Chapter

1

Functional Materials

1.1 INTRODUCTION

The term 'ceramic' originates from the Greek word 'Keramikos' meaning 'burnt stuff' which implies that the properties are obtained through processes at high temperature. Traditional ceramics such as porcelain, bricks and tiles have clay as one of the important constituents while on the contrary, modern ceramics are made of oxides and nonoxides of metals and nonmetals.

> The word 'ceramic' comes from the Greek word 'Keramikos' meaning 'pottery,' or 'potter's clay' is also related to an old Sanskrit word meaning 'to burn'

These materials are considered to be one of the popular industrial materials as they are hard, inert and thermally stable. These materials are neither composed of only organic compounds nor metals. Since ceramics are composed of more than one element, the crystal structure is complex with bonds ranging from being completely ionic to fully covalent. However, when the ionic character predominates, crystal structure may be considered as being composed of electrically charged ions with equal number of cations and anions rather than atoms. Also a stable structural framework is achieved when anions surrounding the materials are a part of the diversified group of industry products composed of silicates, including refractories, cements, abrasive clay products, lime, plaster, glass, high and low tension electrical insulators.

> The oldest human-made ceramics date back to about 24000 BC and were found in Czechoslovakia.

Ceramics are versatile in nature which are crystalline, glassy, insulating or semiconducting and used as spark plugs, fiber optics (Al_2O_3 and ZrO_2 are the ceramics popularly used), artificial joints, space shuttle tiles, cooktops, race car brakes, micro positioners, chemical sensors, self-lubricating bearings, body armor, skis, etc.

Raw Materials of Ceramics

The important raw material required in the manufacturing of ceramic materials are:

i. **Clay:** It is made of aluminum silicate formed during weathering of igneous rocks which contains feldspar. In presence of water, clay gains plasticity and can be easily moulded.

$$\underset{\text{Potash Feldspar}}{K_2O\ Al_2O_3\ 6SiO_2} + 2H_2O + CO_2 \longrightarrow K_2CO_3 + 4SiO_2 + \underset{\text{Kaolinite Clay}}{Al_2O_3\ 2SiO_2 \cdot 2H_2O}$$

On heating, water is eliminated to result a glassy, vitreous hard material.

$$Al_2O_3 2SiO_2 \cdot 2H_2O \xrightarrow{873\,K} Al_2O_3 2SiO_2 + 2H_2O$$

$$\underset{\text{China Clay}}{Al_2O_3 2SiO_2 \cdot 2H_2O} \xrightarrow{1200\,K} \underset{\text{Mullite}}{3Al_2O_3 2SiO_2} + 6H_2O + 4SiO_2$$

ii. **Silica:** Added in the form of quartz or flint, it provides a firm skeletal structure to the ceramic materials and is highly resistant to heat.

iii. **Feldspar:** These are aluminosilicates of sodium, potassium or calcium having a low fusion temperature acting as binding material. The three common type of feldspar are:

- Potash feldspar: $K_2O\ Al_2O_3\ 6SiO_2$
- Soda feldspar: $Na_2O\ Al_2O_3\ 6SiO_2$
- Lime feldspar: $Ca_2O\ Al_2O_3\ 6SiO_2$

iv. **Fluxing agents:** These are alkaline oxides that promote liquification such as borax, soda ash and lead oxide.

v. **Refractory agents:** Imparts thermal stability often in the form of ThO_2 or ZrO_2

vi. **Colouring agents:** Oxides of cobalt, chromium, nickel and manganese impart colour.

1.2 PROCESSING OF CERAMICS

A great deal of research has gone into developing fabrication methods of ceramic, as it decides the cost, durability and cost of the ceramic end products as well. Powder processing and shaping technique are the two important fabrication steps often employed in the processing of ceramics.

1.2.1 Powder Processing

In solid phase, the raw materials in the form of hydroxides, oxalates or carbonates are blended and allowed to solidify. Synthesis in liquid phase is preferred to prepare ceramic fibers and thin films which can be achieved through sol-gel or co-precipitation methods. High purity ceramics are synthesized in the vapor phase where the raw materials are vaporized and homogeneously mixed in the form of fine nonaggregated particles using the technique of chemical vapor or physical vapor deposition.

1.2.2 Shaping

Popularly referred to as forming, the ceramic in the powdered form is given a formation under an ambient temperature, and can be subjected to dye pressing, slip casting or extrusion at room temperature called as cold forming or hot isostatic pressing and injection moulding called as hot forming.

1.3 CLASSIFICATION OF CERAMIC MATERIALS

As ceramics have achieved broader applications, classification is necessary to gain a systematic view of these materials.

1.3.1 Classification Based on Composition

Class 1: Silicate ceramics

These constitute Si and O as the prime components and are generally produced by glass ceramic techniques. They have a low thermal expansion and are available in coarse and fine textures with high mechanical strength.

Example: Porcelain, steatite.

One type of advanced ceramic, called 'shuttle ceramic tiles', has been created to withstand temperatures upto 1280°C (2336 F). Space shuttles are covered in 30000 of these lightweight tiles. They protect the shuttle from heat when it re-enters Earth's atmosphere from space.

Class 2: Oxide ceramics

This category includes oxides of Si, Al, Zr, Ti, Mg and other metals. They possess high melting point with exclusive electrical properties and are manufactured by modeling process.

Example: Magnesia, silica.

Class 3: Nonoxide ceramics

Generally produced by conventional dry-pressing processes, they include carbides, nitrides, borides and silicide possessing high thermal conductivity and abrasive properties.

Example: B_4C, WC

Class 4: Glass ceramics

These are materials produced by controlled crystallisation constituting a structure with dimension of 1 μm, existing between amorphous and highly crystalline state possessing high impact resistance and translucency.

Example: Li_2O Al_2O_3 SiO_2

1.3.2 Classification Based on Applications

Class 1: Classic ceramics

These are the traditional ceramics which are highly porous, made for everyday use with basic components such as clay, feldspar and silica are made in large quantities by inexpensive manufacturing methods.

Example: Abrasives, refractories, clay and cement

Calcium carbonate ($CaCO_3$) is used as a polishing agent or an abrasive in tooth paste.

Class 2: Electroceramics

Ceramic materials which are used to execute electronic functions such as insulators and conductors are termed as electroceramics. These materials have specifically designed formulation with highly controlled processing. They can be subdivided into two classes as follows:

a. *Dielectrics or insulator ceramics:* Popularly used in capacitors, as these materials resist the flow of electrons.
   Example: Al_2O_3, $BaTiO_3$
b. *Conducting ceramics:* Popularly used in spark igniters, accelerometers and sonar imaging, as these materials contain electrically polarized domains in their structure which respond to any electric field applied.
   Example: Piezoceramics, magnetoceramics

Class 3: Modern ceramics

These are the recently developed inorganic ceramics with high commercial value include a broad spectrum of materials which can withstand high temperature, high strength and hardness, wear and corrosion resistance, biocompatibility, with unique optical and electronic properties.

Example: Nuclear ceramics, bioceramics

1.3.3 Classification Based on Functionality

Based on the performance and purpose of use, ceramics can be classified as traditional and advanced ceramics.

> The blade of a ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped if dropped on a hard surface

Traditional Ceramics

Class 1: Clay products

These are made of natural materials with 45% quartz acting as filler and 55% feldspar providing the shape. As they exhibit load bearing ability, they are pressed or extruded into shape while in a wet plastic state and then dried and fired.

Example: Bricks and tiles

> Ceramic cement is successful in Portland cement replacement range upto 40% by mass and thus considered to be ecofriendly

Class 2: Bricks and tiles

A homogeneous mixture of alumina (aluminum oxide), silica (silicon oxide), and dolomite (calcium magnesium carbonate) constitutes bricks or tiles with clay being fired in a kiln to increase hardness.

Example: Construction materials

Class 3: Abrasives

Hard materials used to provide shape or finishing to an object through rubbing, often referred to as polishing or buffing.

Example: Diamond, boron nitride

Class 4: Refractories

These are oxides of Al, Si, Mg and Ca, are heat-resistant materials used in making furnaces, crucibles, kilns, boilers, stills for cracking petroleum, ladles for pouring molten metal into moulds, electrolytic cells and incinerators which operate upto 2150°C.

Example:

i. Acidic refractories (Al_2O_3 and SiO_2)—resistant towards acids, but attacked by base.
ii. Basic refractories (MgO)—resistant towards bases, but attacked by acids.
iii. Neutral refractories (Cr_2O_3)—resistant towards both acid and base.

Special refractories are high purity oxides, relatively expensive, with very little porosity which includes beryllia (BeO), zirconia (ZrO_2), mullite ($3Al_2O_3.2SiO_2$) and silicon carbide (SiC). Carbon and graphite can act as refractories but rarely used due to its susceptibility to oxidation at high temperatures of about 800°C.

Class 5: Cements

Ceramic dust which is a nonrecyclable byproduct in ceramic industry is used as a supplementary binder in Portland cement that hardens the concrete. The lack of Ca^{2+} ions, decreases the porosity, and thus makes it denser and leads to the formation of fine aggregate. This cost effective cementitious material popularly used in making hollow bricks, has decreased the energy consumption and CO_2 production associated with the production of portland cement.

Example: MgO SiO_2 Al_2O_3 dust

Silicate Structure in Traditional Ceramics

Silicates are occasionally considered as discrete molecules but exist as arrays where ceramic materials can exist in any of the following forms with a combination of covalent, ionic and metallic bonding.

Silicon oxygen tetrahedron $[SiO_4]^{4-}$: Here one silicon atom is bound interstitially to 4 oxygen atoms. Each oxygen atom has only 7 electrons in its outermost shell. Thus to reach the octet structure, it takes the electron from a metal or shares an electron pair with the 2nd silicon and becomes double tetrahedron silicate $[Si_2O_7]^{6-}$.

