UNIT–IV

ENGINEERING MATERIALS

Nanomaterials: Introduction - Fullerenes-graphene-Carbon nano tubes-types (single walled carbon tubes and multi walled carbon nanotubes) advantages and applications- Nano composites.

Polymeric composites: Introduction - types of composites - Particle reinforced - fibre reinforced-structural composites.Abrasives-Classification and properties, Refractories-Classification and properties, Lubricants- Classification and properties.

NANO MATERIAL

Nanomaterials describe, in principle, materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometres (10^{-9} meter) but is usually 1—100 nm (the usual definition of nanoscale.

Properties

- Strength
- Electrical
- Thermal
- Defects
- One-Dimensional Transport
- Toxicity

Strength: Carbon nanotubes have the strongest tensile strength of any material known.It also has the highest modulus of elasticity

- If the nanotube structure is armchair then the electrical properties are metallic
- If the nanotube structure is chiral then the electrical properties can be either semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor
- In theory, metallic nanotubes can carry an electrical current density of 4×10^{9} A/cm^{2} which is more than 1,000 times greater than metals such as copper

Thermal properties:

- All nanotubes are expected to be very good thermal conductors along the tube, but good insulators laterally to the tube axis.

- It is predicted that carbon nanotubes will be able to transmit up to 6000 watts per meter per Kelvin at room temperature; compare this to copper, a metal well-known for its good thermal conductivity, which transmits 385 watts per meter per K.
- The temperature stability of carbon nanotubes is estimated to be up to 2800^{o}C in vacuum and about 750^{o}C in air.

Applications:

- Nanotubes hold the promise of creating novel devices, such as carbon-based single-electron transistors, that significantly smaller than conventional transistors.
- Nanotubes' excellent strength to weight ratio creates the potential to build an elevator tospace.
- Nanotubes and other Fullerenes can be filled with molecules that have either an electronic or structural property which can be used to represent the quantum bit (Qubit) of information, and which can be associated with other adjacent Qubits.
- carbon nanotubes shorter than about 200 nanometers readily enter into human lung cells similar to the way asbestos does, and may pose an increased risk to health.
- Carbon nanotubes along with the majority of nanotechnology, are an unexplored matter, and many of the possible health hazards are still unknown.

Synthesis:

- **Arc discharge**
  - CNTs Can be found in the carbon soot of graphite electrodes during an arc discharge involving high current. This process yields CNTs with lengths up to 50 microns.
- **Laser Ablation**
  - In the laser ablation process, a pulsed laser vaporizes a graphite target in a high-temperature reactor while an inert gas is inserted into the reactor. Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses.
  - Other methods where CNTs are created
  - **Chemical Vapor Decomposition**
  - **Natural, incidental, and controlled flame environments**

There are two main approaches to synthesize nanomaterial or nanoparticle. One is top-down approach and another is the bottom-up approach.

1. **Top-down approach:**

As the name suggests, the top-down approach means from top(larger) to bottom(smaller). This approach is similar to making a statue made of stone. As in making of a statue, a bulk or big piece of stone is taken, similarly in top-down approach; a bulk piece of material is taken. Then carving and cutting is done until desired shape is achieved. Example: Different kinds of lithographic techniques cutting (such as electron beam, photo ion beam or X-ray lithograph cutting), etching, grinding, ball milling and sol gel technique.

2. **Bottom-up approach:**

As the name suggests, the bottom-up approach means from bottom(smaller) to top or up(larger). In this technique, a nanometric structure is taken then using methods of assembly or self assembly, a mechanism is developed which is larger than where it is started.

Example: all cell use enzymes to create DNA by taking constituent molecules and binding them together to make the final component.

