Combination of two or more atoms in a definite proportion.
- Combination of positive and negative valence elements.
- After forming a compound the elements lose their individual identity and properties.
- Some compound behaves like pure metals having a definite melting point with narrow limits of temperature. So cooling curve for a compound is similar to that of a pure metal. It is referred to as a congruent melting phase.
- Chemical composition of intermediate alloy phase is intermediate between the two pure metals and generally has crystal structure different from those of pure metals.

Intermetallic compounds

- If two elements have high difference in electronegativity, they tend to from a system called intermetallic compound.
- Intermetallic compounds like MgSe, PbSe, Mg2Si, Cu2S are cubic whereas NiAs, MnSe, CuSn are hexagonal.

Electron or Hume Rothery phases

- These compounds have wide range of solubility and occur at certain values of valence electrons to atom ratio such as 3:2
- (CuZn), 21:13 (Cu5Zn8), 7:4 (CuZn3).

- **URLs/Hyperlinks for further study:**

  https://nptel.ac.in/courses/113106032/5

  https://nptel.ac.in/courses/113106032/6

  https://nptel.ac.in/courses/113106032/8

ENGINEERING METALLURGY

UNIT – III

PHASE DIAGRAMS

SYLLABUS:

Phase Diagrams: Construction of equilibrium diagrams involving complete and partial solubility, Gibbs phase rule, lever rule. Different types invariant reactions – Eutectic, Eutectoid, Peritectic, Peritectectoid reactions etc.

Iron carbon equilibrium diagram: Description of phases- steels, cast iron, Different reactions of the Iron-Iron Carbide equilibrium system, Alloy groups -Properties, Composition and uses (Wrought iron, Grey cast iron, malleable iron, SG iron and steels)

PHASE DIAGRAMS

- Equilibrium diagrams can also be called as Phase Diagrams, Constitutional diagrams.
- Phase is physically distinctive form but chemically same substance.
  Example:
  - Water as solid → ice } Two distinct physical forms but chemically same.
  - Water as gas → vapour }
- Phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature, pressure and composition.

  (or)
- A phase diagram is a graphical representation to show the conditions at which distinct phases of a material can occur at equilibrium.
- With pressure assumed to be constant, the equilibrium diagram indicates the structural changes due to variations of temperature and composition.
- Interpretations from phase diagram: Concentration of solution, Fractions and development of microstructure under equilibrium.
- These diagrams do not indicate the dynamics when one phase transforms into another.

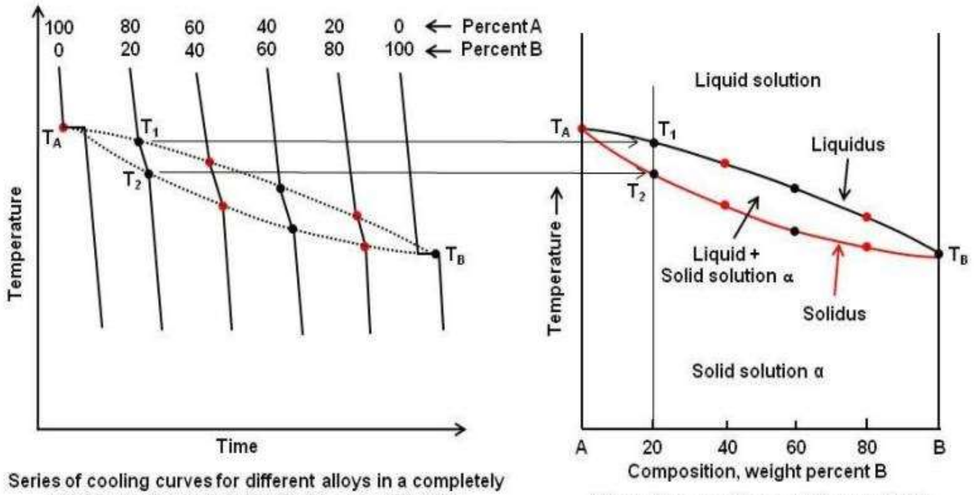
- **Classification of phase diagram:**

  1. Isomorphous system 2. Eutectic system
  3. Eutectoid system 4. Peritectic system 5. Peritectoid system

- **The classification of phase diagrams based on the solubility of solute and solvent :**
  - ✓ **Components completely soluble in liquid state:**
    1. Complete soluble in liquid and solid states**.** **[Isomorphous System]**
    2. Complete soluble in liquid and insoluble in solid. **[Eutectic System]**
    3. Complete soluble in liquid and partial soluble in solid. **[Partial Eutectic System]**
    4. Congruent melting intermediate alloy phases.
    5. Incongruent melting alloy system. **[Peritectic System]**
  - ✓ **Components partly soluble in liquid state**. **[Monotectic System]**
  - ✓ **Components insoluble in both liquid and solid state.**
  - ✓ **Other transformations in solid state:**
    1. Eutectoid system
    2. Peritectoid system
    3. Order-disorder
    4. Allotropic change

- **Construction of Equilibrium diagrams:** Equilibrium diagrams are constructed experimentally by various methods as: Thermal analysis, Metallographic methods, X-ray diffraction and Electrical resistivity e.t.c.

  Thermal Analysis:
    - It uses the concept of cooling curves plotted at constant composition.
    - Cooling curve will show the change in slope when a phase change occurs.



Series of cooling curves for different alloys in a completely soluble system both in the liquid and solid states

Phase diagram of two metals completely soluble in the liquid and solid states

Construction of Phase Diagram from Series of Cooling Curves

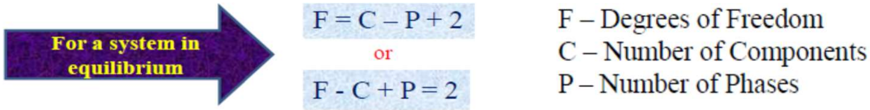
- **Metallographic Methods:**
  - This method consists in heating samples of an alloy to different temperatures, waiting for equilibrium to be established, and then quickly cooling to retain their high temperature structure.
  - The samples are then examined microscopically.
  - This method is difficult 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:**
  - 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 enunciated by J.W. Gibbs relating number of phases *P*, number of components *C*, and number of degrees of freedom *F* has a simple form:
  - The phase rule connects the Degrees of Freedom, the number of components in a system and the number of 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.

Degrees of Freedom: The degree of freedom, F, is 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.

$$\boxed{P + F = C + n}$$



For a system in equilibrium

$$F = C - P + 2$$

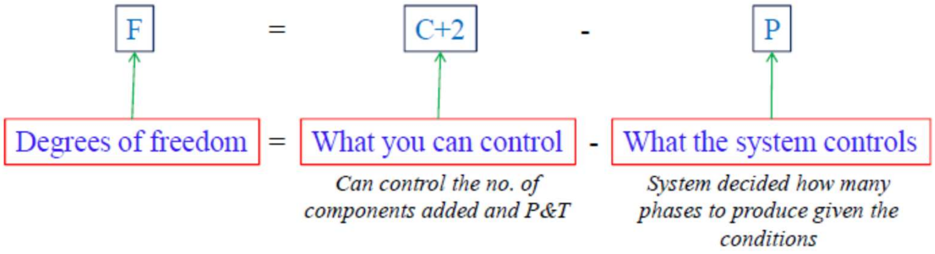
or

$$F - C + P = 2$$

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

n = number of external factors = 2 (temperature and pressure)

- A way of understanding the Gibbs Phase Rule : P + F = C + 2
  - The degrees of freedom can be thought of as the difference between *what you (can) control and what the system controls*



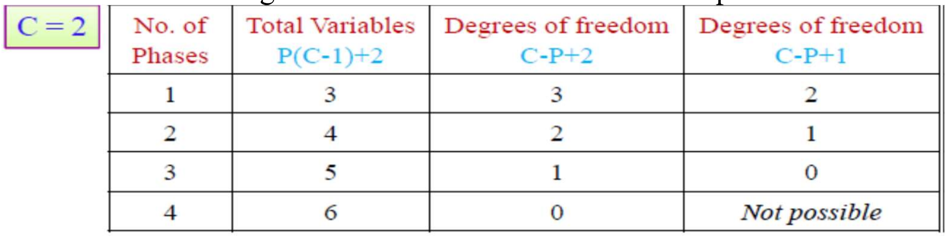
$$F = C+2 - P$$

Degrees of freedom = What you can control - What the system controls

Can control the no. of components added and P&T

System decided how many phases to produce given the conditions

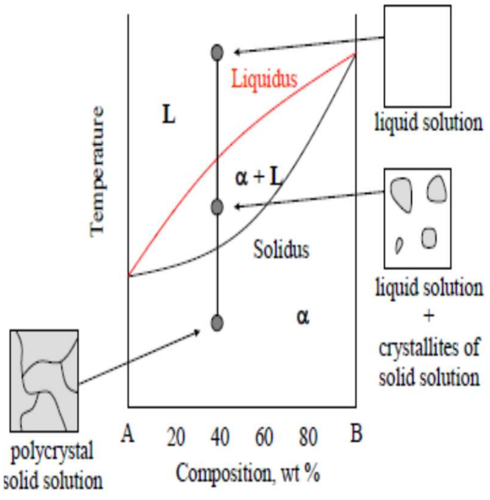
- Variation of the number of degrees of freedom with number of components and number of phases



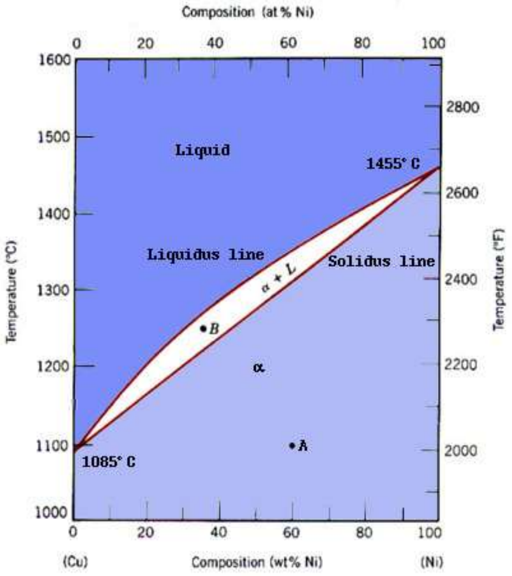
C = 2

No. of Phases	Total Variables P(C-1)+2	Degrees of freedom C-P+2	Degrees of freedom C-P+1
1	3	3	2
2	4	2	1
3	5	1	0
4	6	0	*Not possible*

- **<u>Two metals completely soluble in liquid and solid state</u>**: [Isomorphous System]
  - Solid phase formed should be substitutional solid solution.
  - Two metals will have same crystal structure and differ in atomic radii by less than 8%.
  - Example: Cu-Ni alloy.
  - The complete solubility occurs because both Cu and Ni have the same crystal structure (FCC), near the same radii, electro negativity and valence.
  - The liquidus line separates the liquid phase from solid or solid + liquid phases. That is, the solution is liquid above that line.
  - The solidus line is that below which the solution is completely solid (does not contain a liquid phase.)
  - In one-component system melting occurs at a well-defined melting temperature.
  - In multi-component systems melting occurs over the range of temperatures, between the solidus and liquidus lines.
  - Solid and liquid phases are at equilibrium with each other in this temperature range.



(a) Phase change over a temperature range



(b) Cu-Ni Binary phase diagram

- **Interpretation of a binary phase diagrams:**

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

1) The phases those are present.
2) Compositions of the phases.
3) The relative fractions of the phases.

⇨ Finding the composition in a two phase region:

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

Tie line and Lever rule:

Chemical Composition of Phases *Tie Line Rule*

- 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.

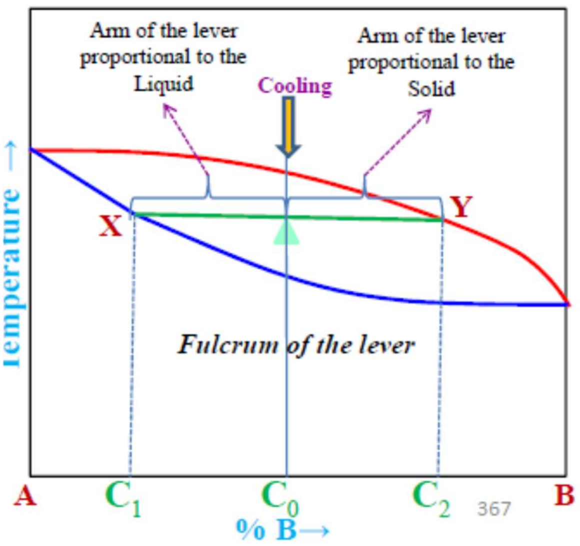
Relative Amounts of Each Phase *Lever Rule*

- To determine the relative amounts of the two phases in equilibrium at any specified temperature in a two phase 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 to the 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.
- 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.

- ✓ The portion of the horizontal line in the two phase region is akin to 'lever' with the fulcrum at the nominal composition (**C0**)
- ✓ 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)

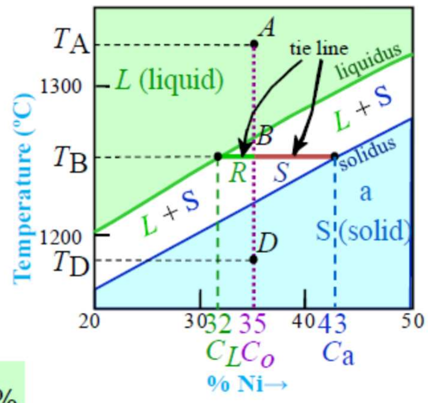
W_L= 0, W solid= 100 wt%

At T_B: Both S and L

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

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

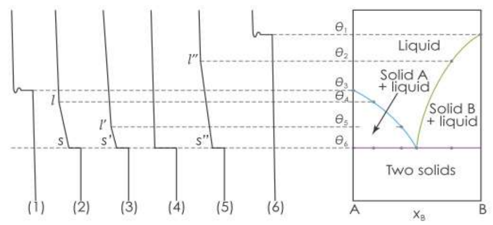
Cu – Ni System



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

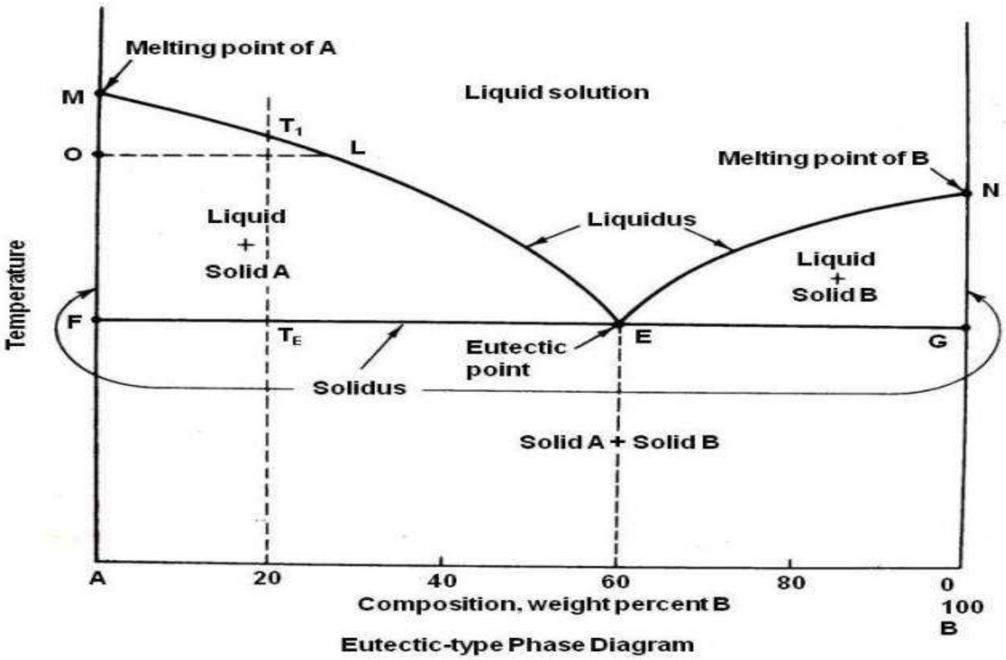
- ➢ **Two metals completely soluble in liquid and insoluble in solid:** [Eutectic System]

- ➢ No two metals are completely insoluble in each other, but the solubility is restricted.
- ➢ **Raoults's law:** It states that freezing point of a pure matter is lowered by adding another matter provided the latter is soluble in liquid and insoluble in solid and the amount of lowering of the freezing point is proportional to the molecular weight of the solute.
- ➢ The experimental cooling curves shows a different kind of behavior as shown in the figure.



Use of thermal analysis. Demonstration of how thermal analysis can be used to determine a phase diagram. Cooling curves (1) and (6) represent behavior for pure A and B, respectively.

- The actual phase diagram now constructed by transfering the breaks on the cooling curves to plot temperature Vs composition. the following digram shows the actual eutectic phase diagram.



- From the above diagram we can note the following points:

  M, N : Melting points of Metals A & B respectively.
  MEN: Liquidus line.
  MFGN: Solidus line.
  E : Eutectic point.

- The phase diagram consists of four regions, they are:
  1. Above liquidus line : Single phase homogenous liquid solution, two metals are soluble in liquid.
  2. Below liquidus line : The remaining 3 are two phase areas. (MFE,EGN and below FGE line).

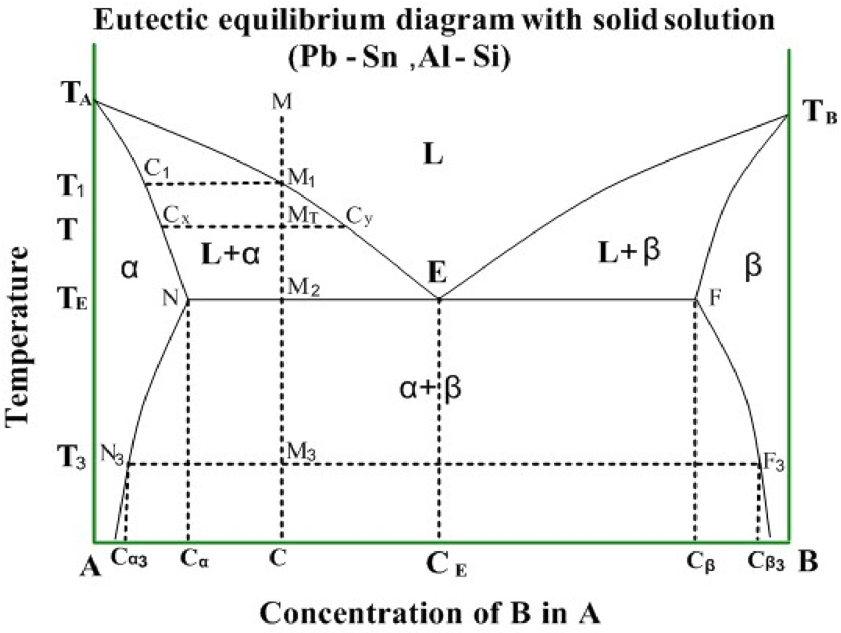
     MFE : Liquid + Solid A
     EGN : Liquid + Solid B
     Below FGE: Solid A + Solid B

- **<u>Eutectic Point: (E)</u>** The point in a phase diagram indicating the chemical composition and temperature corresponding to the lowest melting point of a mixture of components.
  1. Temperature at that point is called Eutectic Temperature ($\mathbf{T_E}$).
  2. Composition at that point is called Eutectic Composition or Eutectic Mixture.
  3. The reaction at that point showing the phase change is know as Eutectic recation and it is given as :

$$\textbf{Liquid} \Rightarrow \textbf{Solid A + Solid B}\text{(eutectic mixture)}$$

- Alloys left to the eutectic point are ***hypoeutectic alloys*** and those to the right are ***hypereutectic alloys.***

- **<u>Two metals completely soluble in liquid but partly soluble in solid state:</u>** [Partial Eutectic system]
  - Most metals show some solubility for each other in solid state henece this is the most common type.
  - Partial eutectic system is as shown below:



Eutectic equilibrium diagram with solid solution (Pb - Sn ,Al - Si)

- From above figure:
  - **T_A & T_B : Melting point of two pure metals.**
  - **T_A E T_B : Liquidus line.**
  - **T_A FEG T_B : Solidus line.**
- Alloys in this system never solidify crystals of pure A or pure B but always forms a solid solution or mixture of solid solutions.