Polytetrahedral structure: When three or more tetrahedral units are linked together, a ring structure evolves, where one oxygen atom is a member of two units. The composition is Si_3O_9 producing $(Si_3O_9)^{6-}$ ions.

Chain structure: Two corners of each tetrahedra when linked, form a single chain structure where one oxygen is common to two adjacent tetrahedra. When two such structure in parallel chain structures are polymerized through a common oxygen atom, results in a double chain structure.

Sheet structure: When a double chain structure extends infinitely, sheets results which are found in clay, mica and talc. The sheets impart plasticity in clay and lubricating characteristics in talc.

Framework structure: The sheet structures when extended to 3D give rise to framework structure results in hard but low density lightweight ceramics.

Example: Roof tiles.

Vitreous structure: A vitreous silicate is a 3D framework with covalent bonds, which provides rigidity.

Example: Glass.

Polymorphism in Ceramics

It is the property of a material to exist in more than one type of crystal structure or space lattice. Silica can exist in three crystalline forms and each differs in their physicochemical properties such as thermal and chemical stability.

(i) Quartz (ii) Tridymite (iii) Cristobalite

Since the change from one form to the other is reversible, they are known as allotropic forms. The change involves breaking of Si-O-Si bonds and the rearrangement of silicon tetrahedral.

$$\begin{array}{ccccc} \text{Quartz} & \xleftrightarrow{870^\circ\text{C}} & \text{Tridymite} & \xleftrightarrow{1470^\circ\text{C}} & \text{Cristobalite} \\ 2655\ \text{kg/m}^3 & & 2270\ \text{kg/m}^3 & & 2300\ \text{kg/m}^3 \end{array}$$

$$\alpha\ \text{Quartz} \xleftrightarrow{573^\circ\text{C}} \beta\ \text{Quartz}$$

$$\alpha\ \text{Tridymite} \xleftrightarrow{120^\circ\text{C}} \beta\ \text{Prime tridymite}$$

$$\alpha\ \text{Prime tridymite} \xleftrightarrow{160^\circ\text{C}} \beta\ \text{Tridymite}$$

$$\alpha\ \text{Cristobalite} \xleftrightarrow{200^\circ\text{C}} \beta\ \text{Cristobalite}$$

1.4 PROPERTIES OF CERAMIC MATERIALS

Due to structural diversity, a strong emphasis is laid on properties of ceramics for its technological functions. The following properties make ceramic materials ideal for engineering applications.

1.4.1 Mechanical Properties

i. Extremely hard and has resistance to wear
   Example: Carborundum 2480 knoop and boron nitride 7000 knoop
ii. Very low tensile strength of 1900 kg/cm^2
   Example: Al_2O_3
iii. High compressive strength 19500–35000 kg/cm^2
   Example: Al_2O_3
iv. Low fracture strength and value of modulus of elasticity for most ceramic range of 7×10^{10} N/m^2 to 40×10^{10} N/m^2

1.4.2 Electrical Properties

i. Most ceramics like procelain, steatite, forsterite and alumina are used as insulators with resistivity of order of 10^{12} Ωm.
ii. A small number of ceramics can conduct electricity and are used as semiconductors.
   Example: Iron oxide, nickel oxide and cobalt oxide
iii. Most ceramics can be made piezoelectric by application of high voltage where the material changes the property of transforming mechanical deformation into voltage changes.
   Example: Barium titanate used in gramophone pickups.

1.4.3 Magnetic Properties

Ceramics consisting of iron oxides have magnetic properties

Example: Ferrites like ferroxcube form soft magnetic materials (used in making inductors and transformers) and ferroxdure form hard magnetic materials (used in making household materials).

1.4.4 Chemical Properties

i. Ceramics show high resistance organic solvent, acids and caustic solutions
ii. Can resist oxidation at high temperatures
iii. Ceramics resist molten metals and hence used as furnace lining
   Example: Magnesia, Al_2O_3

1.4.5 Thermal Properties

Ceramics possess excellent specific heat capacity

Example: Silica and zirconia have specific heat of about 1.1 and 0.6×10^3 W/m°C and thermal conductivity of 1.7 and 2.3 W/m°C respectively.

1.4.6 Optical Properties

i. Glass which is a major class of ceramics is a polycrystalline material in production of windows, bulbs and optical lenses.
ii. Glass with selective absorption and transmission with refraction index varying from 1.46 to 2.0 can be designed.

1.4.7 Nuclear Properties

Ceramics offer a wide range of properties to capture and scatter neutrons thus are used as shields, moderators and chambers used to immobilize and store nuclear wastes.

1.4.8 Biological Properties

Silica ceramic is inert to the tissues and body fluids making it corrosion resistant and biocompatible. It finds applications in making artificial teeth, bones implant and a major part in surgical glue.

1.4.9 Piezoelectric Property

It is the property of a material to transform mechanical deformations into voltage changes and vice versa. Piezoelectric ceramic can be prepared by suitably treating ceramic at a high voltage known as "polarization".
Example: Barium titanate and lead zirconate titanate.

1.5 ADVANCED CERAMIC MATERIALS

Ceramics with extreme hardness, physical and chemical stability, good conductivity and biocompatibility are generally termed as advanced ceramic materials making them one of the most important industrial elements.
Example: Silicon nitride in turbine blades, silicon carbide in bearings, boron nitride in high temperature equipment, titanium diboride used as wear-resistant parts, tungsten carbide used in cutting tools, hot pressed zirconia used as a refractory material, alumina used as abrasion resistant tiles, aluminum titanate used as port liners in automobiles, glass ceramics in vacuum tube components are a few examples.

1.5.1 Alumina (Al_2O_3)

It is a well-known oxide ceramic material with aluminium and oxygen sharing ionic bond in between them, available in both coarse and fine grain sizes. It exists in most stable hexagonal α-phase at high temperatures. It can be used in both oxidizing and reducing atmospheres upto 1925°C.

When alumina is combined with SiO_2, it becomes a part of silicon matrix by dissolving and yields glaze melts. Alumina controls the flow of the glaze, prevents crystallization, imparts chemical stability, increases melting point, improves tensile strength, lowers expansion, reduces phase separation and improves hardness.

Example: Kaolin, pyrophyllite or feldspar are good sources of alumina.

Synthesis

Extraction of Al_2O_3 from Bauxite by Bayer's process (Fig. 1.1): Bauxite is a mixture of Al_2O_3, SiO_2, Fe_2O_3 and other materials.
Step 1: A fine powder of bauxite is made to react with NaOH. Only Al_2O_3 dissolves.

$$Al_2O_3 + H_2O + NaOH \longrightarrow NaAl(OH)_4$$

$NaAl(OH)_4$ on heating decomposes to pure $Al(OH)_3$ and NaOH
Step 2: Calcination

$$2Al_2(OH)_3 \xrightarrow{1100°C} Al_2O_3 + 3H_2O$$

Step 3: Filtration: SiO_2 and Fe_2O_3 do not dissolve in NaOH and are removed by filtration.

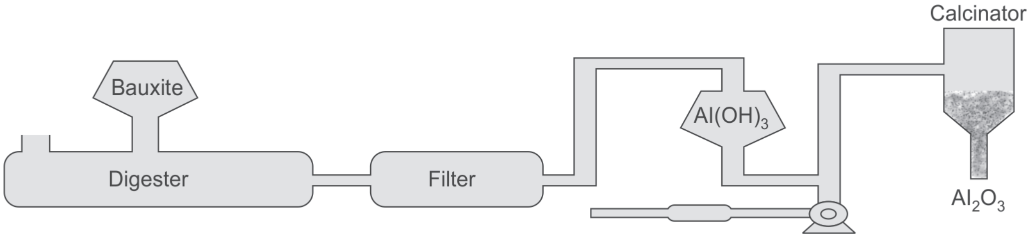

Fig. 1.1: Extraction of Al_2O_3 from bauxite by Bayer's process

Properties

i. Strongest, hardest of all oxide ceramics
ii. Good electrical insulation upto 1 × 1014–1015 Ωcm^{-1}
iii. Good thermal conductivity upto 20–30 W/mK
iv. Highly resistant to flammability, acids, alkali and oxidation.
v. High melting point of about 2369 K and specific heat of 955 J/kgK
vi. Excellent dielectric constant of 11. 1.

Applications

General applications

i. Used in electronics, high voltage insulators and thermometry sensors
ii. Used as thermometry sensors and furnace lining
iii. Used in water purification
iv. Used as abrasives
v. Used as a filler material in pharmaceuticals and cosmetics

Specific applications

i. As it is chemically inert, it is used as filler in cosmetics
ii. As it is highly porous, it is used to remove water from vapours
iii. It is used as a catalyst support in Ziegler-Natta polymerisation and also used as a catalyst in dehydration of alcohols.
iv. Electronic industry material: Used as an insulating barrier in capacitors and spark plugs
v. Fibres of Al_2O_3 such as fibre FP, Nextel 610 and 720 are used in composites
vi. Abrasive: Sandpaper with Al_2O_3 crystals are popularly used as abrasive. Fine powder of Al_2O_3 is used in scratch-repair kits.

1.5.2 Carborundum or Silicon Carbide (SiC)

Composed of carbon and silicon in 1:1 ratio, SiC occurs in nature as a part of rare mineral called *moissanite* in various form as 2H-SiC(β-cubic form), 4H-SiC (hexagonal form) and 6H-SiC (α-hexagonal form) (Figs 1.2 and 1.3). The hexagonal crystal structure being the most common forms, has a predominantly covalent character with the molecular structure Si-C. It is a popular semiconductor with high thermal conductivity which is highly stable, chemically inert, and has Mohs hardness rating of 9, close to that of the diamond.