Nanotubes

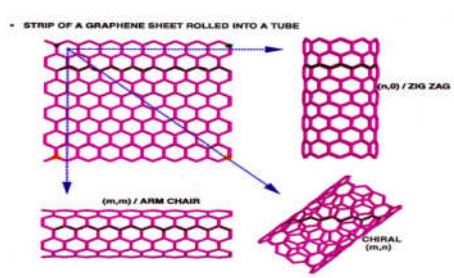
Structure

- Carbon exists in many allotropic forms, diamond, graphite, fullrenes, and carbon nanotubes. Thus carbon nanotube (CNT) is one of the allotropic forms of carbon.
- It has a hollow cylindrical form formed by hexagonal cells of carbon and is constitutionally equivalent to rolled up graphene sheets and closed ends but can be open ends.
- The flat separated layer (monolayer) of graphite called graphene rolled to form tubular structure, is essentially the carbon nano tube.

Depending on the number of graphene sheets that is rolled together

(i) single –walled nanotubes (SWNT) when only one graphene sheet is rolled into cylindrical tube (diameter-1 atom thick~1-3nm)and

(ii) multiwalled nanotube (MWNT) when 2^{+n} graphene sheets (50 layers) are rolled to form one tubular structure (diameter ~ 2-100nm)



Depending on the way the rectangular sheet of graphene is rolled to form a tube, the SWNT'sare further classified into **armchair, zig-zag or chiral single-walled nanotubes**.

- Depending on the way of rolling of graphene sheets (as shown in Fig),single- walled nanotubes of different types, viz. armchair, zig-zag and chiral could be produced.
- They can be represented using the method given by Hamada.
- These points coincide to form the (n, m) nanotube.
- Thus armchair, zig-zag and chiral nanotubes can be represented as (n, n), (n, 0) and (n, m) respectively

Properties:

- CNTs have Very High Tensile Strength.
- CNTs are Highly Flexible- can be bent considerably without damage.
- CNTs are Very Elastic ~18% elongation to failure.
- CNTs have High Thermal Conductivity.
- CNTs have a Low Thermal Expansion CoefficientMechanical properties
- Carbon nanotubes are very strong and their elastic flexibility is indicated by young modulus. Young modulus of CNT is 10 times greater than stee
- Electrical properties:

Electrical properties of CNT vary between metallic to semiconducting material. It depends on the diameter and chirality of the nanotubes. The high electrical conductivity of CNT is due to minimum defects in the strcture

Due to well-defined geometry, exceptional mechanical properties and extradinary electrical characteristics of CNTs are used as nanoelectric circuits, nanoelectrochemical systems, nanorobots etc.

Mechanical strength

- Carbon nanotubes have a very large Young modulus in their axial direction.
- The Nano tube is very flexible because of the great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties.
- Table gives the comparison of Young's modulus, tensile strength and density of carbon nanotubes with some other materials

Optical activity

- Theoretical studies have revealed that the optical activity of chiral nanotubes disappears if the nanotubes become larger.
- It is expected that other physical properties are influenced by these parameters too.
- Use of the optical activity might result in optical devices in which CNTs play an important role.

Applications of CNT

Metallic SWNTs with high current densities and semiconductor MWNTs AND SWNTs have found lot of applicationsin the electronic field. **As biosensors and as nanorobotics includes**

- Transistors / oscillators / diodes - Interconnects
- Logic circuits, - Displays/emitters
- Memory and CMOS integration
- Transparent conductors
- Conductive plastics / EM shielding

1. **Storage device**;
   Important role in batter technology. It act as charge carriers which can be stored inside the nanotube. Eg; CNT in fuel cells and lithium batteries.
2. **ProtectiveSheilds**:Shielding materials for protective electronic equipment against electromagnetic radiation.
3. **Sensors for gases:**The gases like NO_2 and NH_3 can be detected on the basis of increase in electrical conductivity of CNTS.
4. Dry delivery system
5. Reinforcing elements in composites.
6. Catalysis in chemical reaction

CARBON NANOTUBE

Carbon nanotubes (CNTs) have been fundamental for various developments in our current technology ever since it discovered. Nanotechnology is one such field which had tremendous advances. The unique structure of carbon nanotube, combined with its unique mechanical and electrical properties makes it a ‘wonder material’ in the real sense.