- The single phase α & β solid solutions are formed ,which are called as ***terminal solid solutions.***
- FH & GJ are called ***solvus lines,*** which indicated the maximum solubility (saturated solution) of B in A and A in B.
- Point E is eutectic point ,at this point the eutectic reaction that takes place is :

$$\textbf{Liquid} \Rightarrow \alpha + \beta$$

- In above diagram two different eutectic mixtures are formed and the corresponding reactions are shown as:

$$\textbf{Liquid} \Rightarrow \alpha + \textbf{AmBn}$$

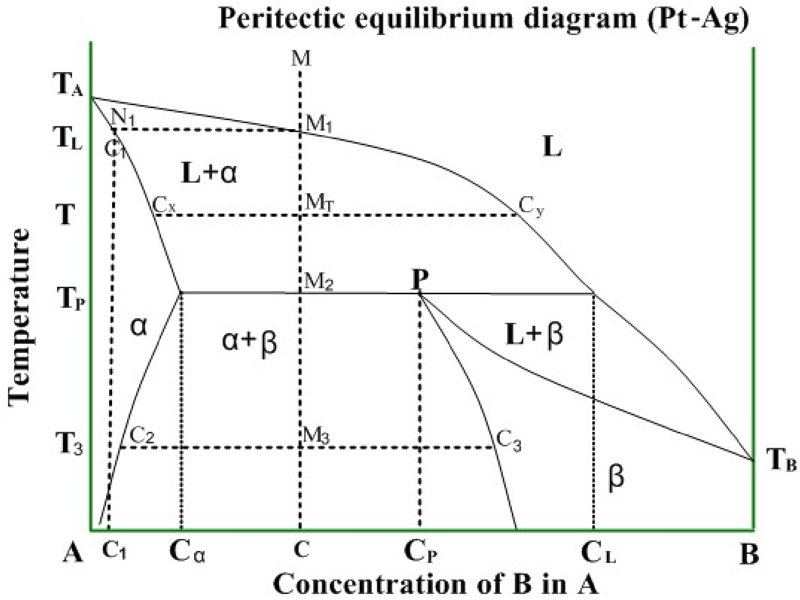
$$\textbf{Liquid} \Rightarrow \textbf{AmBn} + \beta$$

- **The Peritectic reaction:**

- In peritectic reaction a liquid and solid reacts isothermally to form a new solid on cooling. The reaction is expressed as

Liquid + Solid ⇨ New Solid(AmBn)

- The phase diagram showing peritectic reaction is as below:


Peritectic equilibrium diagram (Pt-Ag)

- At Point 'P' the peritectic reaction takes place.
- Peritectic reaction is just the reverse of eutectic reaction.

- **Eutectoid reaction:**
  - This is a common recation in solid state.
  - It is similar to eutectic recation but does not involves liquid.
  - In this reaction solid phase is transformed into two new solid phases.
  - The eutectic reaction is written as:

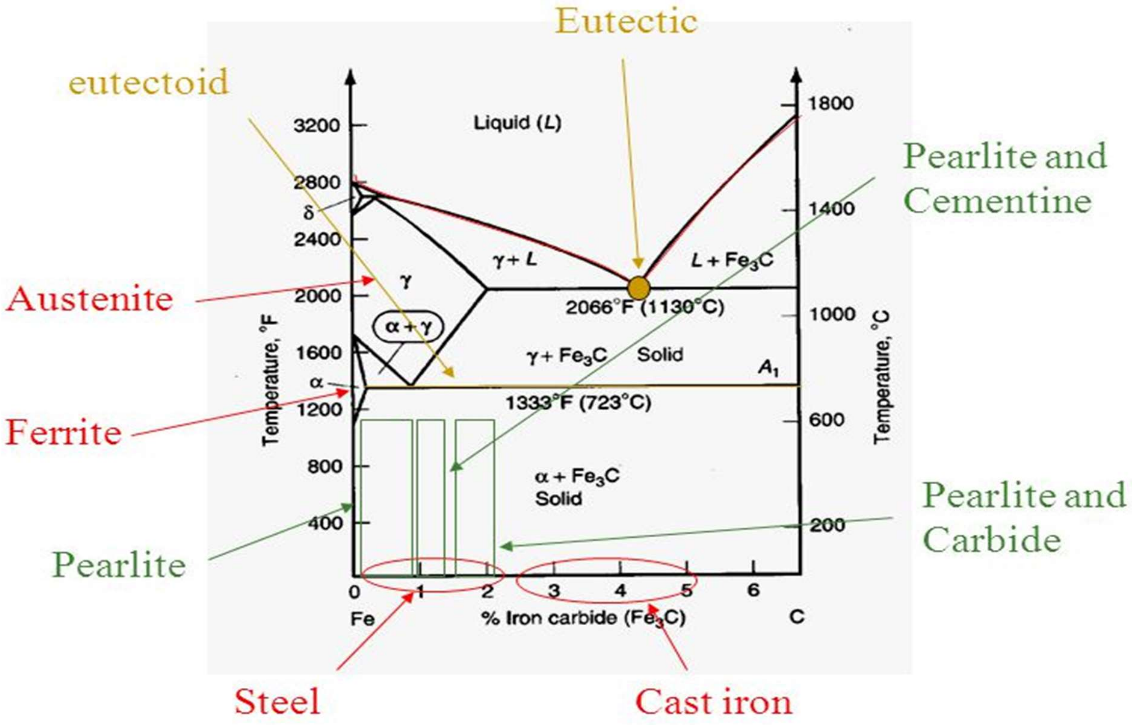
Solid1 ⇨ Solid2 + Solid3(Eutectoid mixture)

- ***Peritectoid reaction:**
  - This is also a common reaction in solid state.
  - It is written as:

Solid1 + Solid2 ⇨ Solid3

Iron carbon equilibrium diagram: (Fe-Fe_3C)

- A study of iron-carbon system is useful and important in many respects. This is because
    (1) steels constitute greatest amount of metallic materials used by man
    (2) solid state transformations that occur in steels are varied and interesting.
- These are similar to those occur in many other systems and helps explain the properties. Iron-carbon phase diagram shown in figure is not a complete diagram. Part of the diagram after 6.67 wt% C is ignored as it has little commercial significance.
- The 6.67%C represents the composition where an inter-metallic compound, cementite (Fe3C), with solubility limits forms.
- In addition, phase diagram is not true equilibrium diagram because cementite is not an equilibrium phase. However, in ordinary steels decomposition of cementite into graphite never observed because nucleation of cementite is much easier than that of graphite. Thus, cementite can be treated as an equilibrium phase for practical purposes.



- The Fe-Fe_3C is characterized by five individual phases and four invariant reactions. Five phases that exist in the diagram are: ***α***–ferrite (BCC) Fe-C solid solution, ***γ***-austenite (FCC) Fe-C solid solution, ***δ***-ferrite (BCC) Fe-C solid solution, Fe_3C (iron carbide) *or* cementite - an inter-metallic compound and liquid Fe-C solution. Four invariant reactions that cause transformations in the system are namely eutectoid, eutectic, monotectic and peritectic.

- As depicted by left axes, pure iron upon heating exhibits two allotropic changes.
  One involves ***α***–ferrite of BCC crystal structure transforming to FCC austenite, ***γ***-iron, at 910 °C. At 1400 °C, austenite changes to BCC phase known as ***δ***-ferrite, which finally melts at 1536 °C.

- Based on %C dissolved in it, a Fe-C solution is classified as: *commercial pure irons* with less than 0.008%C; *steels* having %C between 0.008-2.11; while *cast irons* have carbon in the range of 2.11%-6.67%.

- Thus, commercial pure iron is composed of exclusively ***α***–ferrite at room temperature. Most of the steels and cast irons contain both ***α***–ferrite and cementite. However, commercial cast irons are not simple alloys of iron and carbon as they contain large quantities of other elements such as silicon, thus better consider them as ternary alloys.

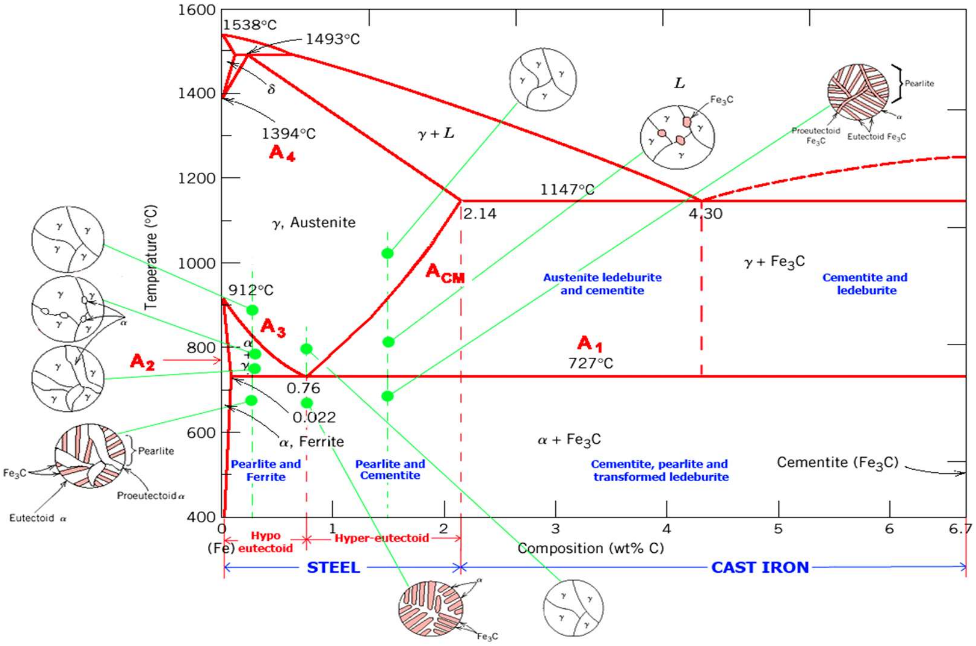
- The presence of Si promotes the formation of graphite instead of cementite. Thus, cast irons may contain carbon in form of both graphite and cementite, while steels will have carbon only in combined from as cementite.

- **Fe-C system constitutes four invariant reactions:**
  - peritectic reaction at 1495 °C and 0.16%C, *δ*-ferrite + *L* ↔ *γ*-iron (austenite)
  - monotectic reaction 1495 °C and 0.51%C, *L* ↔ *L* + *γ*-iron (austenite)
  - eutectic reaction at 1147 °C and 4.3 %C, *L* ↔ *γ*-iron + Fe3C (cementite) [ledeburite]
  - eutectoid reaction at 723 °C and 0.8%C, *γ*-iron ↔ *α*–ferrite + Fe3C (cementite) [pearlite]

Different phases:

- Product phase of eutectic reaction is called ledeburite, while product from eutectoid reaction is called pearlite. During cooling to room temperature, ledeburite transforms into pearlite and cementite. At room temperature, thus after equilibrium cooling, Fe-C diagram consists of either ***α***–ferrite, pearlite and/or cementite.
- Pearlite is actually not a single phase, but a micro-constituent having alternate thin layers of ***α***–ferrite (~88%) and Fe3C, cementite (~12%). Steels with less than 0.8%C (mild steels up to 0.3%C, medium carbon steels with C between 0.3%-0.8% i.e. hypo-eutectoid Fe-C alloys) i.e. consists pro-eutectoid ***α***–ferrite in addition to pearlite, while steels with carbon higher than 0.8% (high-carbon steels i.e. hyper-eutectoid Fe-C alloys) consists of pearlite and pro-eutectoid cementite.
- Phase transformations involving austenite i.e. processes those involve eutectoid reaction are of great importance in heat treatment of steels.

- **The following phase diagram gives complete details of different phases:**



- **URLs/Hyperlinks for further study:**
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ENGINEERING METALLURGY

UNIT-IV

HEATTREATMENT OF STEELS

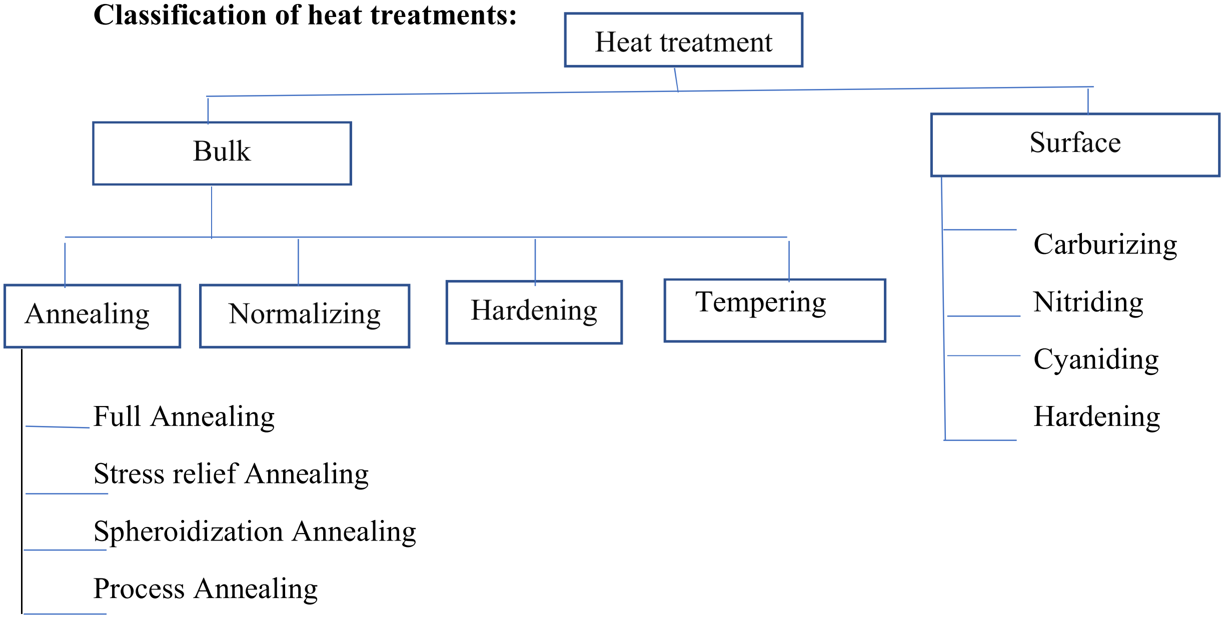
Syllabus: - TTT curves, continuous cooling curves, heat treatment processes – annealing, normalizing, hardening, tempering, martempering, austempering, hardenability, surface hardening methods - carburizing, cyaniding, nitriding, flame hardening and induction hardening, age hardening.

Definition: Heat treatment is defined as an alternative heating and cooling of the component to attain the desired properties to it.

Heat Treatment of Steel

Heat treatment of steel refers to time- and temperature-controlled processes that relieve residual stresses and/or modifies material properties such as hardness (strength), ductility, and toughness. Other mechanical or chemical operations are sometimes grouped under the heading of heat treatment. The common heat-treating operations are annealing, quenching, tempering, and case hardening.

Classification of heat treatments:



STAGES of HEAT TREATMENT:

- Stage 1 — Heat the metal slowly to ensure a uniform temperature.
- Stage 2 — Soak (hold) the metal at a given temperature for a given time.
- Stage 3 — Cool the metal to room temperature.

Heating Stage: -

- In the heating stage, the primary objective is to heat uniformly, and you attain and maintain uniform temperatures by slow heating. If you heat unevenly, one section can expand faster than another, resulting in a distorted or cracked part.

Soaking Stage:

- In the soaking stage, the objective is to hold the metal to the proper temperature until the desired internal structural changes take place. “Soaking period” is the term you use for the time the metal is held at the proper temperature.
- The chemical analysis of the metal and the mass of the part will determine the appropriate soaking period. (Note: For steel parts with uneven cross sections, the largest section determines the soaking period.)

Cooling Stage:

- In the cooling stage, the objective is self-explanatory, but there are different processes to return a metal to room temperature, depending on the type of metal.
- To cool the metal and attain the desired properties, you may need to place it in direct contact with a cooling medium (a gas, liquid, solid, or a combination), and any cooling rate will depend on the metal itself and the chosen medium.
- Therefore, the choice of a cooling medium has an important influence on the properties desired. Cooling metal rapidly in air, oil, water, brine, or some other medium is called quenching.

ANNEALING

Annealing, the material to be annealed is heated to a temperature that is approximately 50°C above the critical temperature. It is held at this temperature for a time that is enough for the carbon to become dissolved and diffused through the material.

The object being treated is then allowed to cool slowly, usually in the furnace in which it was treated. If the transformation is complete, then it is said to have a full anneal.

Annealing is used to soften a material and make it more ductile, to relieve residual stresses, and to refine the grain structure.

Full Annealing: -

- Full annealing is the process of slowly raising the temperature about 50 ºC (90 ºF) above the Austenitic temperature line A3 or line ACM in the case of Hypoeutectoid steels (steels with < 0.77% Carbon) and 50 ºC (90 ºF) into the Austenite-Cementite region in the case of Hypereutectoid steels (steels with > 0.77% Carbon).
- It is held at this temperature for enough time for all the material to transform into Austenite or Austenite-Cementite as the case may be.
- It is then slowly cooled at the rate of about 20 ºC/hr (36ºF/hr) in a furnace to about 50 ºC (90 ºF) into the Ferrite-Cementite range.
- At this point, it can be cooled in room temperature air with natural convection. The grain structure has coarse Pearlite with ferrite or Cementite (depending on whether hypo or hyper eutectoid). The steel becomes soft and ductile.

Stress relief annealing:

- Stress Relief Anneal is used to reduce residual stresses in large castings, welded parts and cold formed parts. Such parts tend to have stresses due to thermal cycling or work hardening.
- Parts are heated to temperatures of up to 600 - 650 ºC (1112 - 1202 ºF) and held for an extended time (about 1 hour or more) and then slowly cooled in still air.

Spheroidization Annealing:

- Spheroidization is an annealing process used for high carbon steels (Carbon > 0.6%) that will be machined or cold formed subsequently.
- This is done by one of the following ways: Heat the part to a temperature just below the Ferrite-Austenite line, line A1 or below the Austenite-Cementite line, essentially below the 727 ºC (1340 ºF) line. Hold the temperature for a prolonged time and follow by slow cooling.

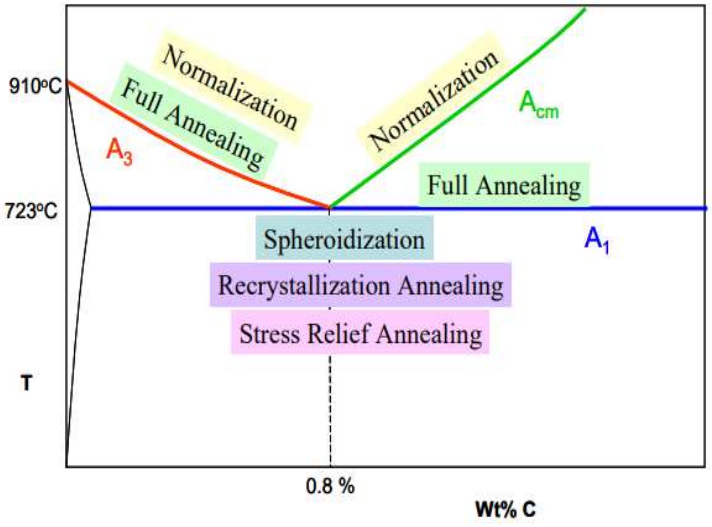
Or

- Cycle multiple times between temperatures slightly above and slightly below the 727 ºC (1340ºF) line, say for example between 700 and 750 ºC (1292 - 1382 ºF), and slow cool. Or For tool and alloy steels heat to 750 to 800 ºC (1382-1472 ºF) and hold for several hours followed by slow cooling.
- All these methods result in a structure in which all the Cementite is in the form of small globules (spheroids) dispersed throughout the ferrite matrix. This structure allows for improved machining in continuous cutting operations such as lathes and screw machines. Spheroidization also improves resistance to abrasion.

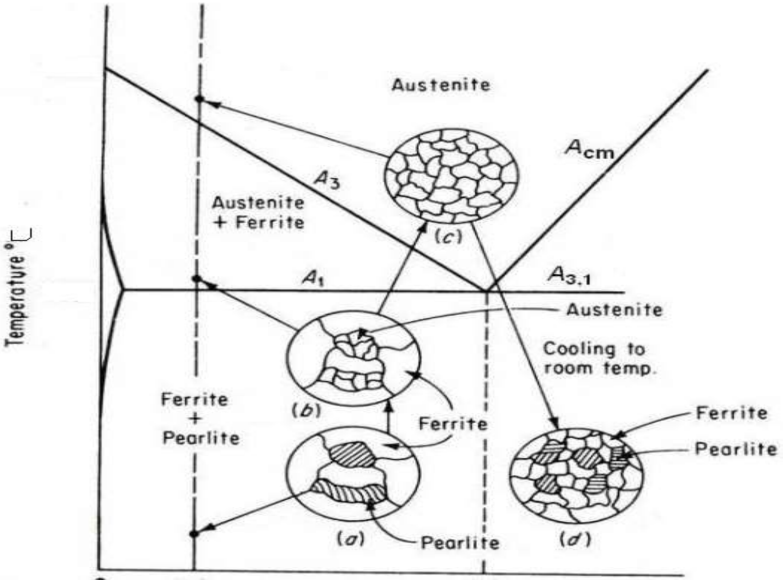
Process Annealing:

- Process Annealing is used to treat work-hardened parts made out of low-Carbon steels (< 0.25%Carbon). This allows the parts to be soft enough to undergo further cold working without fracturing.
- Process annealing is done by raising the temperature to just below the Ferrite Austenite region, line A1on the diagram. This temperature is about 727 ºC (1341 ºF) so heating it to about 700 ºC (1292 ºF) should suffice. This is held long enough to allow recrystallization of the ferrite phase, and then cooled in still air.
- Since the material stays in the same phase throughout the process, the only change that occurs is the size, shape and distribution of the grain structure. This process is cheaper than either full annealing or normalizing since the material is not heated to a very high temperature or cooled in a furnace.