Synthesis

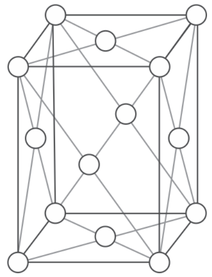

Fig. 1.2: Cubic form

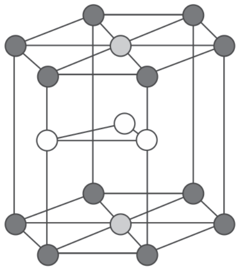

Fig. 1.3: Hexagonal form

- **Synthesis by Acheson process:** It is a process used in the large scale production of carborundum in an Acheson graphite electric resistance furnace. Silica and quartz is mixed with coke and heated to about 2000°C in furnace, where the following chemical reactions take place.

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

$$SiO_2 + CO \longrightarrow SiO + CO_2$$

$$SiO + 2C \longrightarrow SiC + CO(g)$$

$$C + CO_2 \longrightarrow 2CO$$

$$2C + SiO \longrightarrow SiC + CO$$

  Note: Addition of NaCl to furnace prevents corrosion of steel furnace. Addition of sawdust to furnace stops emissions. The product formed is a mixture of different grades of Si which requires further separation.

- **Synthesis by physical vapour transport:** Popularly known as seeded sublimation growth or Lely method, it is a simple process to obtain large sized SiC single crystal. At low Argon pressure, a source is placed to close proximity of seed of SiC, maintaining a temperature gradient which facilitates the movement of material vapour. However, this method has a disadvantage that an uncontrollable nucleation and dendrite-like growth may be observed.
- **Synthesis by chemical vapour deposition:** This method is most suitable for generating SiC thin films, powders, whiskers and nanorods. The process implements hermolysis, hydrolysis, oxidation, reduction, nitration and carboration, depending on the precursor species used. The gaseous species and the substrate are kept in close proximity which allows a slow diffusion controlled absorption of species.

$$2\,SiH_4(g) + C_2H_2(g) \longrightarrow 2SiC(g) + 5H_2(g)$$

- **Synthesis by sol-gel process:** This method is most suitable for generating SiC in highly pure form with extremely uniform and dispersed nanostructures.

Step 1: Hydrolysis: An alkoxide is mixed with a suitable solvent to produce siloxane (SiOSi).

Step 2: Polycondensation: Formation of gel by shrinkage and densification is achieved by heating and removing the solvent. The product is a network of nanostructures of SiC in the pure form.

> Tungsten carbide begins as a fine powder during the jewelry-making process, but after heating, it's approximately 10 times harder than 18K gold and two times denser than steel!

Properties

i. Extremely hard due to tetrahedral crystal lattice of covalently bonded silicon and oxygen
ii. Good thermal conductivity but low thermal expansion and hence can resist thermal shock

iii. Has semiconductor characteristics
iv. Remain undamaged up to 1800°C

Applications

i. Used as a structural material in composite armor, brake disc and plastic alloys for automobiles and microelectronics
ii. SiC fibers are used in gas temperature
iii. Used as a diamond substitute in jewellery
iv. Used in heat treatment of metals, melting of glass and production of electronic components
v. Used in making pallets that connects power lines and earth.

> Carbide cutting tools remain sharp, not only at ordinary cutting temperatures of 1700 to 2000 F, but even at temperatures of upto 3000 F, which can exist at the interface between the cutting tip and the metal being cut.

1.6 SUPERHARD CERAMICS

Ceramic materials having extreme hardness to withstand more than 40 GPA with high thermal and chemical stability are generally termed *superhard ceramics*.

Precision ceramics are made using superhard ceramics which play a major role among technical ceramics over-ridden only by diamond in terms of toughness.

Example: B_4O known for abrasion resistance are used in pumping nozzles, SiC known for chemical resistance and low thermal expansion. Two of the superhard ceramics popularly used in industries are discussed below.

1.6.1. Tungsten Carbide

Its molecular formula is WC, an important compound of carbon with some other equivalents being titanium carbide, molybdenum carbide, tantalum carbide and chromium carbide. With a high density and Young's modulus of about 530–700 GPa, it overrides the stiffness of steel and is considered to be one of the hardest material. Its unique thermal stability makes it an excellent material for a wide range of industrial applications which includes metal cutting, mining, dental drills, bearings, dyes and seal rings. Available as grey fine powder, it exists in two forms:

i. **Hexagonal form** (α-WC): Distance between tungsten atoms is 291 pm and between layers is 284 pm. Tungsten-carbon bond length is 220 pm. The hexagonal state is stable from a range between 2670–2720 K to 3000–3050 K.
ii. **Cubic form** (β-WC): Generally formed at lower temperatures, exists as thin films made of grains with granular size 400–500 Å.

Properties

1. Twice as hard as to deal with Young's modulus of 530–700 GPA and twice as dense as steel.
2. Refractory grade WC has hardness of 2000–2700 HV with a score of 9 in mohs scale
3. Highly resistant to strong acids
4. Has melting point 2870°C and boiling point 6000°C with thermal conductivity 110 $Wm^{-1} \cdot K^{-1}$ and coefficient of thermal expansion 5.5 $\mu m^{-1} \cdot K^{-1}$
5. Low electrical resistivity of 0. 2 $\mu\Omega m$
6. High resistance to galling and welding

Applications

i. Cutting tools for machining
ii. Used in armor piercing ammunition and rock drill bits.
iii. Used as an effective neutron reflector.
iv. Tyres with WC studs provide a good traction on ice.
v. Used in manufacturing of guage blocks.

Synthesis

Method 1: Dry tungsten powder blend with carbon black and fired in hydrogen atmosphere at 1400 to 2650°C.

$$W + C \xrightarrow{1400-2650^\circ C} WC$$

Method 2: Tungsten hexachloride is reduced with H_2 and made to react with CH_4 which acts as a source of carbon.

$$WCl_6 + H_2 + CH_4 \xrightarrow{670^\circ C} WC + 6HCl$$

Method 3: To achieve higher reaction rates tungsten hexafluoride is reduced with H_2 and made to react with CH_3OH acting as a source of carbon.

$$WF_6 + 2H_2 + CH_3OH \longrightarrow WC + 6HF + H_2O$$

1.6.2 Boron Nitride

The structural variety in BN is similar to carbon solids as the pairs of boron and nitrogen atoms is isostructural and isoelectronic.

It is a popularly used broadband semiconductor compound with extreme chemical and thermal stability having strong covalent bonds and equal number of boron and nitrogen atoms. Due to dipolar nature of B-N bond, it is also considered as a good material for adsorption of hydrogen and hydrogen storage applications. BN can exist in amorphous and crystalline forms varying in the arrangement of atoms.

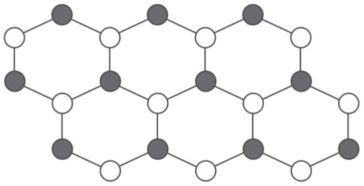
Fig. 1.4: Hexagonal BN

Amorphous form: No regularity in the structure and resembles amorphous carbon.

Crystalline form: Atoms have fixed position and regularity in structure.

Hexagonal form (h-BN or α-BN): It is the most stable form resembling graphite, has ABAB… stacking structure. The hexagonal rings of the basal planes directed above each other are rotated by 180° angle between alternative layers (Fig. 1.4).

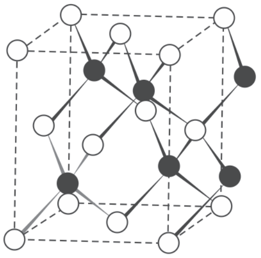
Fig. 1.5: Cubic BN

Cubic form (c-BN or β-BN): It is a less stable form resembling diamond has ABCABC… stacking structure. The cubic structure has tetrahedrally coordinated boron and nitrogen atoms with {111} planes arranged in a three layer stacking (Fig. 1.5).

Wurtzite form (ω-BN): These are six membered rings constituting boron and nitrogen and have chair configuration with two layers of stacking planes ABAB… (Fig. 1.6).

Synthesis

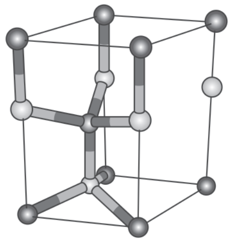

Fig. 1.6: Wurtzite BN

i. Pure ammonia is passed onto borax at elevated temperature.

$$B_2O_3 + 2NH_3 \xrightarrow{900°C} 2BN + 3H_2O$$

ii. Boric acid may be used to obtain BN at *in-situ* (lab) temperature

$$B(OH)_3 + NH_3 \longrightarrow BN + 3H_2O$$

iii. Boron oxide reacted with urea

$$B_2O_3 + Co\ (NH_3)_2 \longrightarrow 2BN + 2H_2O + CO_2$$

Properties

i. **High thermal stability:** Stable upto 1000°C in air, 2800°C in inert atmosphere and 1400°C in vacuum.
ii. **Electrical conductivity:** Band gap is wide with 5.9 eV and hence used as an electrically insulating filler material.
iii. **Chemical stability:** Insoluble in acids and it resists oxidation upto 1300°C, if it undergoes oxidation at about 1300°C to B_2O_3, further oxidation is prevented by a thin layer of oxidized product.