Types of Carbon Nanotubes

There are mainly two types of carbon nanotubes that are in use today:

- **Single-walled carbon nanotube (SWCNT)**

A single-walled carbon nanotube (SWCNT) is a seamless cylinder which consists of only one layer of graphene. It shows impressively unique electrical properties.

- **Multi-walled carbon nanotube (MWCNT)**

The multi-walled carbon nanotube (MWCNT) is also cylindrical in shape, with multiple concentric layers of graphene composing it. These are comparatively complex structure and variety.

Difference between SWCNT and MWCNT

These are the stark differences between single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT)

- **Layers**

Single-walled carbon nanotubes are composed of a single layer of graphene which forms a cylindrical shape. It observed as two planes under a transmission electron microscope. While the Multi-walled carbon nanotubes made of multiple layers of graphene, which formed in a concentric pattern around the smallest nanotube.

- **Allotropic**

Single-walled carbon nanotubes are allotrope of SP2 hybridized carbon, which is much similar to fullerenes. The structure forms six-atom carbon rings in a hexagonal shape, which is identical to that in graphite. On the other hand, multi-walled carbon nanotubes involve several tubes which set in concentric layers in a cylindrical shape.

- **Strength**

Research studies have proven that multi-walled carbon nanotubes are remarkably stronger than the impressively strong single-walled carbon nanotube.

- **Efficiency**

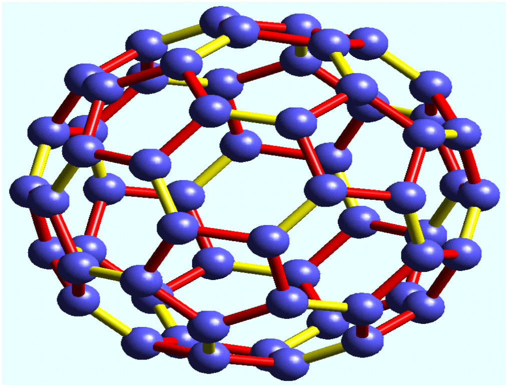
It also shows that multi-walled carbon nanotubes are significantly better at working in the highly corrosive atmosphere. The MWCNTs show lowered loss or oxygen reduction when used as a catalyst for fuel cells as compared to SWCNT.

Fullerene

- ***The Buckminsterfullerene,named after the American architect Buckminster Fuller, The most symmetrical large molecule,*** discovered in 1985 got Nobel prize Chemistry 1996.
- The structure of the C_{60}Buckyball is a combination of 12 pentagonal and 20 hexagonal rings, forming a spheroid shape with 60 vertices for 60 carbons. Figure shows the structure of the molecule, which reveals how the pentagonal rings sit at the vertices of an icosahedron such that no two pentagonal rings are next to each other.
- The average C-C bond distance measured using nuclear magnetic resonance (NMR) is 1.44A°.
- A diameter of 7.09 A° is calculated for the C_{60} based on the fact that the C-C distance is equal to 1.40 A° for the hexagon bonds and 1.46 A° for the pentagonal bonds length.

Properties:

- Quite stable from chemical and physical points of view (breaking the balls requires temperatures of about 1000 °C).
- Highest tensile strength of any known 2D structure or element.
- Highest packing density of all known structures.
- Impenetrable to all elements under normal circumstances, even to a helium atom **with an** energy of 5 eV.
- Symmetric shape
  → **lubricant**
- Large surface area
  → **catalyst**
- High temperature (~500^{o}C)
- High pressure
- Hollow
- → **caging particles**



Applications:

- Designing high performance MRI contract agents,
- Xray imaging contract agents,
- Photo dynamic theraphy and hrug
- Gene delivery.