The following diagram shows the general regions of different annealing processes on iron carbide phase diagram.



Annealing of Hypoeutectoid steel: - A coarse-grained 0.20 percent carbon steel (hypoeutectoid steel) can be refined by full annealing as explained below.

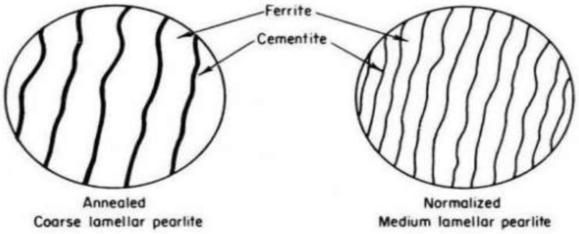


- The microstructure of the coarse grain 0.2 percent carbon steel is shown at (a) in the above figure. When this steel is heated, no change will occur until it crosses lower critical temperature line A1. At that temperature, by eutectoid reaction pearlite areas will transform to small grains of austenite but the original large ferrite grains will remain unchanged as shown at (b) in above figure.
- To refine these large ferrite grains the material shall be further heated. Continued heating between the A1 and A3 lines will transform large ferrite grains to small grains of austenite so that above the A3 line (upper critical temperature line), the entire microstructure will show only small grains of austenite as shown at (c) in above figure.
- Now furnace cooling (very slow cooling) from this state will result in small grains of proeutectoid ferrite and small areas of coarse lamellar pearlite as shown at (d) in above figure. Therefore, the proper annealing temperature for full annealing of hypoeutectoid steels is approximately 50°C above the A3 line.
- Refinement of the grain size of hypereutectoid steel will occur approximately about 50°C above the lower critical temperature (A3,1) line. Heating above this temperature will coarsen the austenitic grains, which, on cooling, will transform to large pearlite areas.
- The microstructure of annealed hypereutectoid steel will consist of coarse lamellar pearlite areas surrounded by a network of a proeutectoid cementite. Because this excess cementite network is brittle and tends to be plane of weakness, full annealing should never be a final heat treatment process for hypereutectoid steels. The presence of a thick and hard grain boundary will also result in poor machinability.

NORMALIZING

- The normalizing of steel is carried out by heating approximately 100°C above the upper critical temperature line (A3 or Acm) followed by cooling in still air to room temperature. The normalizing temperatures range is shown in the figure given earlier for annealing temperature.
- It may be noted that for hypereutectoid steels, it is necessary to heat it above the Acm line to dissolve the cementite network.

- The purpose of normalizing is to produce harder and stronger steel than full annealing, so that for some applications normalizing may be a final heat treatment. Normalizing is also carried out to improve machinability.
- The increase in cooling rate due to air cooling as compared to furnace cooling in case of full annealing affects the transformation of austenite and the resultant microstructure. Since the cooling is not carried out under equilibrium conditions, the iron-iron carbide diagram cannot be used to predict the proportions of proeutectoid ferrite and pearlite (in case of hypoeutectoid steel) or proeutectoid cementite and pearlite (in case of hypereutectoid steel) that will exist at room temperature.
- There is less time for the formation of the proeutectoid constituent; consequently there will be less proeutectoid ferrite in normalized hypoeutectoid steels and less proeutectoid cementite in hypereutectoid steels as compared with annealed ones. For hypereutectoid steels, normalizing will reduce the continuity of the proeutectoid cementite network, and in some cases it may be suppressed entirely. Since it was the presence of the cementite network which reduced the strength of annealed hypereutectoid steels, normalized steels should show an increase in strength.
- Apart from influencing the amount of proeutectoid constituents that will form, the faster cooling rate in normalizing will also affect the temperature of austenite transformation and the fineness of the pearlite. In general, the faster the cooling rate, the lower the temperature of austenite transformation and the finer the pearlite.The difference in spacing of the cementite plates in the pearlite between annealing and normalizing is shown schematically in the figure given below.



HARDENING

In this process, austenite is transformed to martensite because of quenching (rapid cooling) from furnace to room temperature.

- The recommended austenitizing temperature for hypoeutectoid steels is about 50°C above the upper critical temperature line. This is the same as the recommended annealing temperature. For plain-carbon hypereutectoid steel the recommended austenitizing temperature is usually between the Acm and A3,1 lines (about 50° above the A3,1 line, same as the recommended annealing temperature); therefore, undissolved carbides would tend to be present in the microstructure at room temperature.
- The Acm line rises so steeply that an excessively high temperature may be required to dissolve all the proeutectoid cementite in the austenite. This tends to develop undesirable coarse austenite grain size, with danger of cracking on cooling.
- Under slow or moderate cooling rates, the carbon atoms can diffuse out of the austenite structure. The iron atoms then move slightly to become b.c.c. (body-centered cubic). This gamma to alpha transformation takes place by a process of nucleation and growth and is time dependent. With a still further increase in cooling rate, insufficient time is allowed for the carbon to diffuse out of solution, and although some movement of iron

atoms takes place, the structure cannot become b.c.c. while the carbon is trapped in solution. The resultant structure, called martensite is supersaturated solid solution of carbon trapped in a less dense (than b.c.c.) body-centered tetragonal structure. In this structure, two dimensions of the unit cell are equal, but the third is slightly extended because of the trapped carbon. This highly distorted lattice structure is the prime reason for the high hardness of martensite. After drastic cooling (quenching), martensite appears microscopically as a white needle like or acicular structure sometimes described as a pile of straw.

Quenching Medium: -

- **Water:** Quenching can be done by plunging the hot steel in water. The water adjacent to the hot steel vaporizes, and there is no direct contact of the water with the steel. This slows down cooling until the bubbles break and allow water contact with the hot steel. As the water contacts and boils, a great amount of heat is removed from the steel. With good agitation, bubbles can be prevented from sticking to the steel, and thereby prevent soft spots. Water is a good rapid quenching medium, provided good agitation is done. However, water is corrosive with steel, and the rapid cooling can sometimes cause distortion or cracking.
- **Salt Water:** Salt water is a more rapid quench medium than plain water because the bubbles are broken easily and allow for rapid cooling of the part. However, salt water is even more corrosive than plain water, and hence must be rinsed off immediately.
- **Oil:** Oil is used when a slower cooling rate is desired. Since oil has a very high boiling point, the transition from start of Martensite formation to the finish is slow and this reduces the likelihood of cracking. Oil quenching results in fumes, spills, and sometimes a fire hazard.

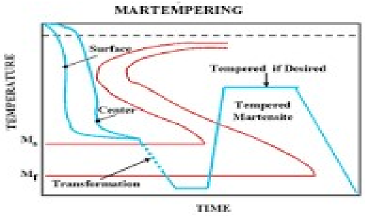
TEMPERING

Steels can be heat treated to high hardness and strength levels. Hardening is carried out because structural components subjected to high operating stress need the high strength of a hardened structure. Similarly, tools such as dies, knives, cutting devices, and forming devices need a hardened structure to resist wear and deformation.

However, the as-quenched hardened steels are too brittle for most applications. Tempering is a heat treatment process that reduces the brittleness of hardened steel without significantly lowering its hardness and strength. In view of this, all hardened steels are tempered before use.

Austempering:- Heat treatment that is applied to ferrous metals, most notably steel and ductile iron. In steel it produces a bainite microstructure whereas in cast irons it produces a structure of acicular ferrite and high carbon, stabilized austenite known as ausferrite.

Martempering :-It is used to describe an interrupted quench from the austenitizing temperature of certain alloy, cast, tool, and stainless steels. The purpose is to delay the cooling just above the martensitic transformation for a length of time to equalize the temperature throughout the piece.



TTT Diagrams

- TTT diagram stands for “time-temperature-transformation” diagram. It is also called isothermal transformation diagram.
- These are also called as S-Curves.

TTT diagram gives information about: -

i) Nature of transformation-isothermal or athermal (time independent) or mixed

ii) Type of transformation-reconstructive, or displacive.

iii) Rate of transformation

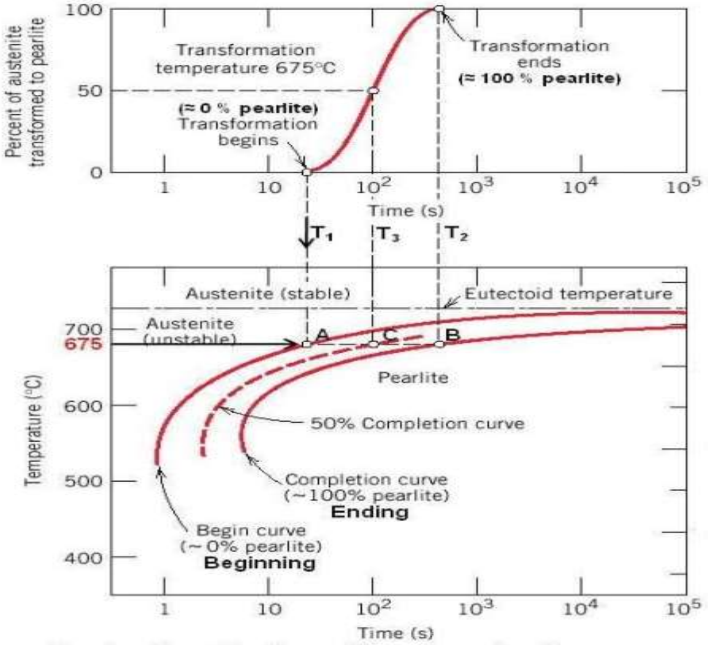
iv) Stability of phases under isothermal transformation conditions

v) Temperature or time required to start or finish transformation

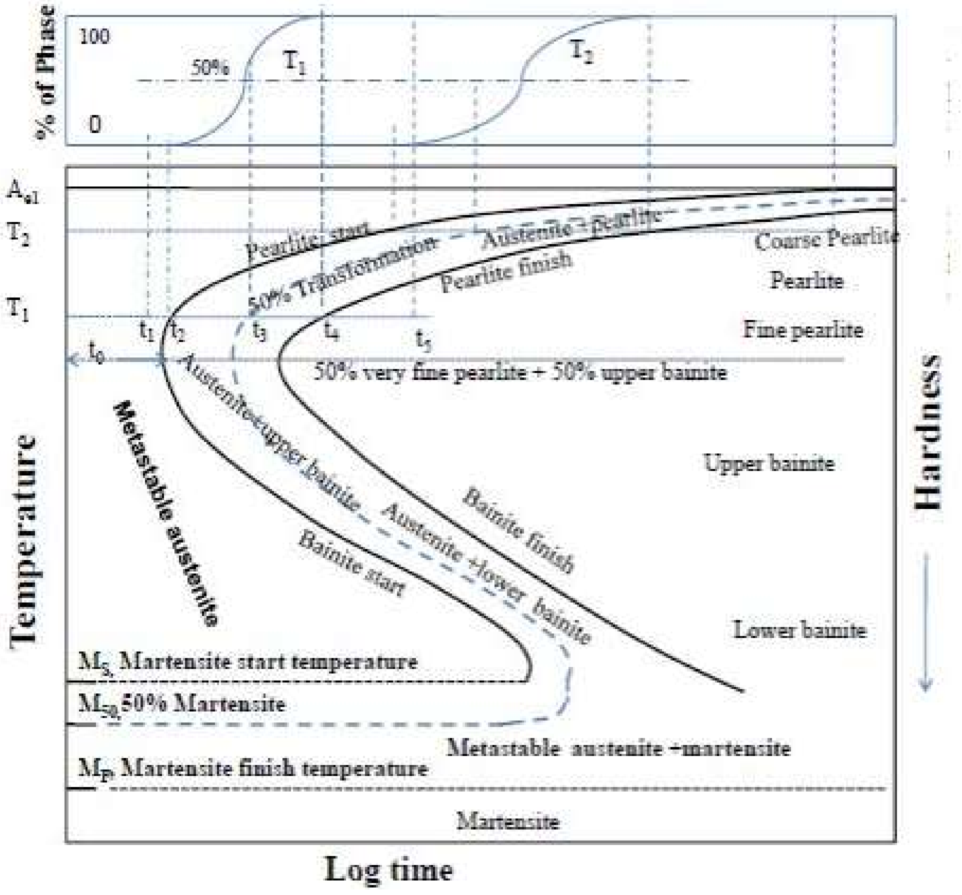
vi) Qualitative information about size scale of product Hardness of transformed products.

Construction and Study of I-T Diagram: -

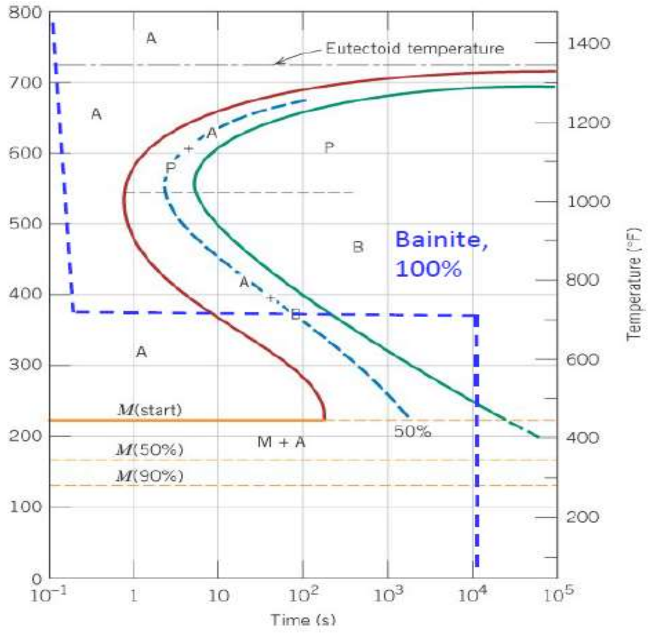
Step 1: Prepare many samples cut from the same bar. Their cross section has to be small in order to react quickly to change in temperature.
Step 2: Place the samples in a furnace or molten salt bath at the proper austenitizing temperature. For 1080 (eutectoid) steel, this temperature is approximately 1425Â°F. They should be left at the given temperature long enough to become completely austenite.
Step 3: Place the samples in a molten salt bath which is held at a constant subcritical temperature (a temperature below the Ae1 line), for example, 675Â°C.
Step 4: After varying time intervals in the salt bath, each sample is quenched in cold water or iced brine.
Step 5: After cooling, each sample is checked for hardness and studied microscopically.
Step 6: The above steps are repeated at different subcritical temperatures until enough points are determined to plot the curves on the diagram.



TTT Diagrams with various phases:-



Bainite transformation:



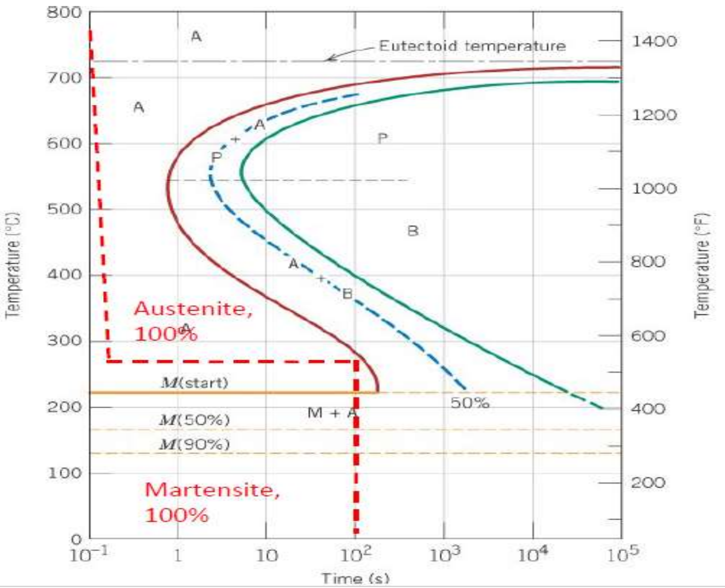
Iron-carbon alloy with eutectoid composition.

- Specify the nature of the final microstructure (% bainite, martensite, pearlite etc) for the alloy that is subjected to the following time–temperature treatments:
- Alloy begins at 760˚C and has been held long enough to achieve a complete and homogeneous austenitic structure.

Treatment (a)

- Rapidly cool to 350 ˚C
- Hold for 104 seconds
- Quench to room temperature

Martensite transformation:



Iron-carbon alloy with eutectoid composition.

- Specify the nature of the final microstructure (% bainite, martensite, pearlite etc) for the alloy that is subjected to the following time–temperature treatments:
- Alloy begins at 760˚C and has been held long enough to achieve a complete and

homogeneous austenitic structure.

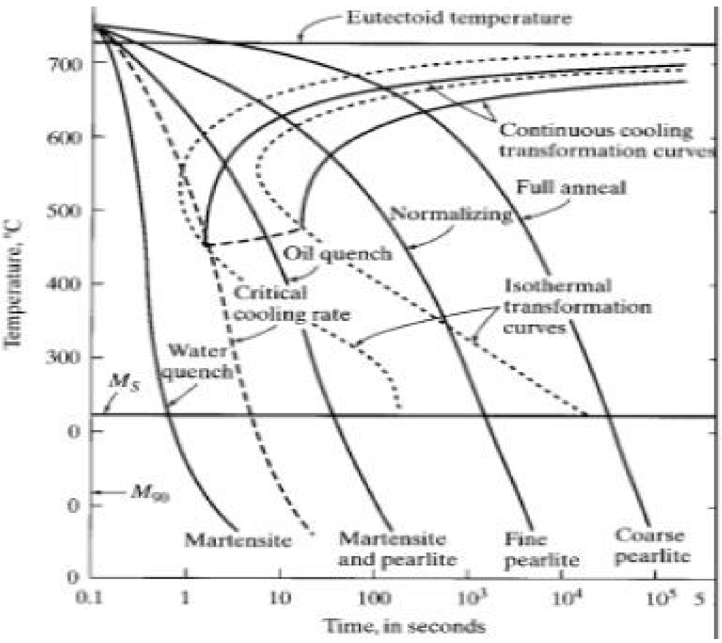
Treatment: -

- Rapidly cool to 250 ˚C
- Hold for 100 seconds
- Quench to room temperature

CONTINUOUS COOLING CURVES

A continuous cooling transformation (CCT) phase diagram is often used when heat treating steel. These diagrams are used to represent which types of phase changes will occur in a material as it is cooled at different rates.

- These diagrams are often more useful than time-temperature-transformation diagrams because it is more convenient to cool materials at a certain rate than to cool quickly and hold at a certain temperature.
- The CCT diagram for steel is slightly differ from TTT, it is as shown in figure.



- The products formed by continuous cooling procedures can be predicted using a continuous cooling diagram which differs from the isothermal transformation diagram in that the beginning and the end of the transformation are generally shifted to lower temperatures and longer times. Different rates of cooling, and hence different microstructures are achieved through the use of different cooling media, as shown in Fig. Essentially as the cooling rate is increased the hardness and the strength of the steel increases.

HARDENABILITY

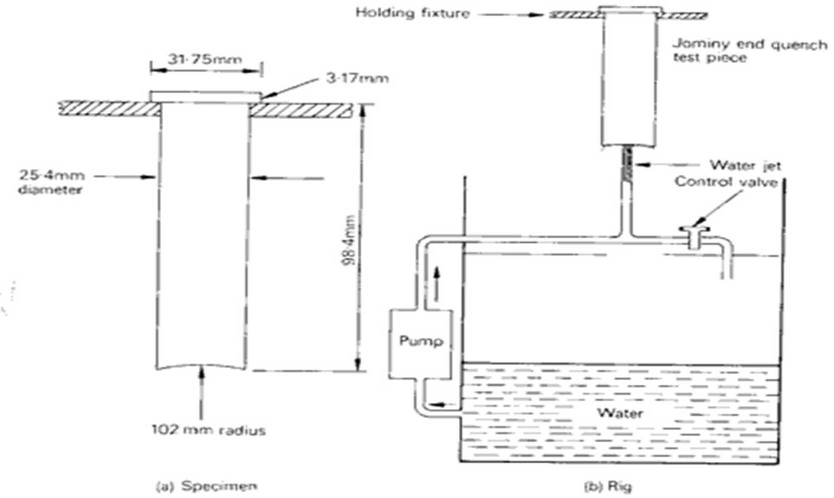
Hardenability is a way to indicate a material's potential to be hardened by thermal treatment. Hardness is resistance to penetration. Hardenability describes how deep the steel may be hardened upon quenching from high temperature. The depth of hardening is an important factor in a steel part's toughness.