Application

i. Hexagonal BN is an excellent lubricant and is a good alternative for graphite
ii. It imparts self-lubricating properties used as a constituent of plastics, resins, ceramics and alloys
iii. Used as a semiconductor base because of its excellent dielectric property.
iv. Used as a charge leakage barrier layer of photo drum in laser print
v. Nanosheets of BN serve as proton conductors and hence used in water electrolysis process

1.6.3 Transparent Ceramics

Glass and polymers, considered being optically transparent or "see through" materials are of high importance in industry, but generally lacks mechanical and chemical stability. Hence, transparent ceramics are excellent candidates to replace conventional transparent materials in optoelectric devices, biomedical materials, scintillation processes and solid-state lighting owing to their chemical durability.

Transparency is imparted by crystallographic orientation through different fabrication methods. As grains are the main phase of ceramics, the transparency of ceramics is governed by grain boundaries where scattering of light occurs and impurities reside. Ceramics materials with high degree of crystallinity with cubic, tetragonal and hexagonal structures can lead to isotropic scattering and are preferable, despite their laborious processing routes. Among the three steps involved in ceramic making namely, preparation of powder, body forming and sinctering, the capacity of light transmittance of the ceramics depends on temperature of sintering which decides the grain size.

Sintering is a process of compacting the ceramic material with homogeneous microstructure by application of pressure and heat below its melting point, to reduce the water content and porosity.

To achieve transparency in ceramics, sintering is generally done to optimize the grain size to about 200 μm through spark plasma sintering, hot isostatic pressing and cold isostatic pressing. The best materials for the preparation of transparent ceramics are mechanically and chemically stable oxides such as Al_2O_3, MgO, ZrO_2, Y_2O_3, Sc_2O_3, Lu_2O_3. Further, pre-sintering, calcination and doping can enhance the controllability of grain size. Some of the fabrication methods adopted are

- **Nonaqueous tape casting:** Thin ceramic flat tapes are produced using organic solvents.
- **Vacuum tape casting:** Long thin ceramic tapes are produced using a vacuum pump.
- **Slip casting:** A liquid consisting of ceramic solid particles is molded into a shape without application of heat.

1.7 COMPOSITES

These are materials comprising two or more constituent material with different physical or chemical properties, which on combination, lead to new properties that were absent in the individual component. However, they remain separate and distinct from finished structure. These materials are a combination of matrix acting as a binder and reinforcement.

1.7.1 Matrix

It is a continuous phase which surrounds the fiber dispersed phase. Matrix helps in retaining the composite mass, shape, configuration and binds the fiber together retaining its entity. Matrix protects the surface of composites from corrosion, mechanical damage, temperature changes and decides the distribution of structural and environmental load transfer which affects the efficiency of the composite.

Matrix Used in Composites Include

Thermosetting resins: These materials which sets at a high temperature are irreversibly hardened and imparts specific tensile strength and stiffness properties. They can be further processed only by chemical dissociation.

Example: Epoxides, furan resins, polyimides, silicones, polyamides, vinyl esters, polyesters, etc.

Thermoplastic resins: These are moldable at a specific temperature when intermolecular forces weaken and impart flexibility but solidify on cooling.

Example: Polymethylmethacrylate, acrylonitrile butadiene styrene, polylactic acid, polyimide sulphone, ether imide, poly benzimidazole, etc.

1.7.2 Reinforcement

It is a component which can be particulates, fibre particulates or whiskers. The most commonly used reinforcement is fiber. Fibers are molecules with long chain polymers of varying length and diameter of a few microns. The strength and stiffness of fibers reflects the strength and stiffness of the composites. Fibres used in a composite include the following.

i. **Glass fibers:** Imparts chemical resistance to composites
   Example: Sodium silicate glass
ii. **Carbon fibers:** Imparts high modulus and strength to composites.
   Example: Rayon carbon filament, polyacrylonitrile fibers

iii. **Boron fibers:** Imparts elasticity and strength to composites
Example: Boron filaments

iv. **Polyolefin fibers:** Imparts low dielectric properties and good microwave transparency
Example: Polybutene-1

v. **Silicon carbide fibers:** Imparts high thermal stability to the composite.
Example: Sintered SiC fibres

1.7.3 Classification

Classification of Composites Based on Occurrence

i. Natural composites: These are compounds derived from nature and are renewable.
Example:
   1. Wood containing lignin acts as matrix and binds the cellulose fibre reinforcement materials.
   2. Bone containing calcium phosphate matrix, binding the collagen protein reinforcement material.

ii. Synthetic composites: These are manmade artificial composites with better properties than natural composites.
Example:
   1. Reinforced cement concrete containing cement as matrix and metal rod as reinforcement material
   2. Fiber glass containing polymethylmethacylate matrix and fine threads of glass as fiber.
   3. Carbon fiber containing polystyrene matrix and carbon fibre as reinforcement.

Classification of Composites Based on Matrix

Composites are generally classified based on the matrix used. Thermoplastics when used as a matrix tend to lose strength at elevated temperature. However, qualities like rigidity and toughness it imparts make it industrially important.

i. **Metal matrix composites:** Most metal and metal alloys can be used as matrix. Ti, Al and Mg are used as are lightweight elements with high modulus. Metal matrix composites are popularly used as conducting materials and the strength to weight ratio is higher than traditional alloys.
Example: Copper reinforced with tungsten particles

ii. **Ceramic matrix composites:** These materials when used as matrix imparts high melting point and load bearing capacity with high compressive strength making them good materials for high temperature application.
Example: SiC reinforced with carbon fibre

iii. **Polymer matrix composites:** Polymers qualify as excellent matrix materials owing to light weight and desirable mechanical properties. Thermosets and thermoplastics are widely used as matrix materials.
Thermosetting polymers like epoxy polyesters, phenolic and polyimides which do not melt but decompose on hardening and hence used as a premixed and moulding component.
Example: Glass strand reinforced polyurethane

iv. **Carbon matrix composites:** Carbon and graphite are highly superior elements as they have high strength rigidity and temperature resistance upto 2300°C.
Example: Graphite with Cu particles

Classification of Composites Based on Reinforcement

i. **Fibre reinforced composite:** Strength and stiffness of fiber used as reinforcement decides the properties of composite.
ii. **Particulate reinforced composite:** These are small compact molecules which when used as reinforcement can impart special properties such as colour and flexibility.
iii. **Whisker reinforced composite:** These are short fibers of length ranging from 3–5. 5 mm and popularly used for its zero defects
iv. **Flakes reinforced composite:** Light weight, inexpensive flakes are used in place of fibers which are densely packed. When metal flakes are used, conducting properties are induced.

1.7.4 Properties of composites

i. High strength to weight ratio
ii. High flexibility and toughness
iii. Fire retarding and fire resisting properties
iv. Good insulators with high chemical resistance
v. Low thermal conductivity
vi. Highly ductile and malleable

1.7.5 Applications

i. Used in making laminates and electronic gadgets
ii. Used in making chimney ducts, chemical storage tanks and boat hulls
iii. Manufacturing of containers used for microwaves and form insert
iv. Used in making fiberglass
v. Used in acoustical insulation

1.8 ADVANCED COMPOSITES

Traditional polymer composites have a bulk polymer and reinforcement. Often, there is a poor interfacial bonding between them resulting in disproportion of properties. To improve the interfacial interaction, a third minor reinforcement component in the nanometre scale is added to the composite as an additive which can disperse homogeneously in the polymer matrix and enhances the properties of the composite.

1.8.1 Polymer-nanoclay Composites

Materials with polymers as continuous matrix with dispersed nanomaterial in the form of fibres, spheroids, pallets of at least one dimension less than 100 nm mixed with clay are termed as polymer-nanoclay composites. The nanoclay dispersion aggregates within the polymer matrix and the polymer chains are separated from the clay layers, formimg an intercalated structure between the clay layers by modifying the geometry of the clay layer.

Example:

1. Montmorillonite nanoclay composed of 1 nm thick aluminio silicate layers gets dispersed in a polymer matrix with interlayer distance of 10 μm enhancing the mechanical strength and flame resistance.

2. Montmorillonite nanoclay coated with siloxane of 50 μm disperses into polymer matrix imparting high cation exchange capacity

Surfboards are made from fibreglass, a cheap composite material of glass fibre and a plastic polymer

1.8.2 Synthesis of Polymer-nanoclay Composite

There are three synthetic methods to prepare polymer nanoclay composites which are popularly in use.

Method 1. Melt blending method

A desired amount of nanomaterial intercalated in the clay is blended with the polymer at a temperature above the polymer's softening point in presence of an inert gas. This method provides a better mixing of the polymer and nanoclay which is compatible with the current industrial process such as extrusion and injection, moulding in thermoplastic and elastomeric industries.

Advantage: No organic solvents are required and hence environmental friendly.

Disadvantage: High temperature is required and sometimes results in aggregation of nanomaterials.

Gore-Tex is a composite which is used to make clothing. It contains layers of different materials which work together to create a fabric which is waterproof and breathable

Method 2. Solution blending method

The polymer and the nanomaterials are dissolved homogeneously in a suitable solvent and added to clay. This causes the layers of the clay to swell. The solvent is later removed by vaporization or precipitation to obtain pure nanoclay composite.

Advantage: Gives a uniform nanoclay dispersion.

Disadvantages:

- Applicable only to a few polymers
- A large quantity of organic solvents are required and hence not eco-friendly

Method 3. *In-situ* polymerization technique

Layered silicates containing nanomaterials is incorporated into the monomers before the polymerization to form monomer-clay sheet. During this polymerization step, clay layers are exfoliated and easily get dispersed.

Advantage: Permits versatile molecular designs and is currently in use.

Disadvantage: Applicable only to slow reactions.