Commercial and biological possibilities exist:

- **Sunscreens**: due to photophysical properties
- **Antibacterials:**due to redox and general chemical reactivity
- **Superconducting materials**: due to physical properties

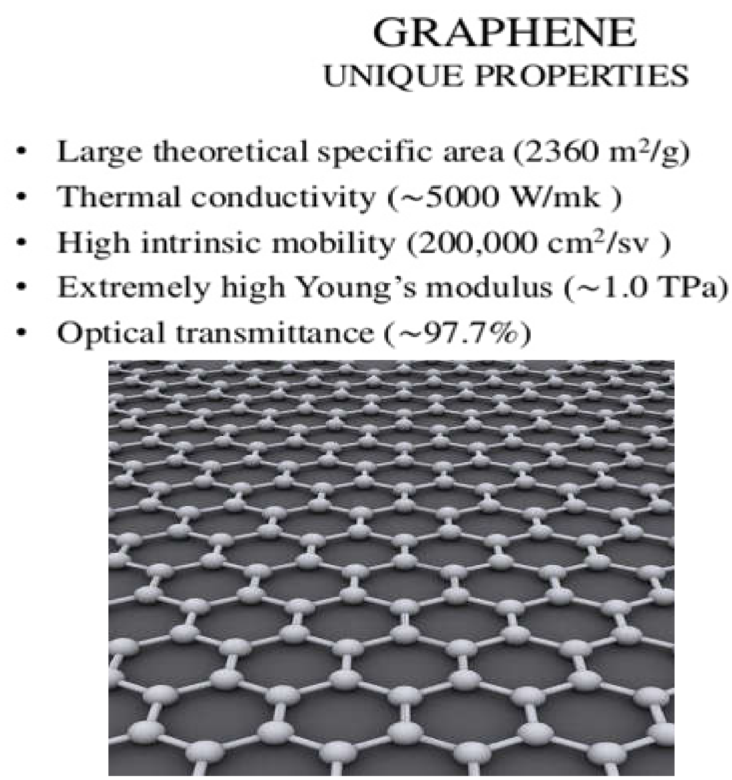
Graphene

Studies on graphite layers for past hundred years, Graphene theory first explored by P.R. Wallce (1947). Graphene, a singular layer of graphite, has been discovered to have unique properties. The high mobility and ability to travel short distances without scattering makes it one of the best materials for electrical applications. Graphene's mechanical and optical properties also allow its use to go beyond electrical applications.

- 2-dimensional, crystalline allotrope of carbon
- Allotrope: property of chemical elements to exist in two or more forms
- A single sheet of graphite is called grapheme, It is sp^2 hybridized $\rightarrow$ covalently bonded and looking Honeycomb (hexagonal) lattice
- The bonding between the graphene sheets in graphite is of van der Walls type
- Bond length is .142 nm long = very strong bond
- Strongest material ever discovered. ultimate tensile strength of 130 gigapascals compared to 400 megapascals for structural steel
- Very light at 0.77 milligrams per square metre, paper is 1000 times heavier
- Also, graphene is very flexible, yet brittle (preventing structural use)
- Graphene physically acts as a 2-Dimensional material. This leads to many properties that are electrially beneficial, such as high electron moblity and lowered power usage. 2-dimensional, crystalline allotrope of carbon

Applications

- OLED Techonologies
- Body Armour
- Lightweight Aircraft/vehicles
- Photovoltaics
- Superconductor/battery
- Transistors
- Computer chips
- Batteries
- Energy generation
- Supercapacitors
- DNA sequencing
- Water filters
- Antennas
- Solar cells
- Spintronics-related products



Composites

All the engineering materials (high polymers, metals and ceramics) possess their outstanding charecteristics as well as limitations.