- The Jominy End Quench Test ASTM A 255 measures Hardenability of steels. Hardenability is a measure of the capacity of a steel to be hardened in depth when quenched from its austenitizing temperature. Hardenability of a steel should not be confused with the hardness of a steel.

The Jominy End Quench Test:

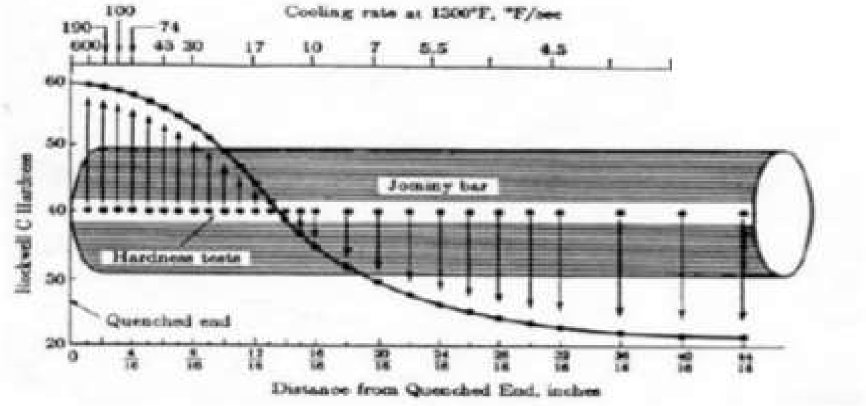
- A sample specimen cylinder either 100mm in length and 25mm in diameter, or alternatively, 102mm by 25.4mm is obtained.
- Second, the steel sample is normalized to eliminate differences in microstructure due to previous forging, and then it is austenitised. This is usually at a temperature of 800 to 900°C.
- Next, the specimen is rapidly transferred to the test machine, where it is held vertically and sprayed with a controlled flow of water onto one end of the sample. This cools the specimen from one end, simulating the effect of quenching a larger steel component in water. Because the cooling rate decreases as one moves further from the quenched end, you can measure the effects of a wide range of cooling rates from vary rapid at the quenched end to air cooled at the far end.

- Jomiey end quench test set up is as shown in figure:



(a) Specimen (b) Rig

- After the experiment the values of hardness are plotted as shown in figure to determine the variations in hardness over the length of the bar.



CASE HARDENING (SURFACE TREATMENT)

In many situations hard and wear resistance surface is required with the tough core. Because of tough core the components can withstand impact load. The typical applications requiring these conditions include gear teeth, cams shafts, bearings, crank pins, clutch plate, tools and dies.

- The combination of these properties can be achieved by the following methods:

1. Changing the composition at surface layers (chemical heat treatment or case hardening)
   (i) Carburising (ii) Nitriding (iii) Carburising and Cyaniding
2. Hardening and tempering the surface layers (surface hardening)
   (i) Flame Hardening (ii) Induction Hardening

CARBURISING

- Carburizing, also referred to as Case Hardening, is a heat treatment process that produces a surface which is resistant to wear, while maintaining toughness and strength of the core. This treatment is applied to low carbon steel parts after machining, as well as high alloy steel bearings, gears, and other components.

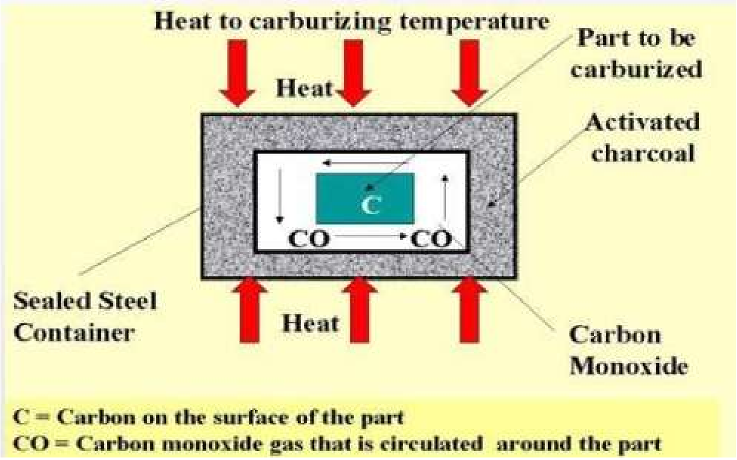
- Carburizing increases strength and wear resistance by diffusing carbon into the surface of the steel creating a case while retaining a substantially lesser hardness in the core. This treatment is applied to low carbon steels after machining.

- Strong and very hard-surface parts of intricate and complex shapes can be made of relatively lower cost materials that are readily machined or formed prior to heat treatment.

CARBURIZING METHODS:

1. Pack carburizing
2. Liquid carburizing.
3. Gas carburizing

- **Pack carburizing:** The schematic representation of pack carburizing is as shown.



Steps & Reactions:

1.FORMATION OF CARBON MONOXIDE.

2.DISSOCIATION OF CO WITH EVOLUTION OF ATOMIC CARBON.

$$2CO \longrightarrow CO2 + C \text{ atom}$$

3.ENRICHMENT OF STEEL SURFACE LAYER WITH CARBON.

$$2CO + 3Fe \longrightarrow Fe3C + Co2$$

Carbon actually gets dissolved in Gamma iron to form Autenite

- **Liquid carburizing: -** Also known as salt bath carburising

  Carburising done by immersing the steel components in a carbonaceous fused salt bath medium containing sodium or potassium cyanide, sodium and potassium chloride and barium chloride which acts as a activator Bath heated in the range of 815 - 900°C

  Reactions:

  $BaCl_2 + 2NaCN \rightarrow Ba(CN)_2 + 2NaCl$
  $Ba(CN)_2 + Fe \rightarrow Fe(C) + BaCN_2$ (Barium cyanamide)

  Some beneficial nitrogen may also diffuse through oxidation of sodium cyanide

  $2NaCN + O_2 \rightarrow 2NaCNO$
  $3NaCNO \rightarrow NaCN + Na_2CO_3 + C + 2N$

  Nitriding helps in increasing hardness and wear resistance. Carburising time of 0.5 to1 hour for case depth of 0.1 to 0.5mm.

- **Gas carburizing: -**

  Components heated in the range of 870 to 950° C in the presence of carbonaceous gases like methane, ethane, propane or butane diluted with a carrier gas containing 40% N_2, 40% H_2, 20% CO, 0.3% CO_2, 0.5% CH_4, 0.8% water vapor and traces of oxygen.

  Reactions:

  $C_3H_8 \rightarrow 2CH_4 + C$ [Cracking]
  $CH_4 + Fe \rightarrow Fe(C) + 2H_2$
  $CH_4 + CO_2 \rightarrow 2CO + 2H_2$
  $2CO + Fe \rightarrow Fe(C) + CO_2$

  Carburising mainly occurs due to CO to CO_2 conversion.
  H_2 reacts with CO_2 and increases CO concentration

  $H_2 + CO_2 \rightarrow CO + H_2O$

  Traces of oxygen are also present due to the following reactions;

  $2CO_2 \rightarrow 2CO + O_2$
  $CO_2 + Fe \rightarrow Fe(C) + O_2$

  To avoid dead spots and formation of soot: Control on gas composition and proper circulation of gas is essential for constant and uniform rate of carbon diffusion.

NITRIDING

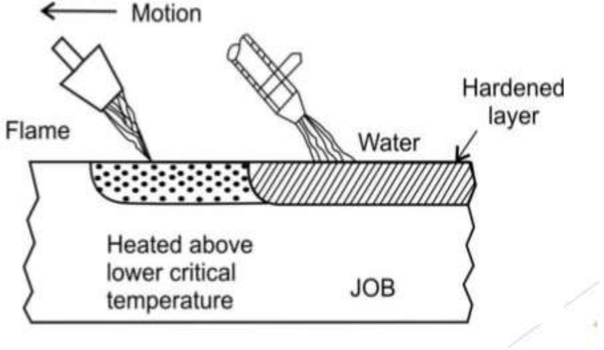
- Nitriding involves diffusion of nitrogen into the product to form nitrides. The resulting nitride case can be harder than the carburized steel. This process is used for alloy steels containing alloying elements (Aluminium, Chromium and Molybdenum) which form stable nitrides.
- Nitriding consists of heating a component in a retort to a temperature of about 500 to 600^{0} C. Through the retort the ammonia gas can circulate. At this temperature the ammonia dissociates by the following reaction.

  $$2NH_3 \rightarrow 2N + 3H_2$$

- The atomic nitrogen diffuses into steel surface, and combines with the alloying elements (Cr, Mo, W, V etc) to form hard nitrides. The depth to which nitrides are formed in the steel depends on the temperature and the time allowed for the reaction. After the nitriding the job is allowed to cool slowly. Since there is no quenching involved, chances of cracking and distortion of the component is less.

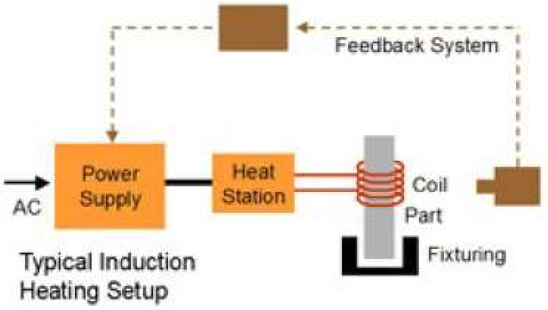
FLAMR HARDENING

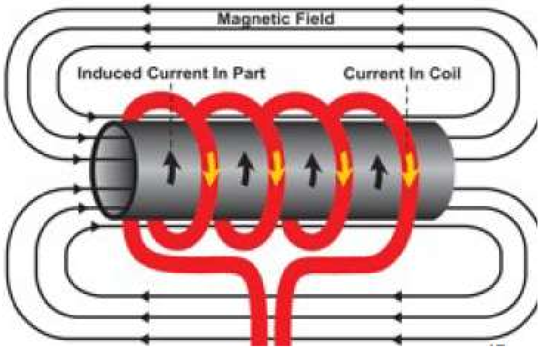
- The flame hardening involves heating the surface of a steel to a temperature above upper critical point (850^0 C) with a oxyacetylene flame and then immediately quenched the surface with cold water.
- Heating transforms the structure of surface layers to austenite, and the quenching changes it to martensite.
- The surface layers are hardened to about 50 – 60 HRC. It is less expensive and can be easily adopted for large and complex shapes.
- Flame hardened parts must be tempered after hardening. The tempering temperature depends on the alloy composition and desired hardness.
- The flame hardening methods are suitable for the steels with carbon contents ranging from 0.40 to 0.95% and low alloy steels.



INDUCTION HARDENING

- Induction hardening involves placing the steel components within a coil through which high frequency current is passed. The current in the coil induce eddy current in the surface layers and heat the surface layers up to austenite state.
- Then the surface is immediately quenched with the cold water to transfer the austenite to martensite.
- Advantages of induction hardening over flame hardening is its speed and ability to harden small parts; but it is expensive.
- Like flame hardening, it is suitable for medium carbon and low alloy steels.
- Typical applications for induction hardening are crank shafts, cam shafts, connecting rods, gears and cylinders.



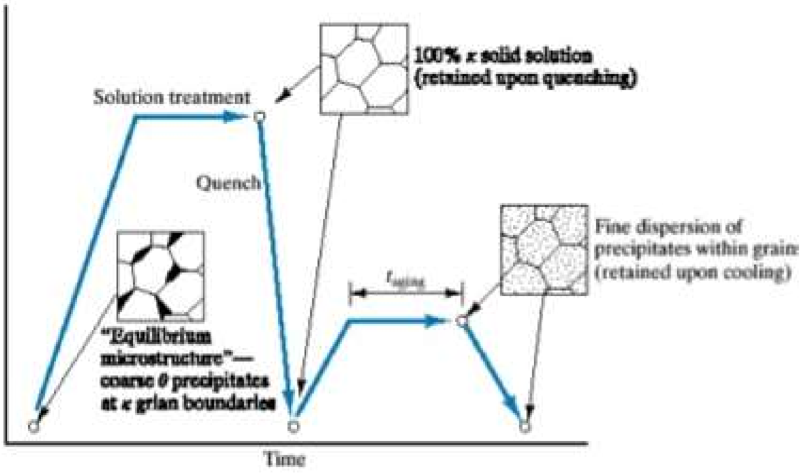


Age Hardening:

- Age hardening, also known as precipitation hardening, is a type of heat treatment that is used to impart strength to metals and their alloys.
- It is called precipitation hardening as it makes use of solid impurities or precipitates for the strengthening process.
- The metal is aged by either heating it or keeping it stored at lower temperatures so that precipitates are formed.

The process of age hardening is executed in a sequence of three steps.

1. First the metal is treated with a solution at high temperatures. All the solute atoms are dissolved to form a single-phase solution. A large number of microscopic nuclei, called zones, are formed on the metal. This formation is accelerated further by elevated temperatures.
2. The next step is the rapid cooling across the solvus line so that the solubility limit is exceeded. The result is a super saturated solid solution that remains in a metastable state. The lowering of temperatures prevents the diffusion.
3. Finally, the supersaturated solution is heated to an intermediate temperature in order to induce precipitation. The metal is maintained in this state for some time.



URLs/Hyperlinks for further study:

https://nptel.ac.in/courses/113105024/31
https://nptel.ac.in/courses/113105024/37
https://nptel.ac.in/courses/113101003/downloads/partVI/module5.pdf

ENGINEERING METALLURGY

UNIT – V

Non-Ferrous Metals and Alloys and Composite Materials

Syllabus: Properties and applications of Titanium - Titanium alloys, Copper – Copper alloys, and Aluminium – Aluminium alloys.
Composite materials: Classification of composites, various methods of component manufacture of composites, particle – reinforced materials, fiber reinforced materials, metal – matrix composites and C – C composites.

Introduction:

- Metallic materials, when considered in a broad sense, may be divided into two large groups, ferrous and nonferrous.
- The ferrous materials are iron-based, and the nonferrous materials have some element other than iron as the principal constituent.
- The bulk of the nonferrous materials is made up of the alloys of copper, aluminium, magnesium, nickel, tin, lead, and zinc.
- Other nonferrous metals and alloys that are used to a lesser extent include cadmium, molybdenum, cobalt, zirconium, beryllium, titanium, tantalum, and the precious metals gold, silver, and the platinum group.

TITANIUM ALLOYS

Introduction:

- Titanium is not actually a rare substance as it ranks as the ninth most plentiful element and the fourth most abundant structural metal in the Earth's crust exceeded only by aluminum, iron, and magnesium.
- Titanium usually occurs in mineral sands containing ilmenite ($FeTiO3$), found in the Ilmenmountains of Russia, or rutile ($TiO2$), from the beach sands in Australia, India, and Mexico. Titanium dioxide is a very versatile white pigment used in paint, paper, and plastic, and consumes most of world production.
- Titanium alloys primarily stand out due to two properties: high specific strength and excellent corrosion resistance. This also explains their preferential use in the aerospace sector, the chemical industry, medical engineering, and the leisure sector .
- Pure titanium, as well as the majority of titanium alloys, crystallizes at low temperatures in a modified ideally hexagonal close packed structure, called α titanium.
- At high temperatures, however, the body-centered cubic structure is stableand is referred to as β titanium.

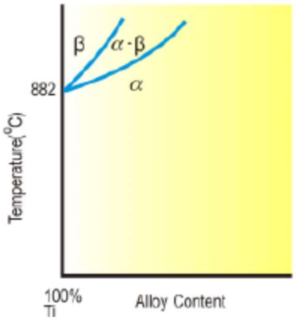
Classification of titanium alloys:

1. α phase titanium alloy.
2.β phase titanium alloy.
3.(α+ β) phase titanium alloy.

- **Alpha alloys**- These are non-heat treatable and are generally very weldable. They have low to medium strength, good notch toughness, reasonably good ductility and have excellent properties at cryogenic temperatures. The more highly alpha or near alpha alloys offer high temperature creep strength and oxidation resistance.

- **Alpha-Beta alloys-** These are heat treatable to varying extents and most areweldable with the risk of some loss of ductility in the weld area. Their strength levels are medium to high. Hot forming qualities are good but cold forming often presents difficulties. Creep strength is not usually as good as in most alpha alloys.
- **Beta alloys-** Beta or near beta alloys are readily heat treatable, generally weldable, and offer high strength up to intermediate temperature levels. In the solution treated condition, cold formability is generally excellent.

  - **Crystallographic Forms**
    - ✓ The metallurgy of titanium is dominated by the crystallographic transformation which takes place in the pure metal at 882°C. Below this temperature, pure titanium has a hexagonal close packed structure known as alpha (α); above it, the structure is body centred cubic and termed beta (β).
    - ✓ The fundamental effect of alloying additions to titanium is alteration of the transformation temperature and production of a twophase field in which both alpha and beta phases are present. Elements having extensive solubility in the alpha-phase characteristically raise the transformation temperature and are called alpha stabilisers.
- **Alpha Stabilisers**
  - The binary phase diagram formed by addition of an alpha stabiliser (such as aluminium, oxygen, nitrogen or carbon) to titanium.
  - Oxygen is added to pure titanium to produce a range of grades having increasing strength as the oxygen level is raised. Aluminium is the only other alpha stabiliser used commercially and is a major constituent of most commercial alloys.
  - It is a very effective alpha strengthening element at ambient and elevated temperatures up to about 550°C. The low density of aluminium is an additional advantageous feature but the amount that can be added is limited because of the formation of a brittle titanium-aluminium compound at aluminium contents exceeding about 8% by weight.



Effect of alpha-stabilising elements on titanium

  - The alpha phase is also strengthened by the addition of tin or zirconium. These metals have appreciable solubility in both alpha and beta phases and as their addition does not markedly influence the transformation temperature they are normally classified as neutral additions.
  - As with aluminium, the beneficial ambient temperature hardening effect of tin and zirconium is retained at elevated temperatures. Figure demonstrates schematically the phase diagram for titanium and a neutral element.

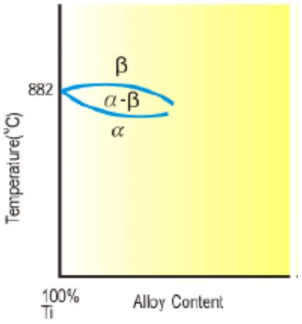


Fig5.17 Effect of neutral elements on titanium.

- **Beta Stabilisers**
  - Elements that depress the transformation temperature, readily dissolve in and strengthen the beta phase and exhibit low alpha phase solubility are known as beta stabilisers. They can be divided into two categories according to their constitutional behaviour with titanium:
    - Beta-isomorphous elements
    - Beta-eutectoid elements.

- **Beta-Isomorphous Elements**
  - Beta-isomorphous elements exhibit complete mutual solubility with beta titanium. Increasing addition of the solute element progressively depresses the transformation temperature to give the characteristic phase diagram shown in Figure 5.18.
  - Molybdenum and vanadium are the most important beta isomorphous elements, while niobium and tantalum have also found application in some alloys.

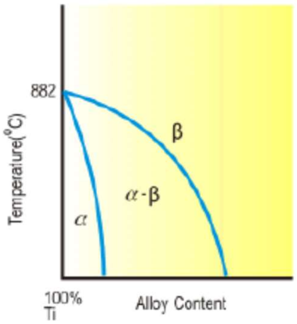


Fig5.18. Effect of beta-isomorphous elements on titanium.

- **Beta-Eutectoid Elements**
  - Beta-eutectoid elements have restricted solubility in beta titanium and form intermetallic compounds by eutectoid decomposition of the beta phase. A representative phase diagram is illustrated in Figure 5.19. Elements of the betaeutectoid type can be further subdivided into sluggish and active elements.
  - Commercially important metals in the sluggish category are iron, chromium andmanganese. Eutectoid decomposition of beta phase in the

titanium-iron, titaniumchromium and titanium-manganese systems is so slow that intermetallic compound formation does not occur during normal commercial fabrication and heat treatment or during service and, therefore, for practical purposes the behaviour of iron, chromium and manganese can be likened to that of beta-isomorphous elements.