1.8.3 Advantages

i. Introducing nanoscale phase increases the strength and imparts corrosion resistance
ii. Nanoparticle enhances dielectric and mechanical properties
iii. Polymer nanoclay composites have good flexural strength barrier properties and excellent heat distortion temperature
iv. Has high sintering property

1.8.4 Applications

i. A base for catalyst in biochemical reaction
ii. A structural material in making chemical sensor capacitors
iii. Used as abrasive and wear resistant coating material
iv. Used in making food grade containers and heat resisting food wraps

1.8.5 Polymer-carbon Nanotube Composites

Materials with polymer as continuous matrix and carbon nanotube dispersed as fibers are termed polymer carbon nanotube composites. Carbon nanotubes are the cylindrical nanostructures which are allotropes of carbon possessing unusual electrical, optical and mechanical properties.

These carbon nanotube fibres are fabricated and dispersed into a continuous polymer matrix like polypropylene, polyimide, polyaniline and polyacrylamide where the nanotubes bond to the polymers by strong π-π stacking which brings dispersion stabilility.

This incorporates many useful properties to the polymers. However, the interfacial bonding between the polymer and the carbon nanotube is still a concern, because of the chemical inertness of carbon nanotubes.

Example:

1. Polyethylene carbon nanotube composite: Incorporated carbon nanotubes, increase the elastic melt properties, strain energy density, viscosity, ductility, toughness and crystallization rate. Hence it is used in fatigue resistant materials.
2. Polyimide carbon nanotube composite: Incorporated carbon nanotubes impart anti-wear capacity, tensile strength, friction resistance and load capacity.
3. Polyaniline carbon nanotube composite: Carbon nanotubes incorporated enhance the conductivity in the composites.
4. Polystyrene carbon nanotube composite: Carbon nanotubes form a network of fibers inside the composite which increases the viscoelastic behavior and loading capacity of the composites.

Synthesis of Carbon Nanotube Composites

i. ***In-situ* polymerization:** An efficient way of synthesis where a catalyst like methylaluminoxane covalently bonded to both carbon nanotube and the polymer melt is added on to the surface of nanotubes. This method provides better crystallization and gives rise to thermal and mechanically stable composites.

ii. **Blending of functionalized carbon nanotube and polymer:** Carbon nanotubes are susceptible to substitution reactions. Hence, they are functionalized with functional groups capable of bridging themselves with polymers.

Advantages

i. Excellent thermal conductivity
ii. Exceptionally high mechanical strength and Young's modulus
iii. Exhibits nonlinear optical properties
iv. Highly versatile and can be fabricated
v. Corrosion resistant and lightweight

Applications

i. Used as components of LED devices
ii. Used as reinforcing and conductive filler
iii. As a structural material in molecular pressure sensor and high temperature gas sensors
iv. Good mechanical strength to replace steel in military equipment
v. Used in making anti-static devices and frequency selective coatings

1.9 ALLOYS

An alloy is a metallic solid obtained from a combination of two or more metals. The metal in larger concentration is the parent metal which is melted in a crucible then solid pieces of alloying metals are added and mixed.

Example: Cu-Ni, Ag-Au, Au-Pt, K-Cs, Ti-Zr, As-Sb

If both the metal atoms are electrochemically same, an ordered solid solution or "superlattice" is formed, called "primary solution".

Example: Cu-Zn, Cu-Au, Cu_3-Au

If both the metal atoms are electrochemically different, the bond among the atoms becomes partially ionic leading to "intermetallic compound", called secondary solutions or "intermediate phase".

Example: $MgCu_2$, KNa_2, $MgNi_2$

Unlike atoms coming together, this is a microscopically heterogeneous mixture often termed phase mixtures where each phase is rich in atoms of one type and are separated by grain boundaries.

1.9.1 Phase Mixture of Solid Solutions

Phase mixtures exists in heterogeneous equilibrium where homogeneous and distinct crystal grains in different phases are mixed together and joined to one another along well defined narrow interfaces. Experimental studies reveal that alloy systems are generally represented as phase diagrams which specifies the range of composition and temperature in which various phases are stable.

The grains in various constituents of a phase mixture in a metallographically prepared section of alloy can be examined under an optical microscope. The quantity of each element present in each phase is defined by a set of equations called *lever rule.*

Consider a binary alloy of components A and B in concentrations c and $(1 - c)$ respectively. Let the alloy consist of two different phases, 1 and 2 in which the concentration of A are c_1 and c_2 respectively. Let the proportion of phase 1 in the alloy be x then phase 2 will be $(1 - x)$. If there are N atoms, we have for the A atoms,

$$\begin{aligned} Nc &= Nxc_1 + N(1-x)c_2 \\ x &= (c-c_2)/(c_1-c_2) = m/l \\ (1-x) &= (c_1-c)/(c_1-c_2) = n/l \\ x/(1-x) &= (c-c_2)/(c_1-c) = m/n \end{aligned}$$

where l, m and n are the lengths defined in the diagram below.

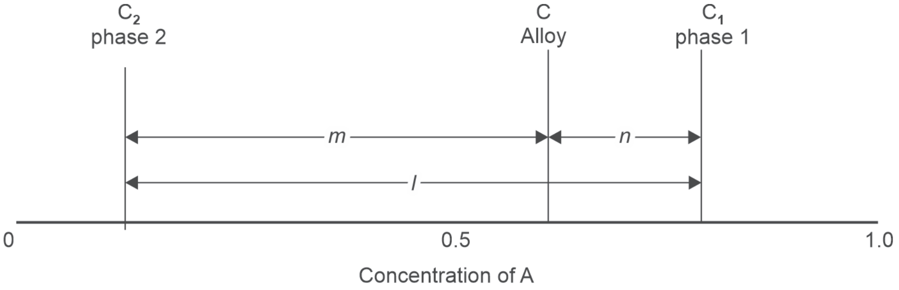

Fig. 1.7: Representation of parameters in lever rule

These relations are the lever rule and necessary for determining the constitution of phase mixtures. In a metallurgical study, it is often important to determine the proportion of phases present in the alloy which can be determined in several ways (Fig. 1.7).

Method 1: Area method—the ratio of area of the phases (as view) measured on a random section of the material. The ratio of volumes of the phases considering the analytic section as a wafer slice of material is measured.

Method 2: Line intercepts—straight lines are scribed at random across a metallographic section and the proportion by length of the phases intercepted by them are measured.

Method 3: Point counting—a grid is laid randomly on the section and proportion by volume is measured from the proportion of grid points which fall on various phases.

1.9.2 Factors Affecting Alloying or Solubility of Metal with Each Other

Roofs made of copper alloys undergo a slight atmospheric corrosion and forms a popular 'green platina' with enhanced attractive appearance.

i. **Atomic size:** Solubility of metals decreases with increase and difference in atomic size and if the diameter is more than 14% then the size is unfavorable.

ii. **Electrochemical nature:** If the metals have a large difference in electronegativity, they form compounds and not alloys and thus have low solubility.

iii. **Relative valence:** A metal of low valence dissolves one of higher valency.

iv. **Temperature:** As disordered solution has higher entropy, solubility of metals with each other increases with increasing temperature.

$$\Delta G = \Delta H - T\Delta S$$

as $T\Delta S$ increases, ΔG decreases and the system becomes highly stable.

Alloys can be broadly classified as ferro and nonferro alloys. Due to the abundance and versatile physicochemical properties of iron, ferro alloys constitutes a major class of industrial alloys.

1.9.3 Ferro Alloys

The main ferro alloys produced are steel, ferrosilicon, ferromanganese, ferrochromium, ferrotungsten, ferromolybdenum, ferrovanadium and ferrotitanium. Among all, the ferro alloy with largest production is steel with a high industrial importance.

Steel: Carbon atoms diffused into the surface of the solid iron producing a hard surface layer is called steel. The essence of steel making is tailoring the carbon content to obtain varied properties. The most popular methods used in the industrial production of steel are crucible steel process, Bessemer process, open-hearth process and electric steel making. The elements like Ni, Cr, Mn, V, Mo, W, Nb and Ti are often added to steel to incorporate desired properties.

1.9.4 Copper Alloys

Copper is a very popular alloying metal, it is chemically inert, highly conductive, easy to solder or braze, with high thermal conductivity and good fabricating properties. However, it cannot compete with steel or aluminum in applications.

'Admiralty brass' a popular alloy is used for marine applications (29% Zn, 1% Sn and 0.05% As) has corrosion resistance to sea water.

It is an excellent solvent for many metals like Al, As, Au, Ga, Ge, Mn, Ni, Pd, Pt, Sn, and Zn forming extensive primary solid solutions. Copper alloys are mostly strengthened by solid solution hardening and work hardening. The most common alloying elements added to copper are:

i. **Zinc:** It is the most common alloying metal with copper and a combination of Cu and Zn is termed brass. Addition of Zn to Cu increases the strength of Cu alloy by 50%, ductility by 30%, and also reduces the cost and lowers the melting point. The properties varied drastically with percentage of Zn. 36% Zn in primary solid solution is called alpha brass with high ductility, 5% Zn in primary solid solution is called gilding brass with high corrosion resistance. 15% Zn in primary solid solution is called red brass with high corrosion resistance. 30% Zn in primary solid solution is called cartridge brass with high ductility. 34% Zn in primary solid solution is called yellow brass which is highly economical.

   Beyond 36% of Zn, the BCC β-phase appears along with α-phase, making cold working difficult. 40% Zn in primary solid solution is called muntz metal is drawn into tubes and other irregular shapes like in hard solder by hot extrusion as it cannot be cold worked.

> Pb forms dispersed insoluble soft particles in the matrix of copper alloys to give free-machining properties. It acts as a lubricant for alloys used as sliding bearing.

ii. **Tin:** Popularly called as bronze, increases the elastic limit of Cu alloy by 10%.
iii. **Aluminum:** Increases the corrosion resistance of Cu alloy by 50%.
iv. **Silicon:** Increases the welding properties of Cu alloy.
iv. **Beryllium:** Increases the mechanical strength of Cu alloy.
v. **Nickel:** Increases the corrosion resistance of Cu alloy.