Classification	
Reinforcement:	
• Particles (dispersion strengthened or large particles)	• Fibers (discontinuous - short or continuous - aligned) • Structural (laminates and sandwichstructures)

PARTICLE-REINFORCED COMPOSITE MATERIALS:

- Large particle composites
- Dispersion-strengthened composites

Examples of large particle composites:-Polymers with *fillers* -Concrete (cement + sand/gravel)

Factors: Factors that have an influence in physical and mechanical properties:size, distribution and particle content**.**

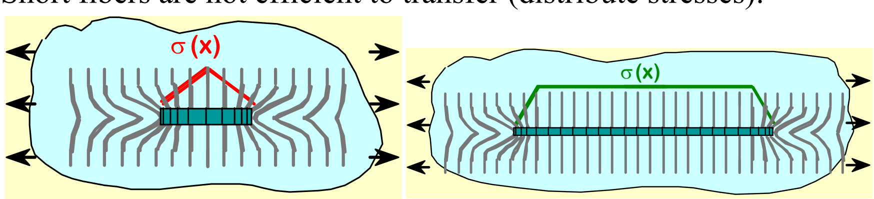
Application:

System	Application	System	Application
Ag-CdO	Electrical connectors	Ni-20%Cr-ThO_2	ThO_2 Turbojet components
Be-BeO	Nuclear reactor and aerospace	Pt-ThO_2	ThO_2 Wires, electrical components

FIBER-REINFORCED COMPOSITE MATERIALS

In general, they are more effective than particle-reinforced composites in the load-transfer and load-alignment characteristics.

Short fibers are not efficient to transfer (distribute stresses):



Fiber orientation and concentration influence the composite general strength and anisotropic behavior.

TYPES OF FIBERS:


glass fibre1

1.Glass Fibers: Used to reinforce plastic matrixes

Composition: Base of SiO_2 (50-70%) + Oxides Ca, Al, B, Na, Mg and K

Properties: Non combustible, good chemical, biological and thermal resistance, thermal insulator, electric insulator. low expansion coefficient and low cost.

Application: Good electrical properties and dimensionalstability (circuit boards), automobile parts, storage tanks, plastic pipes.

2. **Carbon fibers:**Carbon fibers in composites with plastic resins (i.e.: epoxy) good combination ofhigh mechanical strength, stiffness and low weight →aerospace applications

- **Low cost:** sport equipment manufacturing, industrial and commercial products. Very good thermal and physical properties (High electrical conductivity and high thermal conductivity).
Manufactured from organic precursors:
Rayon and isotropic tars (fibers)
Polyacrylonitrile (PAN) and liquid crystal tar (E↑) (easier to orientate)

Nanocomposites

Nanocomposites are a class of materials in which oneor more phases with nanoscale dimensions (0-D, 1-D, and 2-D) are embedded in a metal, ceramic, orpolymer matrix.

Working capacity: Small filler size and distance between fillers
- high surface to volume ratio
-Mechanical Properties :
- Increased ductility with no decrease of strength,
- Scratching resistance

Classification:
General classification;

1. **Organic or inorganic-layered materials:** Exhibit greater stability, in both longer shelf storage lives and uptake times act as host for polymers yielding hydrid variety**.**
2. **Lamellar nanocomposites:** These maximize interface between two phases in nanocomposites.

Classification based on Matrixes:

1. **Metal matrix nanocomposites**: It consist atleast two consitutuent parts, one is metal.

Eg: Fe-Cr/Al_2O_3

2. **Ceramic Matrix Composites**: Ceramic (up to 90%) contained in a metallic matrix
   - Cemented Carbides (tungsten, titanium, chromium)
   - Cutting Tools, Dies, Indenters
3. **Polymer-matrix nanocomposites**: Polymer matrix reinforced with fibresMatrix is typically TP (polyester or epoxy) and TS such as nylons, pvc, polycarbonates and polystyrene.