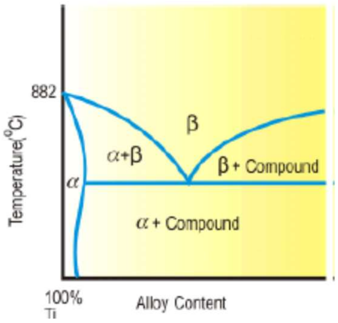


Fig 5.19.Effect of beta-eutectoid elements on titanium.

- **Advantages of Beta Alloys**
    - In addition to strengthening the beta phase, beta stabilisers have two other important advantages as alloying constituents.
    - Beta titanium has an inherently lower resistance to deformation than the alpha modification and therefore elements which increase and stabilise the beta phase tend to improve alloy fabricability during both hot and cold working operations.
    - Addition of sufficient beta stabiliser to titanium compositions also confers a heat treatment capability which permits significant strengthening to be achieved by controlled decomposition of beta phase to alpha phase during the heat treatment process.

Commercially pure titanium is lower in strength, more corrosion-resistant, and less expensive than titanium alloys.

COPPER AND ITS ALLOYS

Introduction

Copper: Copper is non-polymorphous metal with face centered cubic lattice Pure copper is a reddish color, zinc addition produces a yellow color, and nickel addition produces a silver color. Melting temperature is 1083 °C and density is 8900 kg.m-3, which is three times heavier than aluminum. The heat and electric conductivity of copper is lower compared to the silver, but it is 1.5 times larger compared to the aluminum.

Properties:

- High electrical conductivity
- High thermal conductivity
- High corrosion resistance
- Good ductility and malleability
- Reasonable tensile strength

Pure copper electric conductivity is used like a basic value for other metals evaluation and electric conductivity alloys characterization. The pure metal alloying decreased its conductivity .

Physical properties of copper:

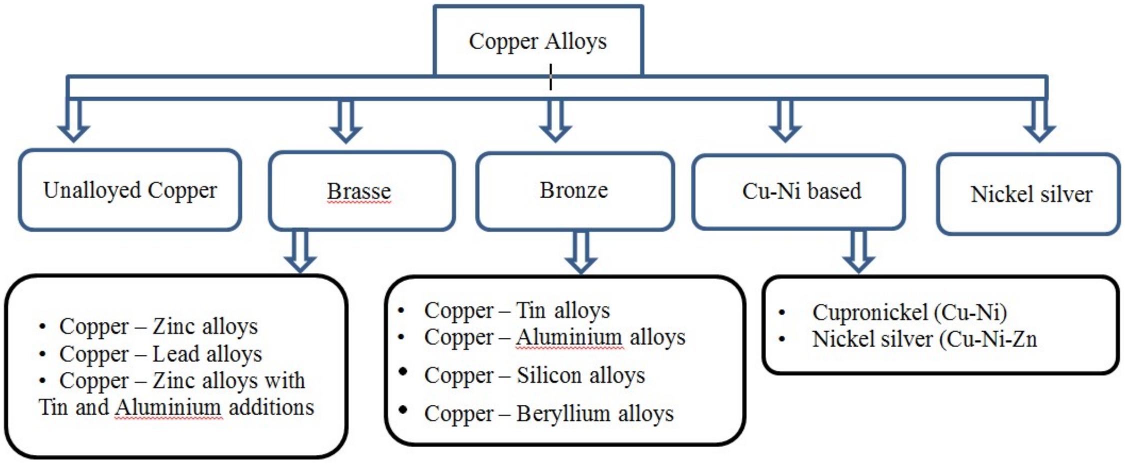
- Crystal structure FCC
- Atomic number 29
- Atomic weight 63.546
- Density (g.cm-3) 8.933
- Melting point (° C) 1084.62

Mechanical properties:

- Coppers mechanical properties depend on its state and are defined by its lattice structure. Copper has good formability and toughness at room temperature and also at reduced temperature.
- Increasing the temperature steadily decreases coppers strength properties. Also at around 500 °C the coppers technical plastic properties decrease. Due to this behavior, cold forming or hot forming at 800 to 900 °C of copper is proper.

- Cold forming increases the strength properties but results in ductility decreasing. In the as cast state, the copper has strength of 160 MPa. Hot rolling increases coppers strength to 220 MPa. Copper has a good ductility and by cold deformation it is possible to reach the strength values close to the strength values of soft steel.

Classification of copper and copper alloys:



Copper and copper alloys are designated according to the Copper Development Association (CDA):

- Wrought alloys(C100-C799)
- Cast alloys (C800-C999)

Unalloyed Copper:

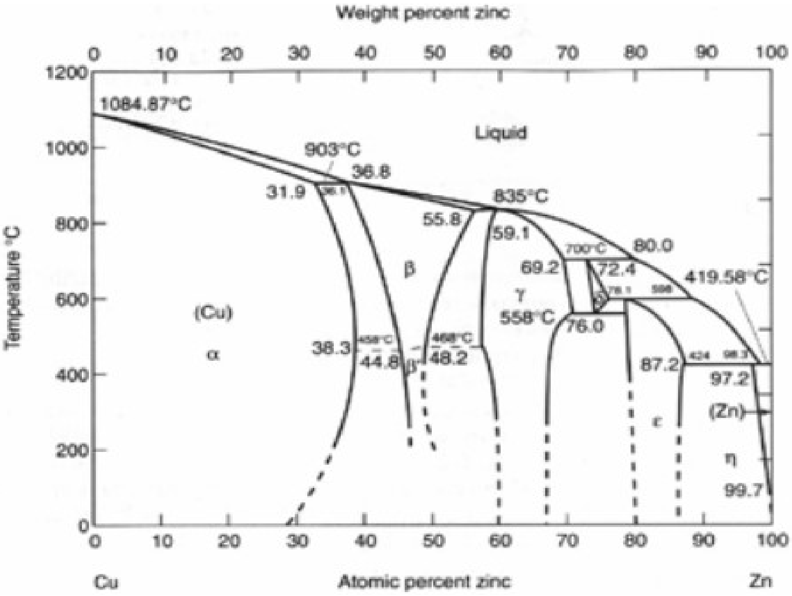
Copper in its pure, unalloyed state is soft, provides high electrical and thermal conductivity and has excellent corrosion resistance. There are various grades of unalloyed copper which differ in the amount of impurities they contain. Oxygen free grades are used for high conductivity and ductility.

BRASSES

Introduction:

- Brasses are alloys made from copper and zinc, they exhibit good strength and ductility and are easily cold worked, properties which improve with increased zinc content up to 35%.
- Brass coloration ranges from red to golden yellow, depending on the amount of zinc the alloy contains. Gilding Metal, Commercial Bronze, Jewelry Bronze, Red Brass and Cartridge Brass are common names given to brass alloys with specific zinc contents.
- Brasses containing between 32% and 39% zinc exhibit excellent hot working characteristics but limited cold workability.
- Brasses containing more than 39% zinc, such as **Muntz Metal**, have high strength and lower ductility at room temperature than alloys with less zinc. Brasses are known for their ease of fabrication by drawability, high cold-worked strength and corrosion resistance.

Brasses are routinely blanked, coined, drawn and pierced to produce springs, fire extinguishers, jewelry, radiator cores, lamp fixtures, ammunition, flexible hose and the base for
gold plate.



Cu-Zn phase diagram

The following table Showing properties and key features of types of brasses

Class	Copper (%)	Zinc (%)	Explanation
Alpha brasses	> 65	< 35	• Alpha brasses are malleable, can be worked cold, and are used in pressing, forging, or similar applications. • They contain only one phase, with face-centered cubic crystal structure. With their high proportion of copper, these brasses have a more golden hue than others
Alpha-beta brasses	55–65	35–45	• Also called duplex brasses, these are suited for hot working. They contain both α and β' phases; the β'-phase isbody-centered cubic and is harder and stronger than α. • Alpha-beta brasses are usually worked hot. The higher proportion of zinc means these brasses are brighter than alpha brasses.
Beta brasses	50–55	45–50	• Beta brasses can only be worked hot, and are harder, stronger, and suitable for casting. • The high zinc-low copper content means these are some of the brightest and least-golden of the common brasses.
Gamma brasses	61–67	33–39	• There are also Ag-Zn and Au-Zn gamma brasses, Ag 30–50%, Au 41%.
White brass	< 50	> 50	• These are too brittle for general use. The term may also refer to certain types of nickel silver alloys as well as Cu-Zn-Sn alloys with high proportions (typically 40%+) of tin and/or zinc, as well as predominantly zinc casting alloys with copper additives. • These have virtually no yellow coloring at all, and instead have a much more silvery appearance.

BRONZES

Introduction:

- **Bronze** is an alloy consisting primarily of copper, commonly with about 12% tin and often with the addition of other metals (such as aluminium, manganese, nickel orzinc) and sometimes non-metals or metalloids such as arsenic, phosphorus or silicon.
- These additions produce a range of alloys that may be harder than copper alone, or have other useful properties, such as stiffness, ductility or machinability.

Properties:

- Bronzes are typically very ductile alloys.
- Bronze only oxidizes superficially; once a copper oxide (eventually becoming copper carbonate) layer is formed, the underlying metal is protected from further corrosion. However, if copper chlorides are formed, a corrosion-mode called "bronze disease" will eventually completely destroy it.
- Copper-based alloys have lower melting points than steel or iron, and are more readily produced from their constituent metals.
- Bronzes have lowerhardness, strength stiffness and elastic modulus
- The cost of copper-base alloys is generally higher than that of steels but lower than that of nickel-base alloys.
- The melting point of bronze varies depending on the ratio of the alloy components and is about 950 °C.
- Bronze may be nonmagnetic, but certain alloys containing iron or nickel may have magnetic properties.

Tin Bronzes or Phosphor Bronzes:

- Phosphor Bronzes, or tin bronzes as they are sometimes called, contain between 0.5% and 11% tin and 0.01% to 0.35% phosphorous.
- Tin increases their corrosion resistance and tensile strength, phosphorus increases wear resistance and stiffness.
- They have super spring qualities, high fatigue resistance, excellent formability and solderability.

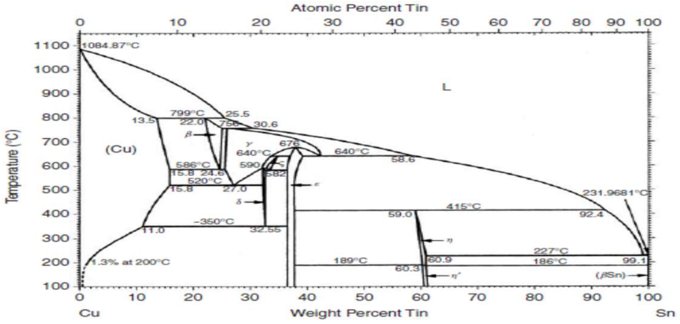
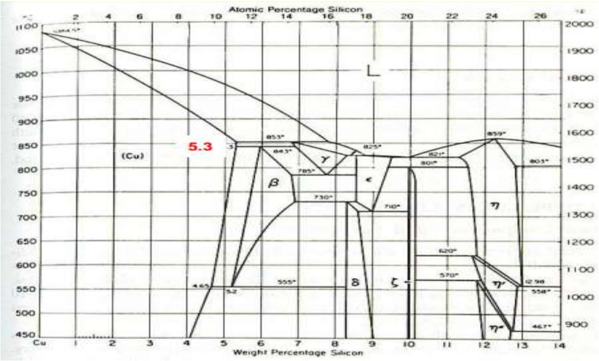


Fig 5.12 Cu-Sn phase diagram

Silicon Bronzes:

- Silicon Bronzes are part of the subgroup of high-strength brasses. They contain less than 20% zinc and upto 6% silicon and are solid solution strengthened.
- Silicon red brasses are used for valve stems where corrosion resistance and high strength are critical. Included in this category are the silicon red bronzes, which are similar to silicon red brasses except for their very low concentrations of zinc.
- They are used to make bearings, gears and intricately shaped pump and valve components.



Cu-Silicon phase diagram

Aluminum bronzes:

- Aluminum Bronzes contain 6% to 12% aluminum, up to 6% iron and nickel and provide high strength and excellent corrosion and wear resistance. S
- Solid solution strengthening, cold work and precipitation of an iron rich phase contribute to these characteristics.
- High aluminum containing alloys can be quenched and tempered. Aluminum bronzes are used in marine hardware, shafts and pump and valve components for handling seawater, sour mine waters, nonoxidizing acids, and industrial process fluids. They are also used as heavy duty sleeve bearings and machine tool ways.
- Aluminum bronze castings have exceptional corrosion resistance, high strength, toughness and wear resistance. They also exhibit good casting and welding characteristics.

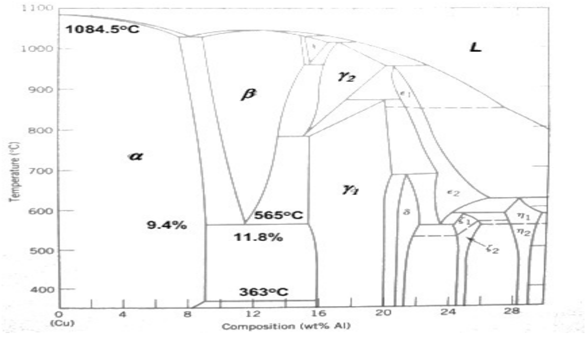


Fig.5.14 Cu-Al alloy phase diagram

Nickel Silvers:

- Nickel Silvers, also called nickel brasses, are alloy containing copper, nickel and zinc. Though they do not contain silver, they have an attractive silver luster, moderately high strength and good corrosion resistance.
- They are used to make food and beverage handling equipmentt, decorative hardware, electroplated tableware, optical and photographic equipment and musical instruments.

Copper Nickel:

- Copper Nickel alloys contain anywhere from 2% to 30% nickel, are highly corrosion-resistant and thermally stable.
- The addition of iron, chromium, niobium and/or manganese can improve their strength and corrosion resistance in steam and moist air.
- They are used to make electrical and electronic products, tubes for condensers in ships, on offshore platforms and in power plants, and various other marine products including valves, pumps, fittings and sheathing for ship hulls.

Speciality copper alloys:

- Specialty Copper Alloys, based, for example, on the copper-nickel-silicon and copper-nickel-tin systems provide unique combinations of properties due to their intrinsic precipitation hardening capability.
- Their high strength coupled with good formability, thermal stability and electrical conductivity make them appropriate to use them in electrical and electronic connectors and hardware.

As we have seen, copper and its alloys constitute a broad range of chemical compositions and are employed widely in applications that enable and enhance our everyday lives. Each application makes effective use of copper's attributes: strength, conductivity, color, formability, joinability and thermal stability.

ALUMINIUM & ITS ALLOYS

Mechanical Properties:

- Persons handling ultrapure Al (99.9999% purity) for the first time often question whether the metal is really Al because it is so much softer (σ yield = 12 MPa) than familiar Al alloys.
- At a more "normal" purity (99.0%), yield strength rises to 40 MPa, and some precipitation-hardening Al alloys can achieve σ yield as high as 625 MPa, a remarkable 50-fold increase over ultrapure Al.
- Pure Al has excellent ductility; 35 to 50% tensile elongation is typical at room temperature. As with most FCC metals, there is no ductile–brittle transition;
- Al remains ductile at cryogenic temperatures with tensile elongation increasing somewhat below −200◦C. Work hardening raises Al's strength quite substantially.
- Commercial purity Al (99.60% pure) has a yield strength of 27 MPa when fully annealed, but if cold worked by swaging or rolling to 75% reduction in area, σy increases to 125 MPa.

Corrosion Behaviour:

- When exposed to O2, Al forms an amorphous oxide layer about 5 nm thick; if heated in air, the oxide layer may thicken to about 20 nm. The oxide is strongly adherent and protective in many corrosive environments. High-purity Al (99.99+% purity) has considerably better corrosion resistance than commercial-purity Al (99.5%), which in turn has better corrosion resistance than most Al alloys.
- A less protective mixed oxide scale forms over second-phase particles in impure Al, and these particles form microscale galvanic cells with the pure Al around them, accelerating corrosive Pure Al resists corrosion in water, seawater, ammonia, most food and beverage solutions, many organic acids, and even concentrated nitric acid.

Reflectance:

- Al has high reflectance for visible and infrared light.
- Al can be deposited on glass by physical vapor deposition to produce smooth surfaces; a 100-nm-thick deposit is sufficient to achieve maximum reflectance.
- Al coatings are used for nearly all vanity and optical mirrors.
  Deep lustre automobile finishes contain high-purity Al powder to reflect light.

Electrical and Thermal Conductivity:

- Al's electrical and thermal conductivities are among the highest of all materials. Although group 11 metals (Ag, Cu, Au) have conductivities higher than Al's, they are heavier and more expensive than Al, making them less desirable for many applications.
- Increased electron–phonon interactions at higher temperatures raise electrical resistivity as temperature rises. Thermal and electrical conductivities are highest for high-purity Al and decrease as impurity content rises. In commercial purity Al, the most common impurities are Fe and Si, which raise electrical resistivity.

Uses of Aluminium:

- Aluminium is used in a huge variety of products including cans, foils, kitchen utensils, window frames, beer kegs and aeroplane parts. This is because of its particular properties. It has low density, is non-toxic, has a high thermal conductivity, has excellent corrosion resistance and can be easily cast, machined and formed.
- It is also non-magnetic and non-sparking. It is the second most malleable metal and the sixth most ductile.
- It is often used as an alloy because aluminium itself is not particularly strong. Alloys with copper, manganese, magnesium and silicon are lightweight but strong. They are very important in the construction of aeroplanes and other forms of transport.
- Aluminium is a good electrical conductor and is often used in electrical transmission lines. It is cheaper than copper and weight for weight is almost twice as good a conductor.
- When evaporated in a vacuum, aluminium forms a highly reflective coating for both light and heat. It does not deteriorate, like a silver coating would. These aluminium coatings have many uses, including telescope mirrors, decorative paper, packages and toys.

Types of Aluminium Alloys:

Aluminium alloys are alloys in which aluminium (Al) is the predominant metal. The typical alloying elements are copper, magnesium, manganese, silicon and zinc. There are two principal classifications.

Namely

1. Casting alloys
2. Wrought alloys

- Both of which are further subdivided into the categories heat-treatable and non-heat-treatable. About 85% of aluminium is used for wrought products, for example rolled plate, foils and extrusions.
- Cast aluminium alloys yield cost-effective products due to the low melting point, although they generally have lower tensile strengths than wrought alloys. The most important cast aluminium alloy system is Al–Si, where the high levels of silicon (4.0–13%) contribute to give good casting characteristics.
- Aluminium alloys are widely used in engineering structures and components where light weight or corrosion resistance is required.

Cast aluminium Alloys:

The Aluminium Association (AA) has adopted a nomenclature similar to that of wrought alloys. British Standard and DIN have different designations. In the AA system, the second two digits reveal the minimum percentage of aluminium, e.g. 150.x corresponds to a minimum of 99.50% aluminium. The digit after the decimal point takes a value of 0 or 1, denoting casting and ingot respectively. The main alloying elements in the AA system are as follows.

- 1xx.x series are minimum 99% aluminium
- 2xx.x series copper
- 3xx.x series silicon, copper and/or magnesium
- 4xx.x series silicon
- 5xx.x series magnesium
- 7xx.x series zinc

Heat treatment of cast aluminium alloys

When the term is applied to aluminium alloys, however, its use frequently is restricted to the specific operations employed to increase strength and hardness of the precipitation hard enable wrought and cast alloys.

1. Heat treatable alloy
2. Non heat treatable alloy

Heat treatable alloy:

Aluminium alloy of this type belongs to system with limited solubility in solid solution. These are precipitated hardenable alloy. The main character of this type of alloy system is a temperature dependent equilibrium solid solubility, which increase with increase in temperatue.in addition other requirements are retaining single phase supersaturated solution by quenching and coherent state.

Examples of this group is

- 2xxx Al-Cu alloy and Al-Cu-Mg alloy.
- 6xxx series include Al-Zn, Al-Zn-Mg alloy
- 7xxx series include Al-Zn, Al-Zn-Mg-Cu type alloys

Non heat treatable cast alloys:

These alloys do not respond to heat treatment because these alloys consist of homogeneous solid solution with or without non-coherent precipitate and show low strength and high ductility.

- Pure aluminium (1100), Al-Mn (3003)
- 5xxx Al-Mg alloys
- 6xxx Al-Si alloys

Effect of Alloying Elements:

- Copper (Cu) 2xxx: The aluminium-copper alloys typically contain between 2 to 10% copper, with smaller additions of other elements. The copper provides substantial increases in strength and facilitates precipitation hardening. The introduction of copper to aluminium can also reduce ductility and corrosion resistance. The most common applications for the 2xxx series alloys are aerospace, military vehicles and rocket fins. The maximum solubility of copper in aluminium is 5.56% at 1018oF.