Copper Aluminum or Aluminum Brass (Cu-Al)

The combination of copper and aluminum is referred to as aluminum brass. Cu-Al alloy is homogenous upto 79% Cu. The addition of Al to Cu improves the hardness, strength and corrosion resistance but decreases ductility. The increasing content of Al makes the system heterogeneous and resistant to corrosion and hence used in marine condenser tubes and power stations.

Aluminum content in the range 7.3–9.4% solidifies at eutectic point.

> The name 'Brazing' is derived from the original use of name 'brass'.

Properties

i. Tough and suitable for cold and hot forming
ii. Retains its mechanical strength even at high temperature
iii. Can with stand stress and strain
iv. Highest tensile strength 380 MPa and hardness 70-110 HB

Application

i. Used in shipbuilding, municipal water system and marine hardware
ii. $CuAl_5$ formed by cold forming is used in making stressed gear wheels

> About 6000 years ago, early people made the alloy bronze by roasting together copper and tin ores. Bronze is stronger and longer-lasting than pure copper.

Copper Silicon

Copper has an atomic mass twice as that of silicon and has higher density than silicon. Copper has a valency of 1, whereas silicon has a valency of 4 and hence the lattice bonding of silicon is incomplete thereby increasing the internal energy of the system.

Alloying of Cu-Si

Copper-silicon melt is mixed at 1450°C for an hour in an environment of Ar gas to prevent oxidation. After reaching room temperature, the solid is removed from furnace. As the density difference between copper and silicon is high, a complex system is formed during solidification (Tables 1.1 and 1.2).

Generally for impurity removal, an understanding of phase diagram is necessary.

> Electrum is a naturally occurring alloy of gold and silver with small amounts of copper and other metals

Properties of Cu-Si

i. Highly wieldable
ii. Good semiconducting properties
iii. Good acid resisting, nonrusting and nonmagnetic

Applications of Cu-Si

i. Aquaculture enclosures are made due to their lightweight.
ii. Used in making chemical furnaces.
iii. Used in making semiconducting materials.

Table 1.1: Atomic structure of silicon-copper

	Copper	*Silicon*
Atomic radius	1.57 Å	1.46 Å
Atomic volume	7.1 $cm^3 mol^{-1}$	12.1 $cm^3 mol^{-1}$
Covalent radius	1.17 Å	n/a
Crystal structure	Cubic face centered	Cubic face centered
Electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	$1s^2 2s^2 2p^6 3s^2 3p^6$

Table 1.2: Comparison of physical properties of Cu and Si

	Physical properties of copper	*Physical properties of silicon*
Atomic mass	63.546	28.0855
Density	8.96 $g\ cm^{-3}$ (300 K)	2.329 $g\ cm^{-3}$ (293 K)
Melting point	1358 K	1687 K
Boiling point	2833 K	
Coefficient of linear thermal exapansion	$16.5 \times 10^{-6}\ K^{-1}$	$3.0 \times 10^{-6}\ K^{-1}$
Electrical conductivity	$60.7 \times 10^{6}\ Scm^{-1}$	$1.2 \times 10^{-5}\ Scm^{-1}$
Thermal conductivity	401	149

1.9.5 Aluminium Alloys

In contrast to traditional metals such as iron and copper, the tonnage use of which has remained fairly steady in recent years, aluminum has increased steadily in amount used by about 7% a year and is now the second only to steel in amount produced. Amongst the common materials, only plastics have a faster rate of growth of production and use than Al.

Aluminum is an excellent alloying parental metal as it is corrosion resistant, light, and economical with good fabricating properties. Its strong alloys have a higher strength/weight ratio than steel and hence are a major structural material for aircraft, transport and other engineering uses. The main alloying elements used in aluminium alloys are Si, Mg, Cu and Zn. Other alloying elements like Cu cannot be used frequently as it forms oxide (weak spots) and comes with less corrosion resistance.

Various combinations are:

- Addition of Zn to Al enhances ductility of Al
- Addition of Mg to Al enhances welding properties of Al
- Addition of Ag to Al enhances grain boundary properties of Al

Silumin

The simple eutectic which Al forms with Si at 12% silicon is the basis of important casting alloys that contain 11–13% silicon. This alloy does not have the problem of formation of weak spots and oxide film at the sites of phase boundary and thus have a good corrosion resistance. These have excellent casting fluidity and in making intricate shapes for engine cylinder blocks gear and crank cases, etc.

Alloying Al with Si between 5–20% enhances the casting characteristics. Based on silicone concentration, alloys are of differentiated into three categories:

- ***Hypoeutectic:*** Solidify with Al in primary phase
- ***Eutectic:*** Both Si and Al to 50% in primary phase
- ***Hypereutectic:*** Solidify with silicon in primary phase

Properties of Al-Si

i. Both components are inexpensive
ii. Resistant to humidity
iii. Highly ductile and has low density
iv. High fluidity and low shrinkage
v. Low thermal expansion coefficient
vi. Excellent corrosion resistance, low density, good mechanical properties and excellent weldability.

Applications of Al-Si

i. Used in highwear resistant materials like piston, engine blocks and bearing brushes
ii. Widely used in making castings with fatigue resistance
iii. Can be heat treated to obtain necessary properties
iv. Laser hardening can be achieved to produce chemically resistant surface

Aluminium-Lithium

Li being a light element makes light weight low-density alloy. Every crystal lattice of Al has one atom of Al replaced by Li.

The alloy exists in two forms:

i. **Metastable Al_3-Li (Δ-phase):** Has a coherent crystal structure that strengthens the metal by hampering the dislocation motion at the time of deformation.
ii. **Stable Al-Li (β-beta phase):** Has precipitate free zones at grain boundaries and hence has poor resistance to corrosion.

Properties

i. Poor fatigue strength when compressed
ii. Low density with high castability
iii. Low ductility
iv. Cold work is required for optimum properties

Applications

i. Used in jet linear air frames, fuel and fuel and oxidant tanks
ii. Used in composites to reduce weight
iii. Better alternative for Ti-composite

1.10 GLASS

1.10.1 Introduction

Glass is a transformative material with incredible versatility and is considered to be one of the world's most valuable engineering material. It is considered as an important engineering component due to its high thermal and mechanical stability gained by continual silicon-oxygen bonds, unparalleled transparency, extreme impermeability, no sharp melting point, solidifying to a transparent solid from a liquid state without crystallization. It constitutes a homogeneous mixture of two or more silicates, represented as XR_2O YMO $6SiO_2$, where R = alkali metal and M = bivalent metal.

Example: Ordinary soda glass consists of Na_2O CaO $6SiO_2$

1.10.2 Chemical Constitution of Ordinary Glass

The production of glass involves addition of various chemical compounds, depending upon the properties desired. Generally, the raw materials used are as follows:

i. Quartz sand: SiO_2 forms a network of oxides
ii. Soda: Na_2O enables thermal expansion and is generally obtained by Na_2CO_3 or Na_2SO_4.
iii. Potash: K_2O which imparts hardness to glass.
iv. Feldspar: Aluminosilicate of sodium or potassium which decreases the melting point.
v. Calcium oxide: CaO, generally obtained by $CaCO_3$, imparts thermal stability.
vi. Colouring agents: Transition metal oxides of cadmium, chromium, cobalt, copper, and manganese impart yellow, green, blue, red and violet colour, respectively ranging from 0.1% to 2%.

1.10.3 Classification Based on Application

The properties of glass varies depending upon the manufacturing process and chemical compositon.The popularly used type of glass are:

i. **Sodalime glass:** Most commonly used glass, consists of 74% SiO_2, 14–17% N_2O and 9% CaO in the form of Na_2O CaO $6SiO_2$. The glass has fine pores and light permeable. It can be further hardened by replacing Na with K to obtain K_2O CaO $6SiO_2$ generally referred to as "hard glass".

   Application: Window panes, bottles and inexpensive glassware.

ii. Borosilicate glass: Used as heat proof and chemical resistant glass consisting of 81% SiO_2, 12%B_2O_3, 2% Al_2O_3.

Application: Thermometers, lab apparatus and electronic device parts

iii. **Optical glass:** It has a homogeneous chemical composition of 73% SiO_2, 7 to 15% PbO, 5 to 7% K_2O and is transparent with an optimum refractive index. It is devoid of air bubbles, has a low melting point and is also highly resistant towards moisture and atmospheric gases.

Application: Lenses and prisms for telescopes, microscopes and spectrophotometers.

Optical glass is available under following categories

Flint glass: High density glass used to make cathode ray tubes and x-ray shields.

Crown glass: Highly homogeneous glass used in making prisms, it contains adducts such as BaO, K_2O and ZnO.

Crooke glass: High absorptivity towards UV radition due to addition of CeO_2, it is popularly used in making spectacles.

1.10.4 Manufacture of Glass Using Tank Furnace

Soda glass is prepared in a large scale using tank furnace with a capacity of about 1400–1500 tons, coated inside with refractory bricks. A homogeneous mixture of powdered raw material often referred to as "Batch material" consisting of sand, limestone, soda ash, salt cake and charcoal is fed into a tank furnace heated to 1700 K progressively. The following reactions occur in the tank furnace (Fig. 1.8).

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The molten glass is uniformly mixed, allowed stand for the gas bubbles to escape and the impurities floating on the surface is skimmed off. The viscous molten glass is moulded to a desired shape.