Properties	**Applications**
➢ Mech property: strength, modulus and dimensional strength ➢ Improved electrical conductivity ➢ Chemical resistance ➢ surface appearance ➢ therrmal stability ➢ optical clarity	➢ Thin film capacitors for computer chips ➢ Solid polymer electrolytes for batteries ➢ Automotive engine parts and guel tanks ➢ Impellers and blades ➢ Oxygen and gas barriers ➢ Packaging in food, medical and pharmaceutical industry

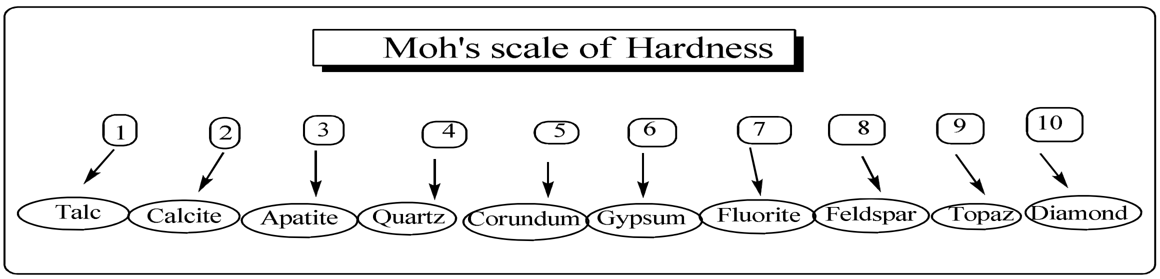
Abrasives

Abrasives are hard substances used for polishing, shaping, grinding operations. They are characterized by high melting point, high hardness and chemically inactive.

Properties:

1. **Hardness:**Hardness of the abrasive is measured on Moh's scale or Vickers's scale. It is the ability of an abrasive to grind or scratch away other materials. The harder the abrasive quiver will be its abrading action.

Measurement of hardness using Moh's scale, in which common abrasives (natural or artificial) are arranged in the order of their increasing hardness.



2. Toughness: Abrasives are generally hard and brittle, which is otherwise known as toughness.

3. Abrasive power:It is the strength of an abrasive to grind away another materials. It depends on hardness, toughness and refractoriness.

Types of Abrasives

NATURAL abrasives

CORUNDUM: It is a white mineral form of Al_2O_3. It is largely replaced by synthetic Al_2O_3 in dentalapplications. It is used primarily for grinding metal alloys.

DIAMOND: It is a transparent, colorless mineral composed of carbon. It is the hardest known substance & is called a *super abrasive* because of its ability to abrade any other known substance.

EMERY: It is a fine-grain grayish black corundum, used for finishing metal alloys & acrylic resin materials.

QUARTZ: It is a hard, colorless, transparent & most abundant mineral. It is used mainly to finish metal alloys but can be used to grind dental enamel.

GARNET: Minerals included in this group are silicates of Al, Co, Fe, Mg & Mn and used in dentistry is usually dark red.

Synthetic Abrasives

SILICON CARBIDE or Carborundum: It is made by subjecting mixture of silica and carbon to high temperature (1650^0C-2200^0C) at electric furnance. It is available in green & blue-black types.

$$SiO_2 + 3C \longrightarrow SiC + 2CO\uparrow$$

ALUMINUM OXIDE: It is made by subjecting mixture of CALCINATED BAUXITE, COKE IRON at high temperature (4000^0C) at electric furnance.It is much harder than corundum (natural alumina) due to its purity. It is used in dentistry to make bonded, coated & air propelled grit abrasives.

Refractories

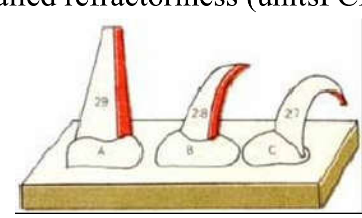
- Refractories are materials that can withstand high temperatures without softening or deformation in shape.
- Refractories are mainly used for the construction of lining in furnances, kilns, converters etc. the main function of a refractory is to withstand and maintain high temperatures and to resist the abrasive and corrosive action of molten, slags and gases.

Properties

1. **Refractoriness:** It is the ability of a materials that can withstand high temperatures without softening or deforation under particular service condition.