Commercial alloys of 2xxx series

The three most widely used wrought aluminium-copper alloys are 2014, 2017, and 2024.

Duralumin 2017 Al-Cu alloy:

The oldest of all the heat treatable aluminium alloys is duralumin (2017) containing 4 percent copper. This alloy is widely used for rivets in aircraft construction. Since this is a natural-aging alloy, after solution treatment it is refrigerated to prevent aging. As a single phase, in the Solution treated condition, it has good ductility so that the rivet head may be easily formed.

2014 Al-Cu alloy

Alloy 2014 has higher copper and manganese content than 2017 and is susceptible to artificial aging. In the artificially aged temper, 2014 has a higher tensile strength, much higher yield strength, and lower elongation than 2017. This alloy is used for heavy-duty forgings, aircraft fittings, and truck frames.

2024 Al-Cu alloy

Alloy 2024, containing 4.5 percent copper and 1.5 percent magnesium, develops the highest strengths of any naturally aged aluminium-copper type of alloy. The higher magnesium content, compared with 2017, makes it more difficult to fabricate. A combination of strain hardening and aging will develop the maximum yield strength attainable in high-strength alloy sheet. Typical uses of 2024 alloy are aircraft structures, rivets, hardware, truck wheels and screw-machine products.

Manganese (Mn) 3xxx:

The addition of manganese to aluminium increases strength somewhat through solution strengthening and improves strain hardening while not appreciably reducing ductility or corrosion resistance.

Commercial alloys of 3xxx

One of the alloys in this group is the popular 3003 alloy, which has good formability, very good resistance to corrosion, and good weldability. Typical applications are utensils, food and chemical handling and storage equipment, gasoline and oil tank, pressure vessels and piping.

Silicon (Si) 4xxx:

The addition of silicon to aluminium reduces melting temperature and improves fluidity. Silicon alone in aluminium produces a non-heat treatable alloy; however, in combination with magnesium it produces a precipitation hardening heat-treatable alloy. Consequently, there are both heat-treatable and non-heat treatable alloys within the 4xxx series. Silicon additions to aluminium are commonly used for the manufacturing of castings. The most common applications for the 4xxx series alloys are filler wires for fusion welding and brazing of aluminium.

Magnesium (Mg) 5xxx:

The addition of magnesium to aluminium increases strength through solid solution strengthening and improves their strain hardening ability. These alloys are the highest strength non heat treatable aluminium alloys and are, therefore, used extensively for structural applications. The 5xxx series alloys are produced mainly as sheet and plate and only occasionally as extrusions. The reason for this is that these alloys strain harden quickly and, are, therefore difficult and expensive to extrude.

Although the solvus line, show considerable decrease in solubility with decrease in temperature of magnesium in aluminium. Some common applications for the 5xxx series alloys are truck and train bodies, buildings, armoured vehicles, ship and boat building, chemical tankers, pressure vessels and cryogenic tanks.

Alloy 5005 (0.8 percent magnesium) is used for architectural extrusions
Alloy 5050 (1.2 percent magnesium) for tubing and automotive gas and oil lines
Alloy 5083 (4.5 percent magnesium) for marine and welded structural applications; and
Alloy 5056 (5.2 percent magnesium) for insect screens, cable sheathing, and rivets for use with magnesium alloys.

Magnesium and Silicon (Mg2Si) 6xxx

The addition of magnesium and silicon to aluminium produces the compound magnesium-silicide (Mg_2Si). The formation of this compound provides the 6xxx series their heat-treatability. The 6xxx series alloys are easily and economically extruded and for this reason are most often found in an extensive selection of extruded shapes.

The wrought alloys include 6053, 6061, and 6063 are mostly used.

- 6061 Al-Mg2Si: Construction of aircraft structures, such as wings and fuselages, more commonly in homebuilt aircraft than commercial or military aircraft. Construction, including small utility boats. Automotive parts, such as wheel spacers. Aluminium cans for the packaging of foodstuffs and beverages.
- 6053 Al-Mg2Si: Aluminium 6053 alloy is chiefly used in the manufacture of rod and wire for rivets. It is also used in several cold heading applications, where it is used in the form of T-temper wire.
-

Zinc (Zn) 7xxx

The addition of zinc to aluminium (in conjunction with some other elements, primarily magnesium and/or copper) produces heat-treatable aluminium alloys of the highest strength. The solubility of zinc in aluminium is 31.6 percent at 527^0 F, decreasing to 5.6 percent at 257^0 F.

Other elements 9xxx:

Iron (Fe): Iron is the most common impurity found in aluminium and is intentionally added to some pure (1xxx series) alloys to provide a slight increase in strength.

Chromium (Cr): Chromium is added to aluminium to control grain structure, to prevent grain growth in aluminium-magnesium alloys, and to prevent recrystallization in aluminium-magnesium-silicon or aluminium-magnesium-zinc alloys during heat treatment. Chromium will also reduce stress corrosion susceptibility and improves toughness.

Nickel (Ni): Nickel is added to aluminium-copper and to aluminium-silicon alloys to improve hardness and strength at elevated temperatures and to reduce the coefficient of expansion.

Titanium (Ti): Titanium is added to aluminium primarily as a grain refiner. The grain refining effect of titanium is enhanced if boron is present in the melt or if it is added as a master alloy containing boron largely combined as TiB2. Titanium is a common addition to aluminium weld filler wire as it refines the weld structure and helps to prevent weld cracking.

Zirconium (Zr): Zirconium is added to aluminium to form a fine precipitate of intermetallic particles that inhibit recrystallization.

Lithium (Li): The addition of lithium to aluminium can substantially increase strength and, Young's modulus, provide precipitation hardening and decreases density.

Lead (Pb) and Bismuth (Bi): Lead and bismuth are added to aluminium to assist in chip formation and improve machinability. These free machining alloys are often not weldable because the lead and bismuth produce low melting constituents and can produce poor mechanical properties and/or high crack sensitivity on solidification.

COMPOSITE MATERIALS

- Many of our modern technologies require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics, and polymeric materials.

- This is especially true for materials that are needed for aerospace, underwater, and transportation applications. For example, aircraft engineers are increasingly searching for structural materials that have low densities, are strong, stiff, and abrasion and impact resistant, and are not easily corroded. This is a rather formidable combination of characteristics. Frequently, strong materials are relatively dense; also, increasing the strength or stiffness generally results in a decrease in impact strength.

- Composite is considered to be any multiphase material that exhibits a significant proportion of the properties of both constituent phases such that a better combination of properties is realized.

- **A composite, in the present context, is a multiphase material that is artificially made, as opposed to one that occurs or forms naturally.** In addition, the constituent phases must be chemically dissimilar and separated by a distinct interface. Thus, most metallic alloys and many ceramics do not fit this definition because their multiple phases are formed as a consequence of natural phenomena.

- Many composite materials are composed of just two phases; one is termed the **matrix,** which is continuous and surrounds the other phase, often called the **dispersed phase.**

- The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase.

- ‘‘Dispersed phase geometry’’ in this context means the shape of the particles and the particle size, distribution, and orientation; these characteristics are represented in Figure 1.

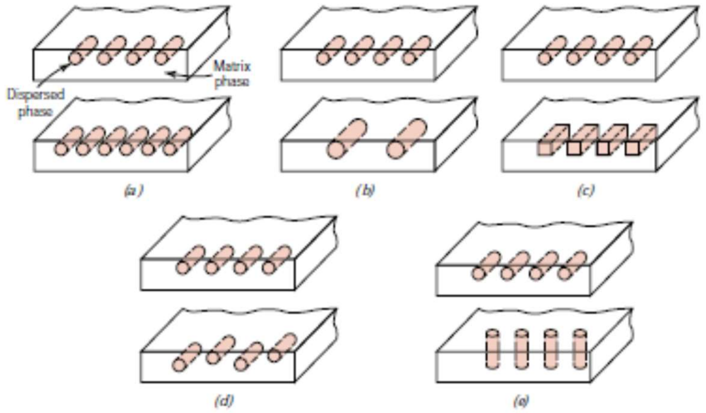
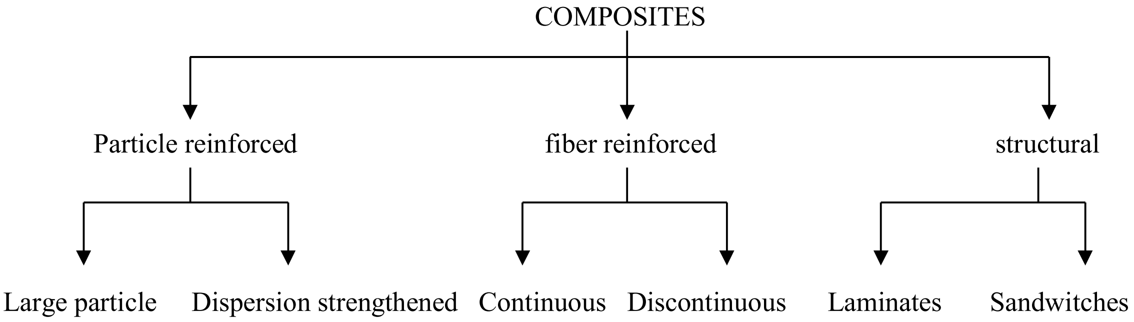


FIGURE .1 (*a*) concentration, (*b*) size, (*c*) shape, (*d*) distribution (*e*) orientation.

- The classification of composite materials is shown in Figure 2, which consists of three main divisions—particle-reinforced, fibre-rein-forced, and structural composites; also, at least two subdivisions exist for each. The dispersed phase for particle-reinforced composites is equiaxed (i.e., particle dimensions are approximately the same in all directions); for fiber-reinforced composites, the dispersed phase has the geometry of a fiber (i.e., a large length-to diameter ratio). Structural composites are combinations of composites and homogenous materials.



PARTICLE REINFORCED COMPOSITES

- **Large-particle** and **dispersion-strengthened composites** are the two subclassifications of particle-reinforced composites.
- The distinction between these is based upon reinforcement or strengthening mechanism. The term ‘‘large’’ is used to indicate that particle–matrix interactions cannot be treated on the atomic or molecular level; rather, continuum mechanics is used.

- For most of these composites, the particulate phase is harder and stiffer than the matrix. These reinforcing particles tend to restrain movement of the matrix phase in the vicinity of each particle.

LARGE-PARTICLE COMPOSITES:

Concrete:

- The most common large-particle composite is concrete, made of a cement matrix that bonds particles of different size (gravel and sand.) The advantage of cement is that it can be poured in place, it hardens at room temperature and even under water, and it is very cheap.
- The disadvantages are that it is weak and brittle, and that water in the pores can produce crack when it freezes in cold weather.
- Concrete is cement strengthened by adding particulates. The use of different size (stone and sand) allows better packing factor than when using particles of similar size.
- Concrete is improved by making the pores smaller (using finer powder, adding polymeric lubricants, and applying pressure during hardening.

Reinforced concrete:

- It is obtained by adding steel rods, wires, mesh. Steel has the advantage of a similar thermal expansion coefficient, so there is reduced danger of cracking due to thermal stresses.

Pre-stressed concrete:

- It is obtained by applying tensile stress to the steel rods while the cement is setting and hardening. When the tensile stress is removed, the concrete is left under compressive stress, enabling it to sustain tensile loads without fracturing. Pre-stressed concrete shapes are usually prefabricated. A common use is in railroad or highway bridges.

Cermets:

- composites of ceramic particles (strong, brittle) in a metal matrix (soft, ductile) that enhances toughness. For instance, tungsten carbide or titanium carbide ceramics in Co or Ni. They are used for cutting tools for hardened steels.

Reinforced rubber:

- obtained by strengthening with 20-50 nm carbon-black particles. Used in auto tires.

DISPERSION-STRENGTHENED COMPOSITES:

- Metals and metal alloys may be strengthened and hardened by the uniform dispersion of several volume percent of fine particles of a very hard and inert material.
- The dispersed phase may be metallic or non-metallic; oxide materials are often used. Again, the strengthening mechanism involves interactions between the particles and dislocations within the matrix, as with precipitation hardening.
- The dispersion strengthening effect is not as pronounced as with precipitation hardening; however, the strengthening is retained at elevated temperatures and for extended time periods because the dispersed particles are chosen to be unreactive with the matrix phase.
- The high-temperature strength of nickel alloys may be enhanced significantly by the addition of about 3 vol% of thoria (ThO2) as finely dispersed particles; this material is known as thoria-dispersed (or TD) nickel.
- The same effect is produced in the aluminium–aluminium oxide system. Avery thin and adherent alumina coating is caused to form on the surface of extremely small (0.1 to 0.2 _m thick) flakes of aluminium, which are dispersed within an aluminium metal matrix; this material is termed sintered aluminium powder (SAP).

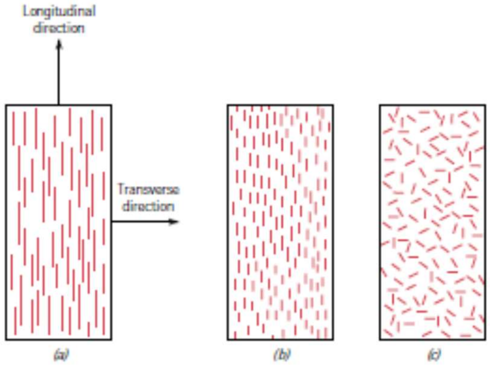
FIBER-REINFORCED COMPOSITES:

- The most important composites are those in which the dispersed phase is in the form of a fiber. Design goals of **fiber-reinforced composites** often include high strength and/or stiffness on a weight basis. These characteristics are expressed in terms of **specific strength** and **specific modulus** parameters.

- Fiber-reinforced composites with exceptionally high specific strengths and moduli have been produced that utilize low-density fiber and matrix materials.

INFLUENCE OF FIBER ORIENTATION AND CONCENTRATION

- With respect to orientation, two extremes are possible:
    - (1) a parallel alignment of the longitudinal axis of the fibers in a single direction
    - (2) a totally random alignment. Continuous fibers are normally aligned
- whereas discontinuous fibers may be aligned randomly oriented or partially oriented. Better overall composite properties are realized when the fiber distribution is uniform.



DISCONTINUOUS AND ALIGNED FIBER COMPOSITES

- Even though reinforcement efficiency is lower for discontinuous than for continuous fibers, discontinuous and aligned fiber composites are becoming increasingly more important in the commercial market.

- Chopped glass fibers are used most extensively; however, carbon and aramid discontinuous fibers are also employed. These short fiber composites can be produced having moduli of elasticity and tensile strengths

DISCONTINUOUS AND RANDOMLY ORIENTED FIBER COMPOSITES

- Normally, when the fiber orientation is random, short and discontinuous fibers are used
- By way of summary, then, aligned fibrous composites are inherently anisotropic, in that the maximum strength and reinforcement are achieved along the alignment (longitudinal) direction.
- In the transverse direction, fiber reinforcement is virtually nonexistent: fracture usually occurs at relatively low tensile stresses.

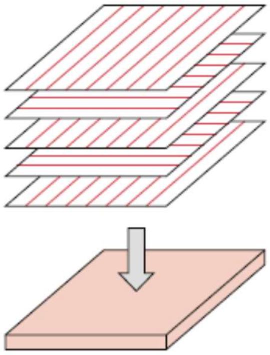
STRUCTURAL COMPOSITES

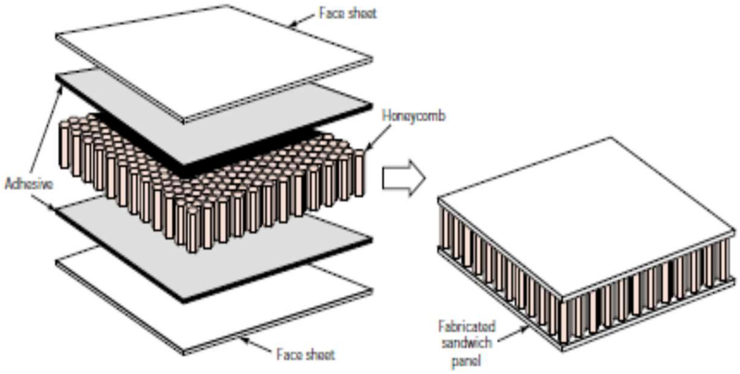
- A **structural composite** is normally composed of both homogeneous and composite materials, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements.
- Laminar composites and sandwich panels are two of the most common structural composites.

LAMINAR COMPOSITES:

- A **laminar composite** is composed of two-dimensional sheets or panels that have a preferred high-strength direction such as is found in wood and continuous and aligned fiber-reinforced plastics.
- The layers are stacked and subsequently cemented together such that the orientation of the high-strength direction varies with each successive layer as figure.

- For example, adjacent wood sheets in plywood are aligned with the grain direction at right angles to each other.





- Laminations may also be constructed using fabric material such as cotton, paper, or woven glass fibers embedded in a plastic matrix.
- Thus a laminar composite has relatively high strength in a number of directions in the two-dimensional plane; however, the strength in any given direction is, of course, lower than it would be if all the fibers were oriented in that direction.
- One example of a relatively complex laminated structure is the modern ski (see the schematic diagram on the chapter-opening page for this chapter).

SANDWICH PANELS:

- **Sandwich panels,** considered to be a class of structural composites, consist of two strong outer sheets, or faces, separated by a layer of less-dense material, or core, which has lower stiffness and lower strength.
- The faces bear most of the in-plane loading, and also any transverse bending stresses. Typical face materials include aluminum alloys, fiber-reinforced plastics, titanium, steel, and plywood. Structurally, the core serves two functions.
- First, it separates the faces and resists deformations perpendicular to the face plane. Secondly, it provides a certain degree of shear rigidity along planes that are perpendicular to the faces.
- Various materials and structures are utilized for cores, including foamed polymers, synthetic rubbers, inorganic cements, as well as balsa wood.
- Another popular core consists of a ‘‘honeycomb’’ structure—thin foils that have been formed into interlocking hexagonal cells, with axes oriented perpendicular to the face planes.
- Sandwich panels are found in a wide variety of applications; they include roofs, floors, and walls of buildings; and, in aircraft, for wings, fuselage, and tailplane skins.

PROCESSING OF FIBER-REINFORCED COMPOSITES

PULTRUSION:

- *Pultrusion* is used for the manufacture of components having continuous lengths and a constant cross-sectional shape (i.e., rods, tubes, beams, etc.).
- continuous fiber *rovings,* or *tows,*3 are first impregnated with a thermosetting resin; these are then pulled through a steel die that preforms to the desired shape and also establishes the resin/fiber ratio.
- The stock then passes through a curing die that is precision machined so as to impart the final shape; this die is also heated in order to initiate curing of the resin matrix.
- Apulling device draws the stock through the dies and also determines the production speed. Tubes and hollow sections are made possible by using center mandrels or inserted hollow cores.

- Principal reinforcements are glass, carbon, and aramid fibers, normally added in concentrations between 40 and 70 vol%. Commonly used matrix materials include polyesters, vinyl esters, and epoxy resins.
- Pultrusion is a continuous process that is easily automated; production rates are relatively high, making it very cost effective. Furthermore, a wide variety of shapes are possible, and there is really no practical limit to the length of stock that may be manufactured.

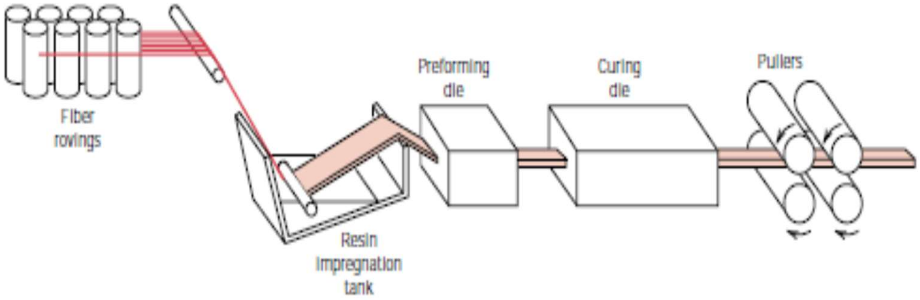


Fig: Pultrusion process

PREPREG PRODUCTION PROCESSES

- **Prepreg** is the composite industry's term for continuous fibre reinforcement preimpregnated with a polymer resin that is only partially cured.
- This material is delivered in tape form to the manufacturer, who then directly molds and fully cures the product without having to add any resin.
- It is probably the composite material form most widely used for structural applications.
- The prepregging process, represented schematically for thermoset polymers in Figure.it begins by collimating a series of spool-wound continuous fiber tows.
- These tows are then sandwiched and pressed between sheets of release and carrier paper using heated rollers, a process termed ''calendaring.''
- The release paper sheet has been coated with a thin film of heated resin solution of relatively low viscosity so as to provide for its thorough impregnation of the fibers.
- A ''doctor blade'' spreads the resin into a film of uniform thickness and width. The final prepreg product—the thin tape consisting of continuous and aligned fibers embedded in a partially cured resin—is prepared for packaging by winding onto a cardboard core.