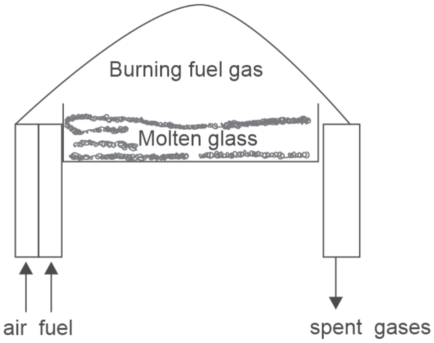

Fig. 1.8: Schematic representation of tank furnace

1.10.5 Manufacture of Glass Using Pot Furnace

High performance special type glass is prepared in a large scale using pot furnace made of alumina (Fig. 1.9) with a capacity of 2 tonnes heated using producer gas. The chemical reactions are the same as in tank furnace except for the fact that the molten glass product does not come in direct contact with products of combustion. Hence a glass of uniform concentration with high quality borosilicate and optical glass can be obtained.

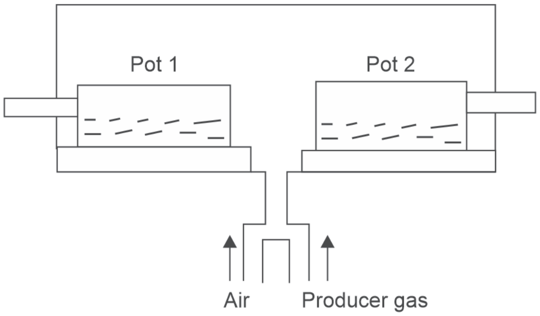

Fig. 1.9: Schematic representation of pot furnace

1.11 LUBRICANTS

Lubricants are substances which decrease the coefficient of friction between two contacting surfaces in mechanical machinery, increasing the efficiency and wear resistance. Economic and ecological factors must be considered during the selection of lubricant to efficiently contribute towards minimizing waste, reducing emission, saving and conserving the natural resources.

1.11.1 Some Properties of Good Lubricants

- High temperature of evaporation and fluidity
- High boiling point
- Low freezing point
- High viscosity index
- High thermal stability
- High hydraulic stability
- High resistance to oxidation and degradation

1.11.2 Some Important Functions of Good Lubricants

- Reduces frictional resistance
- Prevents direct contact and interlocking
- Reduces surface deformation, wear and tear
- Acts as coolant
- Increases the efficiency of the machine and machine life
- Reduces maintenance cost and corrosion
- Acts as sealants for gases

1.11.3 Classification

Lubricants can be classified in different ways

1. **Classification based on the use**
    - Automotive lubricants
      Example: Grease
    - Industrial lubricants
      Example: Mineral oil
    - Special lubricants
      Example: Alkyl benzene
2. **Classification based on the raw material**
    - Petroleum oil
      Example: Mineral oil
    - Vegetable oil
      Example: Olive oil
    - Animal oil
      Example: Whale oil
    - Synthetic oil
      Example: Phosphoric acid ester

3. **Classification based on the origin**
    - Renewable: Vegetable oil
    - Nonrenewable: Mineral oil based
4. **Classification based on the physical state**
    - Solid
      Example: MoS_2, PbO, graphite,
    - Semi solid
      Example: Grease
    - Liquid
      Example: Palm oil
    - Gases
      Example: Compressed air

1.11.4 Solid Lubricants

These lubricants are used when the action of lubrication has to be exerted withstanding high pressure and temperature at a fixed area.

Example: Graphite consists of carbon sheets separated by a distance of 3.4 Å and stacked by weak van der Waals forces. Hence graphite is soapy, slippery, non-inflammable and resistant to oxidation below 375ºC. Suspension of graphite with water is called '*aquadag*', an oil free lubricant prepared using tannin as an emulsifying agent.

Application: Commonly used in air compressors, food industry, ball bearings and railway tracks joints etc.

Example: Molybdenum disulphide (MoS_2)

A sandwich like structure with molybdenum atoms between two layers of sulphur atoms. MoS_2 has a poor interlaminar attraction and hence a low coefficient of friction but has excellent adhesive property, high load carrying capacity and stable in air up to 400ºC.

Application: Commonly used in space vehicles due to its stability towards extreme temperature, low pressure and nuclear radiations.

1.11.5 Semi-solid Lubricants

Liquid lubricants converted to gel by dispersing thickening agents such as soaps of lithium, sodium and calcium, etc. Non-soap thickeners like carbon black, clay, aspaltenes and siloxane are called semi solid lubricants.

Example: Grease

Preparation

Greases are prepared by the saponification of fat with alkali such as NaOH or $Ca(OH)_2$ followed by the addition of hot lubricating oil with constant stirring.

$$\text{Fatty acid} \xrightarrow{\text{Base saponification}} \text{Soap} \xrightarrow{\text{Agitate with hot oil}} \text{Grease}$$

Greases are classified on the basis of the soap used in their manufacture

Calcium based greases: Emulsions of petroleum oils with calcium soaps—it is insoluble in water

Soda-based greases: Petroleum oils thickened by mixing sodium soap—not water resistant because sodium content of soap soluble in water.

Lithium based Greases: Petroleum oil thickened by mixing lithium soap—water resistant but can be used up to 15ºC only.

Non-soap greases: Mineral oil with solids like graphite, carbon black and soap stone

1.11.6 Liquid Lubricants

These are the most popularly used lubricants owing to its capability to form a continuous interface across two surfaces, long life and low cost. Liquid lubricants can be further classified as:

1. Vegetable and animal oils
2. Mineral oils or petroleum oils
3. Blended oil or compound oils

1. **Vegetable and animal oils:** These oils contain glycerides of higher fatty acids which catches up moisture, undergo oxidation or hydrolysis and increases in viscosity. However, they are very expensive due to the associated tedious procedure of extraction. As they have the property of "oiliness", they are blended with mineral oils to make it thinner.

   Example: Olive oil, mustard oil, castor oil, palm oil, whale oil etc.
2. **Mineral oil or petroleum oils:** The residual hydrocarbon fraction constituting a chain of 12 to 50 carbon atoms obtained after fractional distillation of crude petroleum followed by vacuum distillation is referred to as mineral oil or petroleum oil. They are inexpensive, less viscous than vegetable oils and highly resistant towards hydrolysis and oxidation and hence are popularly used as lubricants.
3. **Blended or doped or compound oils:** Introducing additives or other oils to obtain a mixture with desired properties are called the blended oil.

   The following are the common additives

   i. ***Antioxidant or inhibitors:*** These substances preferentially get oxidized and protect other constituents of lubricant

      Example: Amino compounds and aromatic phenolic compounds.

   ii. ***Viscosity index improvers:*** These substances increase the viscosity index by altering the intermolecular forces.

      Example: Hexanol.

   iii. ***Pour point depressants:*** These substances reduce the "pour point" of the oil, the temperature below which the liquid loses its flow characteristics.

      Example: Alkylated naphthalene

   iv. ***Metal deactivators:*** These substances retard the catalytic effect of metals on the oxidation states of constituents undergoing degradation.

      Example: Sulphides or phosphides

   v. ***Antifoaming agents:*** These substances prevent the formation of air bubbles and thereby retard oxidation process.

      Example: Glycol, glycerol etc.

vi. ***Corrosion and abrasion iInhibitors:*** These substances increase the inertness of the lubricant and prevent its erosion.

Example: Organometallic compounds

Example: Tricresyl phosphate

vii. ***Emulsifiers:*** These substances help in the formation of emulsions of lubricating oil with water

Example: Sodium salt of sulphonic acids

1.11.7 Mechanism of Lubrication

Two mechanisms are proposed to explain the working mechanism of lubrication

1. **Boundary lubrication or fluid film lubrication**

Definition: It is a process where a thin molecular layer of lubricant separates the sliding surfaces such that physical and chemical nature of surfaces are retained over a wide range of temperature, pH and other environmental factors.

A film of lubricant generally of 20–30 Å thick is adsorbed through weak Vander Waals forces across two surfaces, preventing surface to surface contact and reducing the friction. This is ideal for lubricants with low viscosity used for low speed and high pressure heavy loading applications.

Example: Zinc dialkyldithophosphate used as engine lubricants

Applications of boundary lubrication

- Bearing of diesel engines and two stroke engines
- Used as hydrodynamic lubrication in Hydraulic pumps
- Used in rotating shaft and rolling components

Properties of boundary lubricants

- High viscocity and adhesiveness
- High thermal stability due to lateral attraction across the long hydrocarbon chains
- High resistance to oxidation
- Low cloud and pour point.

2. **Extreme pressure lubrication**

Defintion: Lubricants used to reduce or prevent the wear of surfaces exposed to high pressures are referred to as extreme pressure lubricants.

Example: Methylenebis(dibutyldithiocarbamate) as an additive to lubricant minimizes the oxidation of metal surface.

Organic compounds introduced as additives, contain Chlorine, Sulphur, and Phosphorus reacts with metal surface and increase the thermal stability and prevent generation of high temperature, surface deformation, vaporization and deformation.

1.11.8 Applications of Lubricants

- As antiwear, antioxidants, demulsifying and antifoaming agents.
- As corrosion inhibitors.
- As engine oils, compressor oils, gear oils, piston oils and gear box fluids
- As cutting fluids in cutting and grinding,

1.12 REFRACTORIES

Compounds which resist extremely high temperatures without fusion or deformation are called refractories.