PCE (Pyrometric Cone Equivalent) Test: Pyrometric Cone Equivalent is the number which stands for softening temperature of a refractory specimen of standard dimension (38 nm height and 19 mm triangular base) and composition.**Pyrometric Cone Equivalent(PCE) Measurement Temperature at which the refractory brick or the cone bend** (ie) thetemperature at which apex touches the base is called refractoriness (unitsPCE)

Cone 29: Stiff at test temperature
Cone 28: Just started Softening
Cone 27: Apex almost touching base

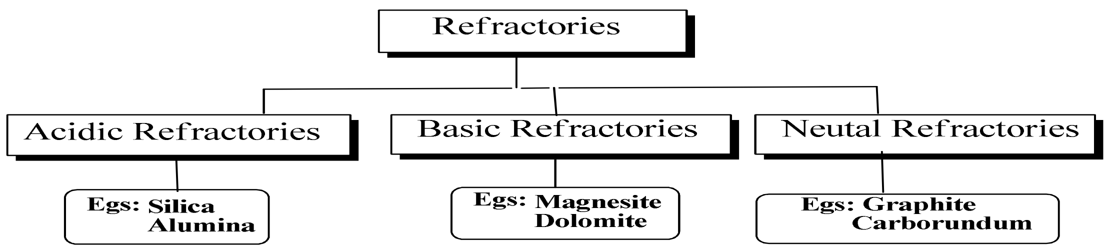


2. **Refractoriness under laod (RUL) or Strength**
   The temperature at which the refractory deforms by 10% is called refractoriness under load. It is conducted by applying a constant laod of 3.5 or 1.5 kg/cm^2 to the test refractory

specimen of size base 5 cm^2 and height 5 cm and heating in a furnace at standard rate of $10^{\circ}C$ per minute.

3. **Porosity:** It is defined as the ratio of its pore volume to the bulk volume.
4. **Thermal Spalling:** It is the resistance of a refractory to any volume changes, when exposed to high temperature over a prolonged time.
5. **Dimensional stability:** it is the resistence to any volumes, when exposed to high temperature over a prolonged time.

Classification



Based on chemical composition:

1. Acidic refractories:

These are used in areas where slag and atmosphere are acidic. They are stable to acids but attacked by alkalis., ex- silica (SiO_2), zirconia (ZrO_2) etc.

2. Neutral Refractories:

These are used in areas where slags and atmosphere are either acidic or basic and are chemically stable to both acids and bases. Examples: alumina (Al_2O_3), chromia (Cr_2O_3) and carbon.

3. Basic refractories:

These are used on areas where slags and atmosphere are basic, stable to alkaline materials but reacts with acids. magnesia (MgO) is a very common example.

Lubricants

Lubricant is a substance used in between two moving surfaces to reduce the friction.

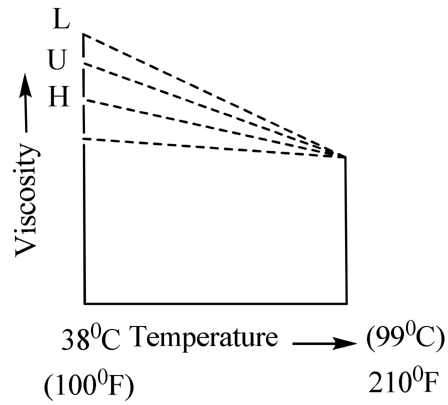
Lubrication:

Lubrication is a process of reducing friction and wear between two moving surface by adding lubricant in between them.

Properties:

1. **Viscosity:** It is a measure of the internal resistance of a liquid during its flow. It is expressed in centipoises. ***Good lubricant must have moderate viscosity***.
2. **Viscosity Index**: the average decrease in viscosity of oil per degree rise in temperature between $100^{\circ}F$ and $210^{\circ}F$.

Viscosity- Temperature Curve



Examples

1. Eg: Gulf coast oil exibits a larger change in viscosity with a increase in temperature and its V. I value is arbitrary assingned as **Zero**
2. Eg: Pennsylvanian oil exibits a smaller change in viscosity with a increase in temperature and its V. I value is arbitrary assingned as **100.**

3. **Cloud and Pour Point:**

   Cloud Point: When an oil is cooled slowly the temperature at which the oil becomes cloudy in appearance is called its cloud point.