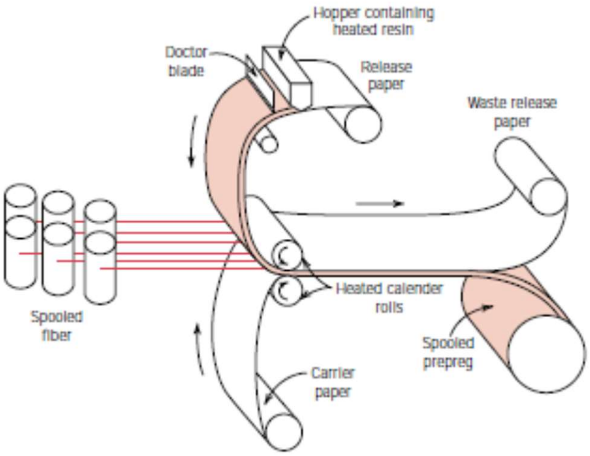
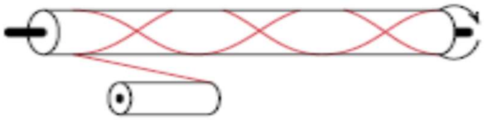


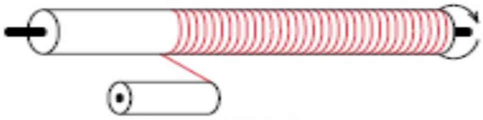
Fig: Prepreg process

FILAMENT WINDING

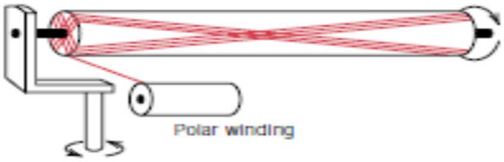
- *Filament winding* is a process by which continuous reinforcing fibers are accurately positioned in a predetermined pattern to form a hollow (usually cylindrical) shape.
- The fibers, either as individual strands or as tows, are first fed through a resin bath and then continuously wound onto a mandrel, usually using automated winding equipment is as shown in Figure
- After the appropriate number of layers have been applied, curing is carried out either in an oven or at room temperature, after which the mandrel is removed. As an alternative, narrow and thin prepregs (i.e., tow pregs) 10 mm or less in width may be filament wound.
- Various winding patterns are possible (i.e., circumferential, helical, and polar) to give the desired mechanical characteristics.
- Filament-wound parts have very high strength-to-weight ratios. Also, a high degree of control over winding uniformity and orientation is afforded with this technique. Furthermore, when automated, the process is most economically attractive.
- Common filament-wound structures include rocket motor casings, storage tanks and pipes, and pressure vessels. Manufacturing techniques are now being used to produce a wide variety of structural shapes that are not necessarily limited to surfaces of revolution (e.g., Ibeams).



Helical winding



Circumferential winding



Polar winding

POLYMER–MATRIX COMPOSITES

- **Polymer-matrix composites** (*PMC*s) consist of a polymer resin1 as the matrix, with fibers as the reinforcement medium. These materials are used in the greatest diversity of composite applications, as well as in the largest quantities, in light of their room-temperature properties, ease of fabrication, and cost.

GLASS FIBER-REINFORCED POLYMER (GFRP)COMPOSITES

- Fiberglass is simply a composite consisting of glass fibers, either continuous or discontinuous, contained within a polymer matrix; this type of composite is produced in the largest quantities.
- Fiber diameters normally range between 3 and 20 _m. Glass is popular as a fiber reinforcement material for several reasons:

    1. It is easily drawn into high-strength fibers from the molten state.

    2. It is readily available and may be fabricated into a glass-reinforced plastic economically using a wide variety of composite-manufacturing techniques.

    3. As a fiber, it is relatively strong, and when embedded in a plastic matrix, it produces a composite having a very high specific strength.

    4. When coupled with the various plastics, it possesses a chemical inertness that renders the composite useful in a variety of corrosive environments.

- There are several limitations to this group of materials. In spite of having high strengths, they are not very stiff and do not display the rigidity that is necessary for some applications (e.g., as structural members for airplanes and bridges).
- Most fiberglass materials are limited to service temperatures below 200C (400F); at higher temperatures, most polymers begin to flow or to deteriorate. Service temperatures may be extended to approximately 300C (575F) by using high-purity fused silica for the fibers and high-temperature polymers such as the polyimide resins.
- Many fiberglass applications are familiar: automotive and marine bodies, plastic pipes, storage containers, and industrial floorings. The transportation industries are utilizing increasing amounts of glass fiber-reinforced plastics in an effort to decrease vehicle weight and boost fuel efficiencies.

CARBON FIBER-REINFORCED POLYMER (CFRP) COMPOSITES:

- Carbon is a high-performance fiber material that is the most commonly used reinforcement in advanced (i.e., non-fiberglass) polymer-matrix composites. The reasons for this are as follows:
  - **1.** Carbon fibers have the highest specific modulus and specific strength of all reinforcing fiber materials.
  - **2.** They retain their high-tensile modulus and high strength at elevated temperatures; high-temperature oxidation, however, may be a problem.
  - **3.** At room temperature carbon fibers are not affected by moisture or a wide variety of solvents, acids, and bases.
  - **4.** These fibers exhibit a diversity of physical and mechanical characteristics, allowing composites incorporating these fibers to have specific engineered properties.
  - **5.** Fiber and composite manufacturing processes have been developed that are relatively inexpensive and cost effective.
- Carbon-reinforced polymer composites are currently being utilized extensively in sports and recreational equipment (fishing rods, golf clubs), filament-wound rocket motor cases, pressure vessels, and aircraft structural components—both military and commercial, fixed wing and helicopters (e.g., as wing, body, stabilizer, and rudder components).

OTHER FIBER REINFORCEMENT MATERIALS

- Glass, carbon, and the aramids are the most common fiber reinforcements incorporated in polymer matrices. Other fiber materials that are used to much lesser degrees are boron, silicon carbide, and aluminum oxide; tensile moduli, tensile strengths, specific strengths, and specific moduli of these materials in fiber form are contained.

METAL–MATRIX COMPOSITES

- **Metal-matrix composites** (*MMC*s), the matrix is a ductile metal. These materials may be utilized at higher service temperatures than their base metal counterparts; furthermore, the reinforcement may improve specific stiffness, specific strength, abrasion resistance, creep resistance, thermal conductivity, and dimensional stability.
- Some of the advantages of these materials over the polymermatrix composites include higher operating temperatures, nonflammability, and greater resistance to degradation by organic fluids.
- Metal-matrix composites are much more expensive than PMCs, and, therefore, their (MMC) use is somewhat restricted.
- The superalloys, as well as alloys of aluminum, magnesium, titanium, and copper, are employed as matrix materials. The reinforcement may be in the form of particulates, both continuous and discontinuous fibers, and whiskers.

- Some matrix–reinforcement combinations are highly reactive at elevated temperatures. Consequently, composite degradation may be caused by high-temperature processing, or by subjecting the MMC to elevated temperatures during service.
- Recently, some of the automobile manufacturers have introduced engine components consisting of an aluminum-alloy matrix that is reinforced with alumina and carbon fibers; this MMC is light in weight and resists wear and thermal distortion.
- Aerospace structural applications include advanced aluminum alloy metal-matrix composites; boron fibers are used as the reinforcement for the Space Shuttle Orbiter, and continuous graphite fibers for the Hubble Telescope.

CERAMIC–MATRIX COMPOSITES

- ceramic materials are inherently resilient to oxidation and deterioration at elevated temperatures; were it not for their disposition to brittle fracture, some of these materials would be ideal candidates for use in high temperature and severe-stress applications, specifically for components in automobile and aircraft gas turbine engines. Fracture toughness values for ceramic materials
- Ceramic-matrix composites may be fabricated using hot pressing, hot isostatic pressing, and liquid phase sintering techniques. Relative to applications, SiC whisker-reinforced alumina are being utilized as cutting tool inserts for machining hard metal alloys; tool lives for these materials are greater than for cemented carbide.

CARBON–CARBON COMPOSITES

- One of the most advanced and promising engineering material is the carbon fiber reinforced carbon-matrix composite, often termed a **carbon–carbon composite;** as the name implies, both reinforcement and matrix are carbon.
- These materials are relatively new and expensive and, therefore, are not currently being utilized extensively. Their desirable properties include high-tensile moduli and tensile strengths that are retained to temperatures more than 2000C (3630F), resistance to creep, and relatively large fracture toughness values.
- Furthermore, carbon–carbon composites have low coefficients of thermal expansion and relatively high thermal conductivities; these characteristics, coupled with high strengths, give rise to a relatively low susceptibility to thermal shock.
- Their major drawback is a propensity to high-temperature oxidation.
- The carbon–carbon composites are employed in rocket motors, as friction materials in aircraft and high-performance automobiles, for hot-pressing molds, in components for advanced turbine engines, and as ablative shields for re-entry vehicles.
- The primary reason that these composite materials are so expensive is the relatively complex processing techniques that are employed. Preliminary procedures are like those used for carbon-fiber, polymer-matrix composites. That is, the continuous carbon fibers are laid down having the desired two- or three-dimensional pattern; these fibers are then impregnated with a liquid polymer resin, often a phenolic; the workpiece is next formed into the final shape, and the resin can cure.

ENGINEERING METALLURGY

UNIT-VI

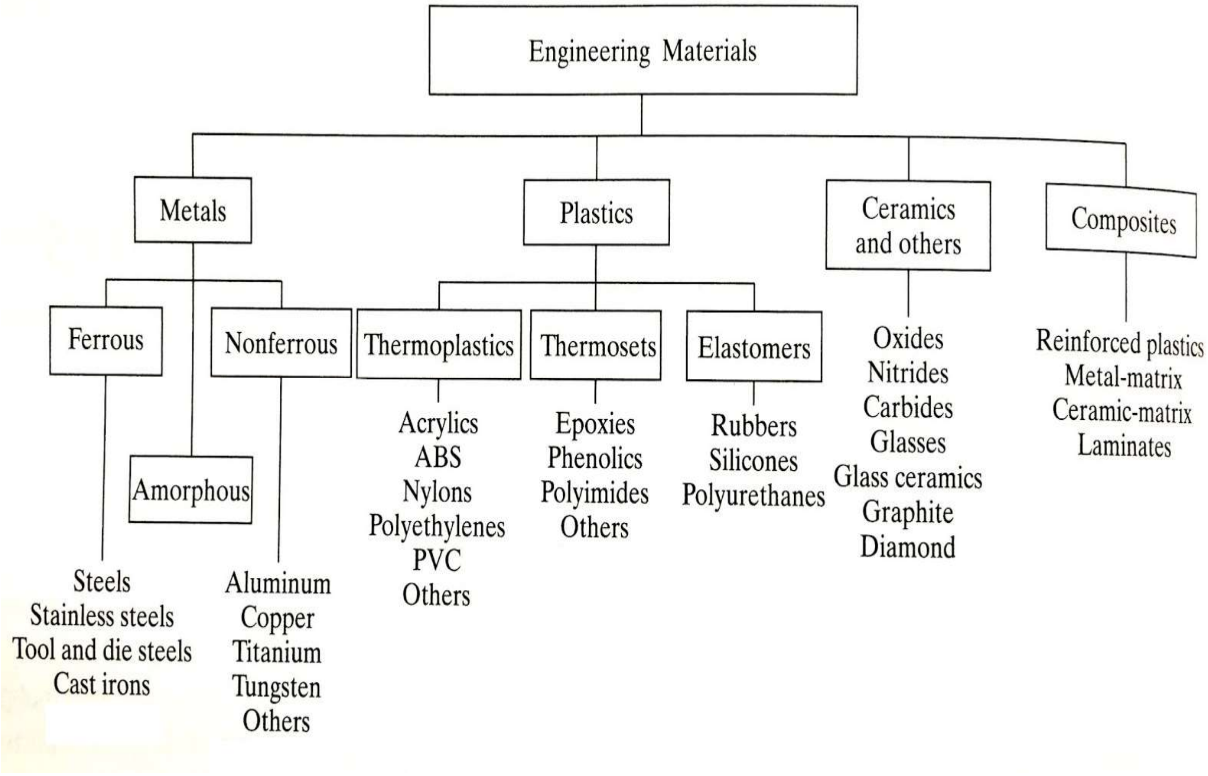
Material Selection & Characterization

Introduction:

Materials are an important aspect of engineering design and analysis. The importance of materials science and engineering can be noted from the fact that historical ages have been named after materials. Therefore, it becomes imperative to highlight the importance of engineering materials for all engineers related to the various aspects of engineering applications.

There is a wide variety of materials available which have shown their potential in various engineering fields ranging from aerospace to house hold applications. The materials are usually selected after considering their characteristics, specific application areas, advantages and limitations. The challenge for designers is to select an optimal material suitable for the specific design requirements. The stringent design requirements generally lead to development of new materials to meet the specific operating conditions and environments.

Classification of Engineering Materials:



Engineering requirements of materials: - There're 3 basic requirements.

(a) Fabrication (b) Service (c)Property of a material

Fabrication: -

- It should be able to get shape or joint with other material without any circumstances.
- The material shouldn't react with fabricated material in any conditions.

Service: -

- The material selected for the purpose must stand up to the service.
- Engineering parts should be made up with least initial cost.

Property of a material: - The important properties of materials are as follows:

1. Mechanical Properties (stress, elasticity, plasticity, strength, ductility, etc.)
2. Chemical Properties (compositions, bonding, melting & boiling point.etc.)
3. Thermal Properties (thermal conductivity, thermal expansion, specific heat.)
4. Optical Properties (absorbtivity, reflectivity, transitivity)
5. Electrical Properties (conductivity, resistivity, semi- conductivity, insulation)
6. Magnetic Properties (permeability, hysteresis)

Introduction to Materials Selection:

The Material Selection Problem Design of an engineering component involves three interrelated problems:

(i) selecting a material
(ii) specifying a shape
(iii) choosing a manufacturing process.

Getting this selection right the first time by selecting the optimal combination your design has enormous benefits to any engineering-based business. It leads to lower product costs, faster time-to-market, a reduction in the number of in-service failures and, sometimes, significant advantages relative to your competition.

But to realize these benefits, engineers have to deal with an extremely complex problem. There are literally tens of thousands of materials and hundreds of manufacturing processes. No engineer can expect to know more than a small subset of this ever-growing body of information. Furthermore, there are demanding and shifting design requirements such as cost, performance, safety, risk and aesthetics, as well as environmental impact and recycle-ability. This document is meant to introduce the material selection process.

Material Selection

The basic question is how do we go about selecting a material for a given part? This may seem like a very complicated process until we realize than we are often restrained by choices we have already made. For example, if different parts must interact then material choice becomes limited. When we talk about choosing materials for a component, we consider many different factors. These factors can be broken down into the following areas.

1. Material Properties
2. The expected level of performance from the material
3. Material Cost and Availability
4. Material must be priced appropriately (not cheap but right)
5. Material must be available (better to have multiple sources)
6. Processing must consider how to make the part.

7. Environment: -

The effect that the service environment has on the part
The effect the part has on the environment
The effect that processing has on the environment

Now clearly these issues are inter-linked in some fashion. For example, cost is a direct result of how difficult a material is to obtain and to machine. And the effect of the environment on the material is clearly related to the material properties. So if we really want to use a novel or unusual material, the choice must be made early in the design process. Then we can do the detailed design work using the correct material properties.

Consider the example of wooden airplanes and metal-framed airplanes. If we were to design an airplane of either material we will have to make the choice early. The end designs are quite different. So, the material choice can radically alter the final design. But the possibility also exists that it may not. After all what is the real difference between a 1045 and a 1035 carbon steel?

.

The following procedure is taken from Material Selection in Mechanical Design by Michael Ashby.

Four Basic Steps: -

1) Translation: express design requirements as constraints and objectives
2) Screening: eliminate materials that cannot do the job
3) Ranking: find materials that best do the job
4) Supporting Info: handbooks, expert systems, web, etc.

Step 1) Translation: -

Function: What does the component do?
Objective: What essentials conditions must be met?
Constraints: What is to be maximized or minimized?
Free Variables: Identify which design variables are free?

Example: Tie Rod
Function: Support a tensile load
Objective: Minimize mass
Constraints: Required length
Load carrying capability without failure
Free Variables: Cross-sectional area Material

$m = A*L*Density$
$F/A < Yield Stress$

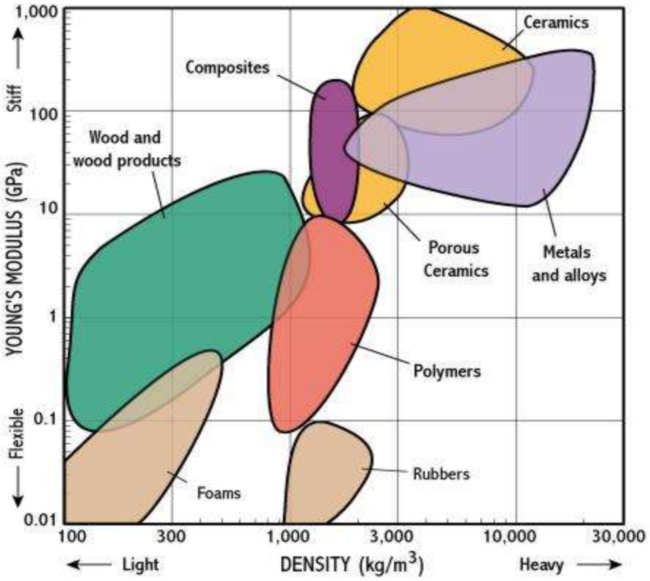
Eliminate free variable

$m >= (F)(L)$ (Density/Yield Stress) therefore minimize weight by maximizing Yield Stress / Density.

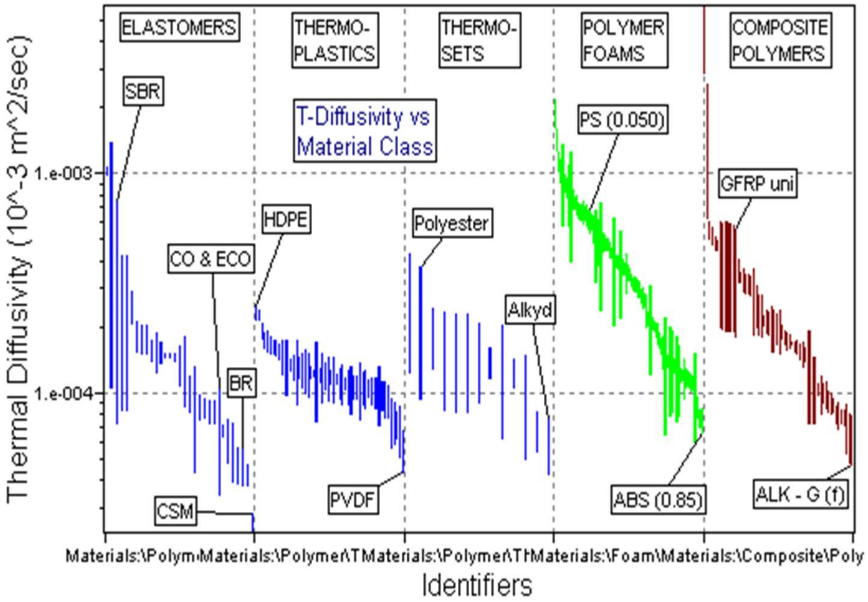
Step 2) Screening: - Methods to evaluate large range of materials

Material Bar Charts
Material Property Charts (density vs. Young's Modulus)
Screen on Constraints
Rank on Objectives

Example: Material Property Chart



Material bar chart:



Step 3) Ranking: - What if multiple materials remain after screening?

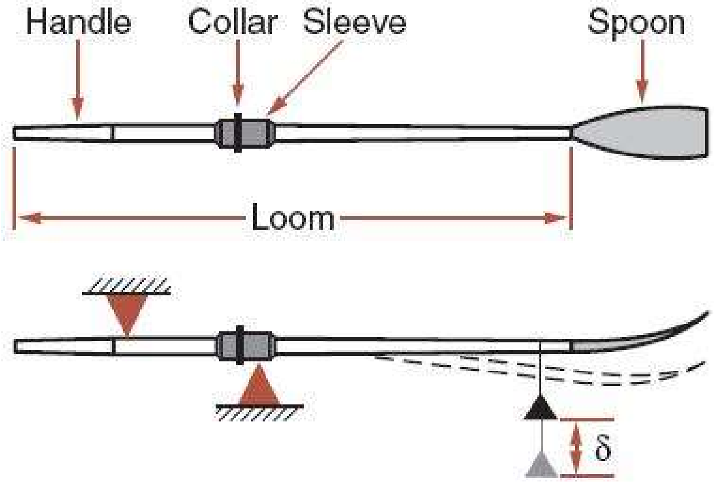
Rank on Objectives

Objectives define performance metrics

Step 4) Select, then verify with any supporting materials.