1.12.1 Properties

A material can be called as refractory if the following conditions are satisfied.

i. **Thermal resistance:** Ability to withstand high temperatures without undergoing deformation. It is represented in terms of pyrometric cone equivalent (PCE) whose value is generally above 26.

ii. **Melting point:** Metal oxides with high melting point acts as a good refractory material such as SiO_2 (mp = 1986), Al_2O_3 (mp = 2290), CaO (mp = 2770), ZrO_2 (mp = 2970) and ThO_2 (mp = 3770)

iii. **Spalling resistance:** Ability to withstand high temperatures without undergoing expansion or contraction.

iv. **Thermal conductivity:** Materials with low prevent heat loss from the walls. Materials such as alumina, silica and dolomite in the form of crucibles and muffle furnace act as refractory materials.

v. **Porosity:** Materials with low porosity prevent diffusion of molten charge, flux, slag and gases and are useful refractories as they resist abrasion and spalling.

vi. **Chemical inertness:** Refractory material must resist the attack of slag, furnace gases, fuel, and ashes inside the furnace. It is preferable to have an acidic refractory when products are alkaline and vice versa.

vii. **Erosion and corrosion resistant:** A good refractory material should have erosion and corrosion resistance.

1.12.2 Measuring Pyrometric Cone Equivalent (PCE) value

Refractory materials are mixtures of metal oxides and hence its thermal stability is conventionally indicated by softening temperature in terms of pyrometric cone equivalent (PCE) value.

To calculate the PCE value, the following procedure is adopted

Step 1: Standard pyramidal pyrometric cones or seger cones of known composition with height 38 mm and triangular base of 19 mm are prepared.

Step 2: Seger cones of material whose PCE value is to be determined are prepared.

Step 3: Temperature of the analyte and standard cones are raised at a rate of 10 degrees per minute.

Step 4: The PCE value of given refractory is noted as temperature at which the standard one softens and bends over the base.

1.12.3 Classification of Refractories

The efficiency of the furnace is affected by the chemical composition and properties of refractory. Refractories can be classified into three types:

Acidic refractories: These are light highly rigid and mechanically strong acidic oxides with low porosity withstanding a load of about 3.5 kg/cm^2 up to 1500ºC– 1600ºC which are resistant towards acidic slags and gases. They are widely used in iron and steel industries for making open hearth furnace, reverberatory furnaces, gas retorts and wall of coke ovens.

Example: SiO_2 and Al_2O_3

Basic refractories: These are basic oxides which are resistant towards basic slags and gases.

Example: CaO, MgO

Neutral or inert refractories: These are neutral refractories which are resistant towards both acidic and basic slags and gases.

Example: SiC, Cr_2O_3 FeO and ZrO_2

1.12.4 Manufacture of Refractories

Manufacture of a refractory consists of the following steps:

1. **Crushing:** Lumps of raw materials are broken into small particles of about 25 mm.
2. **Grinding:** Small pieces of raw material is finely ground to 200 mesh size.
3. **Screening:** The unwanted materials and impurities are removed by screening, settling, magnetic separation and froth flotation.
4. **Blending and mixing:** The raw materials are then mixed to a homogeneous mixture with organic or inorganic binders like molasses starch, shellac, gum and sodium silicates, lime, calcined gypsum.
5. **Moulding:** High pressure is applied either by hand moulding or by mechanical moulding
6. **Drying:** Under an optimum humidity and temperature, applied slowly, the product is dried which removes moisture.
7. **Firing or burning:** This is the last step of the manufacture carried on inside tunnel kilns, shaft kilns or rotary kilns where the refractory is heated to a high temperature to stabilize the refractory through dehydration, calcination, oxidation, shrinkage and crystal structure transformation (verification).

   Example: 1480ºC for high fired super duty bricks; 1700ºC for kaolin bricks and 1870ºC for basic bricks.

CONCEPTUAL QUESTIONS

Justify the followings.

1. Ceramics are bad conductors of heat and electricity.

Ans. Absence of free electrons is responsible for making most ceramics poor conductors of electricity and heat.

2. Metals bend on hammering but ceramics shatter.

Ans. Metals can bend, stretch, and mould into wires because of their rows of regularly packed atoms which will slide past one another. But in ceramics, there are no rows of atoms and atoms are locked in a regularly repeating 3D crystal.

3. Silicon carbide can resist thermal shock.

Ans. High thermal conductivity coupled with low thermal expansion makes them resistant to thermal shock.

4. Surface interaction between matrix and fiber decides the quality of a composite.

Ans. Surface interactions between matrix and fiber enable good binding and load transfer across the composite and hence its properties.

5. Copper is the most popular alloying metal.

Ans. Cu has the best electrical and thermal conductivity.

6. Alloys are preferred over pure metals.

Ans. These are specifically crafted to enhance the properties of the metals and elements they contain and hence preferred over pure metals.

7. Some alloys possess shape memory

Ans. Within recoverable ranges, over a range of temperatures, the alloy undergoes a reversible solid state transformation.

8. Silumin has low plasticity.

Ans. Silicon particles in silumin are in lamellar form and a small force deforms the α-matrix. Also a large volume of silicon particles initiates cracking.

9. Chromium gives the steel resistance to 'stain' in stainless steel.

Ans. Because Cr_2O_3 is a stable corrosion product which resists further corrosion.

10. Composites are promising ecofriendly products.

Ans. Large variety of fibers incorporated in composites is naturally available.

11. Ceramic bio-implants have excellent biocompatibility.

Ans. These do not release ions during degradation and hence are biocompatible.

DESCRIPTIVE QUESTIONS

1. Define (a) superhard ceramics (b) composites (c) matrix (d) fibre.
2. Briefly outline the classification of ceramics with suitable examples.
3. Enumerate the classification of composites based on matrix.
4. Briefly outline the classification of composites based on reinforcement.
5. What are the advantages of composite materials?
6. What is the role of matrix is a composite material?
7. What is the role of reinforcement in composite materials?
8. Explain the various methods to increase surface interaction between matrix and fiber.
9. List the characteristics of matrix and fiber material.
10. List the properties of Al-Si and Al-Li.
11. Define ‘advanced ceramics’. Elaborate on the synthesis of silicon-carbide (SiC) by Acheson process.
12. Differentiate between melt and solution blending methods of synthesis of polymer nanoclay composites.
13. List the factors affecting alloying.
14. Appraise the industrial importance of silumin.
15. List the differences between ferro and nonferro alloys.
16. Describe the synthesis properties and application of (i) BN and (ii) WC
17. Outline the synthesis, properties and applications of (i) Al_2O_3 and (ii) SiC
18. Define an alloy. Elaborate on the composition, properties and applications of Cu-Al and (ii) Li-Al alloys

MULTIPLE CHOICE QUESTIONS

1. Identify which of the following kind of stress ceramics cannot withstand?
(a) Shear (b) Compressive
(c) Tensile (d) Normal

2. Which of the following leads to low tensile strength of ceramics?
(a) Dislocations (b) Structural defects
(c) Grain boundaries (d) Vacancy

3. Which of the following processes is important in fabrication of ceramics?
(a) Sintering (b) Rolling
(c) Forging (d) Casting

4. The raw materials used in the synthesis of BN are
(a) Quartz and coke (b) Quartz
(c) Coke (d) Borax and ammonia

5. The main constituents of composites are
(a) Fibre (b) Matrix
(c) Both a and b (d) None

6. The composition of whiteware ceramics is
(a) Clay (b) Silica
(c) Feldspar (d) All of these

7. Specify the example for natural composite.
(a) Kevlar (b) Bone
(c) Carbon (d) None

8. Ceramic materials can conduct
(a) Heat (b) Electricity
(c) Light (d) None of these

9. Ceramics have properties of
(a) High melting and boiling points (b) Hard
(c) Chemically inert (d) All of these

10. Which of the following carbides are used in cutting tools?
(a) Silicon-carbide (b) Tungsten-carbide
(c) Vanadium-carbide (d) Chromium-carbide

11. Identify the composition of aluminum bronze.
(a) Cu-Sn (b) Cu-Al
(c) Cu-Zn (d) Al-Si

12. Identify the example of high performance fiber.
(a) Carbon fiber (b) Polyester fiber
(c) Kevlar fiber (d) Liquid crystal fiber

13. Identify an example for nonoxide ceramic material.
(a) ZrO_2 (b) Al_2O_3
(c) SiC (d) SiO_2

14. Identify a good ceramic substrate for catalysis
(a) ZrO_2 (b) Al_2O_3
(c) SiC (d) SiO_2

15. Which of the following is a property of porcelain?
(a) Soft
(b) Absorbent
(c) Vitreous
(d) Expensive

16. Which of the following is not an alloy?
(a) Steel
(b) Copper
(c) Brass
(d) Bronze

17. Composite materials are classified based on
(a) Type of matrix
(b) Size and shape of reinforcement
(c) Both
(d) None of these

18. Which of these is the major load carrier in composites?
(a) Matrix
(b) Fiber
(c) Both
(d) Can't be defined

19. Mechanical properties of fiber-reinforced composites depend on
(a) Constituents
(b) Interface strength
(c) Fiber length and orientation
(d) All the above

20. The stronger constituent of a composite is
(a) Matrix
(b) Reinforcement
(c) Both are of equal strength
(d) Can't be defined

21. Which one of the following ceramics can be used as a pigment in paints?
(a) TiO_2
(b) SiC
(c) SiO_2
(d) none

22. Ceramics can conduct
(a) Heat
(b) Electricity
(c) Light
(d) None

23. Ceramics are well known for the properties of
(a) Hardness
(b) Chemical inertness
(c) Corrosion resistant
(d) All of these

24. Identify the alloy which is more suited for aircraft applications
(a) Cu-Si
(b) Si-Al
(c) Al-Li
(d) None

25. Identify the prime constituents of Silicon bonzes
(a) Si and Cu
(b) Cu and Al
(c) Li and Al
(d) Si and Al

ANSWERS

1. c 2. b 3. a 4. d 5. c 6. a 7. b 8. d 9. d
10. b 11. b 12. c 15. c 16. b 17. c 18. a 19. d 20. b
21. a 22. d 23. d 24. b 25. d