   Pour Point: The temperature at which the oil ceases to flow or pour is called pour point.

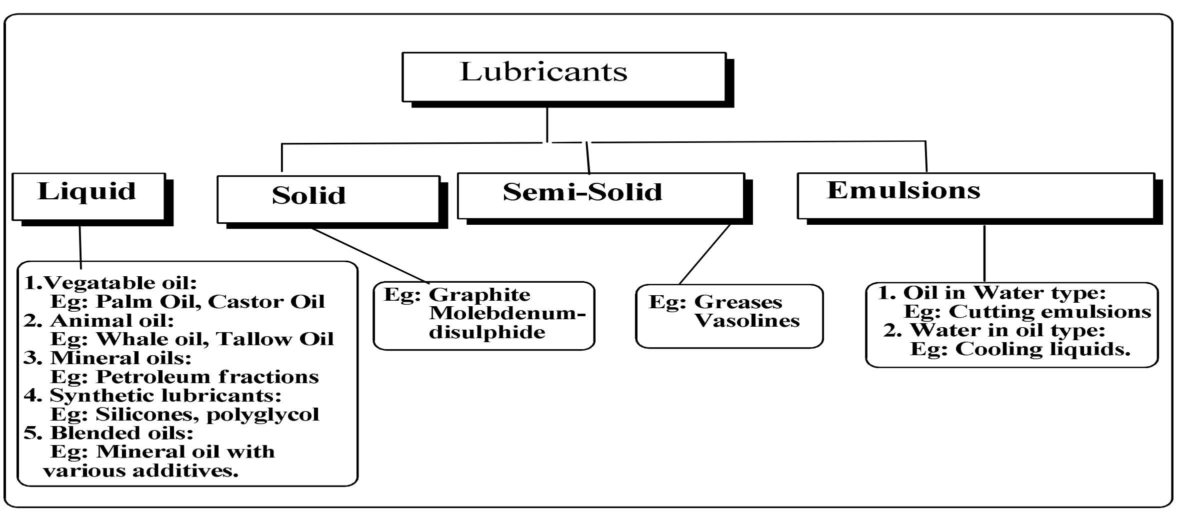
   ***Good lubricant must have low*Cloud and Pour Point.**

4. **Oiliness:** oiliness is the capacity of a lubricating oil to stick on the surface of the machine parts under heavy load and pressure. ***Good lubricant must have good illne.***

5. **Flash point and Fire point**: It is the lowest temperature at which the oil gives off enough vapour that ignite for a moment, small flame is brought near it.

   Good lubricanting oil must have moderate higher Flash point and Fire point than the operating temperature of the machine

Classification:



1. Animal and Vegetables oils: Animal oils are extracted from the crude fat and vegetables oils such as cotton seed oil and caster oils. These oils possess good oiliness and hence they can stick on metal surfaces effectively even under elevated temperatures and heavy loads.

2. Mineral or Petroleum oils: These are basically lower molecular weight hydrocarbons with about 12 to 50 carbon atoms. As they are cheap, available in abundance and stable under service conditions, hence they are widely used.

3. ***Blended oils:*** Addition of proper additives is essential to make them perform well. Such additives added lubricating oils are called blended oils. Examples:

4.**Semi-solid Lubricants or Grease:** The thickeners consist primarily of special soaps of Li, Na, Ca, Ba, Al, etc. Non-soap thickeners include carbon black, silica gel, polyureas and other synthetic polymers, clays, etc. Eg: Grease can support much heavier load at lower speed.

5. **Solid lubricants:** The most common solid lubricants are ***graphite***, ***molybdenum disulphide***, tungsten disulphide and zinc oxide. They can withstand temperature upto650° C and can be applied in continuously operating situations.