CASE STUDY ON MATERIAL SELECTION:

CASE 1: Materials for oars



1. Mechanically speaking, an oar is a beam, loaded in bending.
2. It must be strong enough to carry, without breaking, the bending moment exerted by the oarsman
3. It must have a stiffness to match the rower's own characteristics
4. It must give the right ―feel
5. It must be light the extra weight increases the wetted area of the hull and the drag that goes with it.

Thus, an oar is a beam of specified stiffness and minimum weight

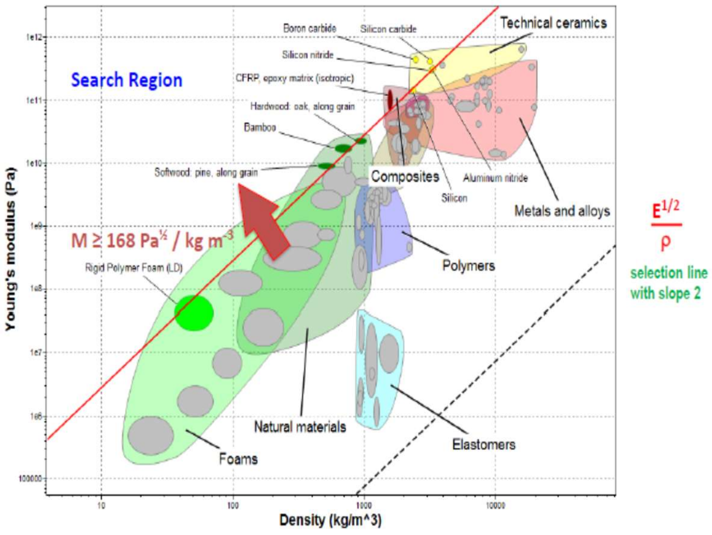
The material index for a light, stiff beam: $M = \dfrac{E^{1/2}}{\rho}$

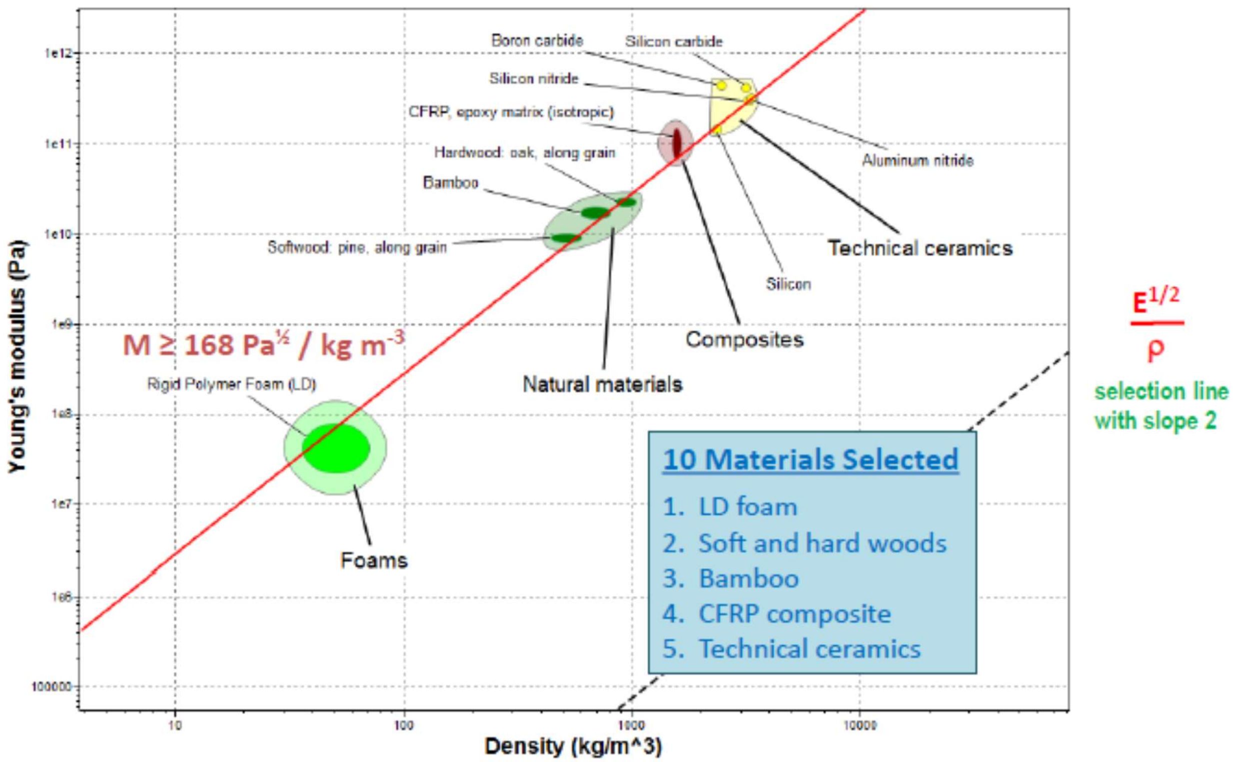
There are other obvious constraints:

Oars are dropped, and blades sometimes clash. The material must be tough enough to survive this. So brittle materials (having toughness G1C less than 1 kJ/m2) are unacceptable.

Design Requirements for the Oar

Function	Oar—meaning light, stiff beam
Constraints	Length L specified Bending stiffness S^* specified Toughness $G_{1c} > 1\ \mathrm{kJ/m^2}$
Objective	Minimize the mass m
Free variables	Shaft diameter Choice of material





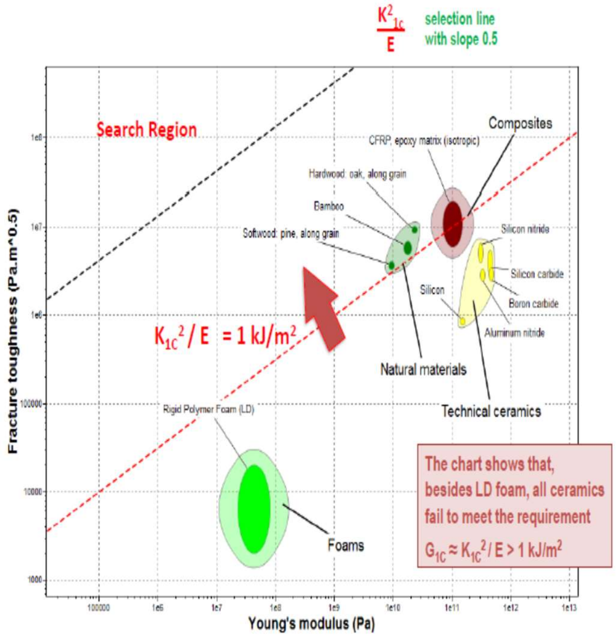
10 Materials Selected

1. LD foam
2. Soft and hard woods
3. Bamboo
4. CFRP composite
5. Technical ceramics

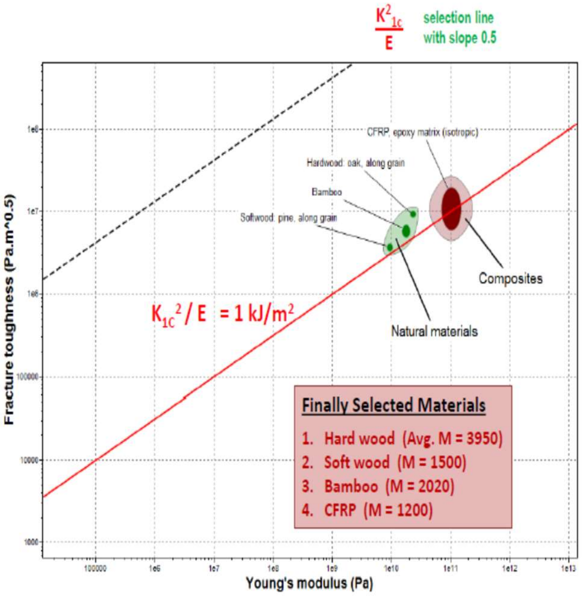
After 1st Criterion,

1. LD foam 2. Soft and hard woods 3. Bamboo 4. CFRP composite 5. Technical ceramics

These selections must satisfy the other constraint (limit on toughness) G1C ≈ K1C2 / E > 1 kJ/m2



The chart shows that, besides LD foam, all ceramics fail to meet the requirement $G_{1C} \approx K_{1C}^2 / E > 1$ kJ/m^2



Finally Selected Materials

1. Hard wood (Avg. M = 3950)
2. Soft wood (M = 1500)
3. Bamboo (M = 2020)
4. CFRP (M = 1200)

Finally, Selected Materials :-

1. Hard wood (M = 3950)	2. Soft wood (M = 1500)
3. Bamboo (M = 2020)	4. CFRP (M = 1200)

So, the recommendation is clear: Make your oars out of hard wood

- Bamboo would only be suitable for the handle in the shape of a tube and could be combined with a spoon of another material (i.e. shaping requirement)
- If the maximum materials index of CFRP is chosen, the oar will be lighter (Wooden oar ~ 4.0 - 4.3 kg; CFRP oar ~ 3.9 kg)
- But this is not necessarily true in all cases as the indices overlap this would require the evaluation of individual products to obtain the desired outcome for the design.

MATERIAL CHARACTRIZATION TECHNIQUES

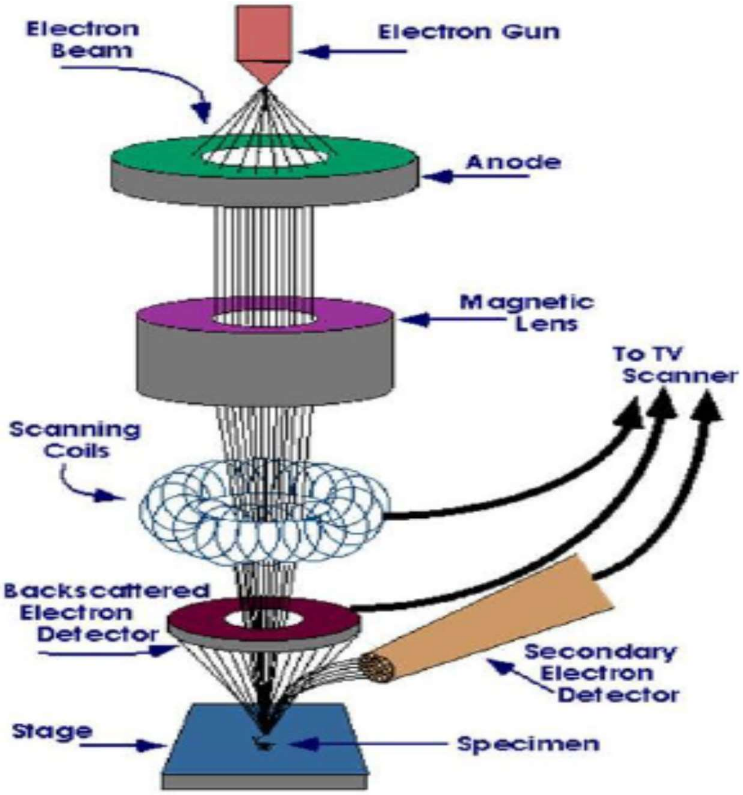
Scanning Electron Microscope:

In this class of microscopes that use electrons are used rather than visible light, to produce magnified images, especially of objects having dimensions smaller than the wavelengths of visible light, with linear magnification approaching or exceeding a million.

Working principle: An electron microscope forms a three-dimensional image on a cathode ray tube by moving a beam of focused electrons across an object and reading both the electrons scattered by the object and the secondary electrons produced by it. High powered indirect microscope produces an image by bombarding a sample with a beam of high energy electrons. The electrons emitted from the sample are then scanned to form a magnified image which allows the examination of the structure, relief and morphology of materials. In addition to its great magnification, the SEM also has a great depth of field. Most SEM also have a facility to analyze the X-rays given off by the target because of its bombardment and, as each element in the periodic table produces its own X-ray spectrum, this can be used to determine the elemental content of the sample.

Scanning electron microscope (SEM) is used for studying the surface topography, microstructure, and chemistry of metallic and nonmetallic specimens at magnifications from 50 up to ~ 100, 000 X, with a resolution limit < 10nm (down to ~ 1nm) and a depth of focus up to several μm (at magnifications ~ 10, 000 X). In SEM, a specimen is irradiated by an electron beam and data on the specimen are delivered by secondary electrons coming from the surface layer of thickness ~ 5nm and by backscattered electrons emitted from the volume of linear size ~ 0.5μm. Due to its high depth of focus SEM is frequently used for studying fracture surfaces.

High resolving power makes SEM quite useful in metallographic examinations. Sensibility of backscattered electrons to the atomic number is used for the detection of phases of different chemistry. Electron channeling in SEM makes it possible to find the orientation of single crystals by electron channeling pattern (ECP) or of grains by selected area channeling pattern (SACP).



X-ray Diffraction (XRD): -

Diffraction occurs when waves interact with a regular structure whose repeat distance is about the same as the wavelength of X-ray waves. X-rays have wavelengths of the order of a few angstroms, the same as typical interatomic distances in crystalline solids so they can interact with atoms and can gain the information at atomic level. Crystalline materials can be described by their unit cell which is the smallest unit describing the material. In the material, this unit cell is then repeated over and over in all directions. This will result in planes of atoms at certain intervals. Fig. 2.3 shows the schematic representation of x-ray diffractometer.

X-ray powder diffraction is a powerful non-destructive testing method for determining a range of physical and chemical characteristics of materials. It is widely used in all fields of science and technology. The applications include phase analysis, i.e. the type and quantities of phases present in the sample, the crystallographic unit cell and crystal structure, crystallographic texture, crystalline size, macro-stress and micro strain, and electron radial distribution functions. X-ray diffraction results from the interaction between X-rays and electrons of atoms.

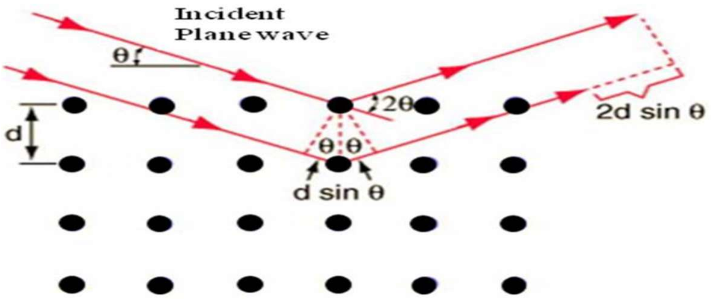
Depending on the atomic arrangement, interferences between the scattered rays are constructive when the path difference between two diffracted rays differs by an integral number of wavelengths. This selective condition is described by the Bragg equation, also called "Bragg's law":

$$n \lambda = 2 d_H \sin \theta_H$$

where dH = inter planar distance (d-spacing),

θH = half angle between incident and reflected beam (or the angle between the incident/reflected beam and particular crystal planes under consideration), n = order of reflection (integer value),

λH = wave length of x-rays. H describes the Miller indices triplet *(h k l)* of each lattice plane.



Schematic representation of diffraction of x-rays by crystallographic plane (Bragg's Law)

Thermogravimetric analysis:

Thermogravimetric (TG) is a branch of thermal analysis examining the mass changes of a sample as a function off temperature (in the scanning mode) or as a function of time (in the isothermal mode). Thermal gravimetric analysis or thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).Changes in the mass of a sample due to various thermal events (desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition) are studied while the sample is subjected to a program of change in temperature. Therefore, it is used in the analysis of volatile products, gaseous products lost during the reaction in thermoplastics, thermosets, elastomers, composites, films, fibers, coatings, paints, etc.

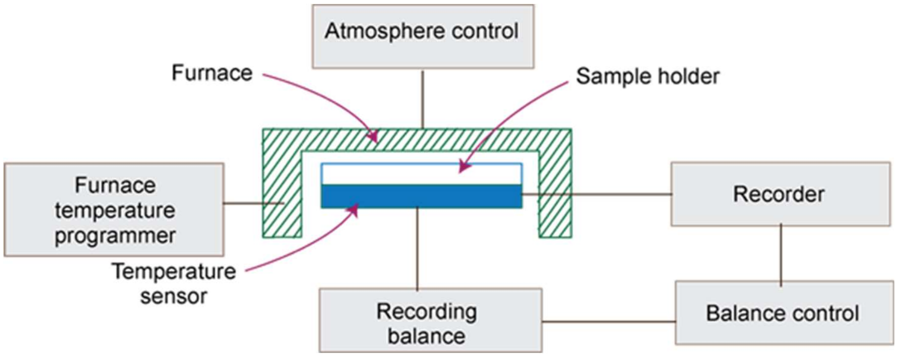
There are different types of TGA available:

i. Isothermal or Static TGA: In this case, sample is maintained at a constant temperature for a period of time during which change in weight is recorded.

ii. Quasi-static TGA: In this technique, the sample is heated to a constant weight at each of a series of increasing temperature.

iii. Dynamic TGA: In this type of analysis, the sample is subjected to condition of a continuous increase in temperature at a constant heating rate, i.e., usually linear with time.

- The instrument used for TGA analysis is a programmed precision balance for a rise in temperature Thermo balance consists of an electronic microbalance (important component), a furnace, a temperature programmer and a recorder.



The plot of mass change in percentage versus temperature or time (known as TGA curves) is the typical result of TGA analysis as shown below.

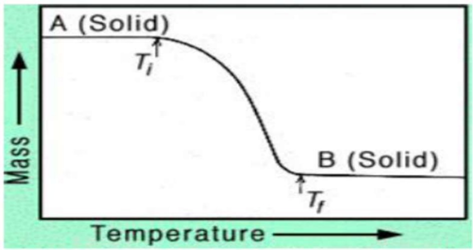


Fig:- The plot of mass change with temperature.

- There are two temperatures in the reaction: T_i (starting of decomposition temperature) and T_f(final temperature) representing the lowest temperature at which the onset of a mass change is seen and the lowest temperature at which the process has been completed, respectively. The reaction temperature and interval (T_f - T_i) strongly depend on the conditions of the experiments. Hence, they cannot have any fixed values.

Interpretation of TGA Curves:

TGA curves are typically classified into seven types according to their shapes. Figure 23.03 shows schematic of various types of TGA curves.

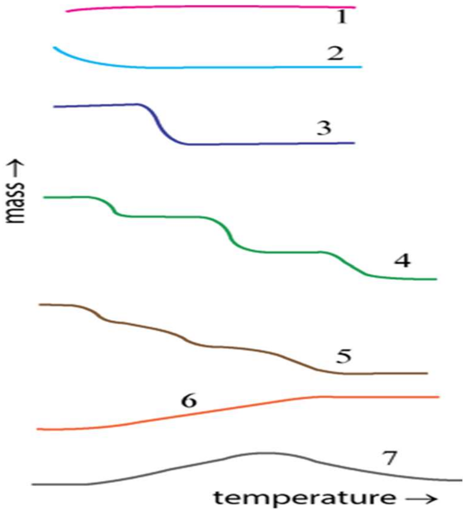


Figure: - Schematic of various types of TGA curves.

- Curve 1: No change: This curve depicts no mass change over the entire range of temperature, indicating that the decomposition temperature is greater than the temperature range of the instrument.
- Curve 2: Desorption / drying: This curve shows that the mass loss is large followed by mass plateau. This is formed when evaporation of volatile product(s) during desorption, drying or polymerization takes place. If a non-interacting atmosphere is present in the chamber, then curve 2 becomes curve 1.

- Curve 3: Single stage decomposition: This curve is typical of single-stage decomposition temperatures having T_i and T_f.
- Curve 4: Multistage decomposition: This curve reveals the multi-stage decomposition processes as a result various reaction.
- Curve 5: Similar to 4, but either due to fast heating rate or due to no intermediates.
- Curve 6: Atmospheric reaction: This curve shows the increase in mass. This may be due to the reactions such as surface oxidation reactions in the presence of an interacting atmosphere.
- Curve 7: Similar to curve 6, but product decomposes at high temperatures. For example, the reaction of surface oxidation followed by decomposition of reaction product(s).

- **URLs/Hyperlinks for further study:**

1. https://nptel.ac.in/courses/112104122/24
2. https://nptel.ac.in/courses/112101005/5