

## 4.5 CERAMIC MANUFACTURING METHODS

The various steps to be considered for the processing are

- (i) **raw material processing,**
- (ii) **fabrication**
- (iii) **densification.**

The raw material powder is thoroughly mixed with water and other ingredients to obtain flow characteristic depending on particular processing technique. The different fabrication processes that are used for many years are

- (a) **casting,**
- (b) **extrusion**
- (c) **dry processing.**

### SLIP CASTING

*Casting* is a familiar process used for ceramic forming. In this process, the raw materials are mixed with a stable suspension of fluid like water in the range of 25 - 30 vol.%. **This suspension is known as slip.**

The slip is poured into a porous mold which is made of plaster of paris. The slip is absorbed into the mold wall leaving behind a solid layer on the mold.

The thickness of solid layer depends on the length of time in mold. This process is continued until the entire mold cavity becomes solid. **This process is known as slip casting** and the various stages are shown in Fig. 4.21.



Fig. 4.5.1- Solid slip casting

Advantages:

The main advantage of slip casting is the ability to form intricate shapes at relatively low cost.

The complex ceramics shapes which are produced using slip casting include turbine engine rotors, automobile wings, etc.

## ISOSTATIC PRESSING

In *isostatic pressing method*, a uniform pressure is applied on all sides.

The raw material is filled in rubber mold and it is sealed with plate and metal mandrel. The sealed rubber mold is inserted into liquid.

The liquid is kept inside the pressure vessel and preferably non compressible. The top of the pressure vessel is closed after inserting the rubber mold.

A hydraulic pressure is applied to the liquid and hence, the uniform pressure is experienced by the rubber mould in all directions. The friction of rubber mould with the walls is eliminated, which results in a uniform density of compacted material.

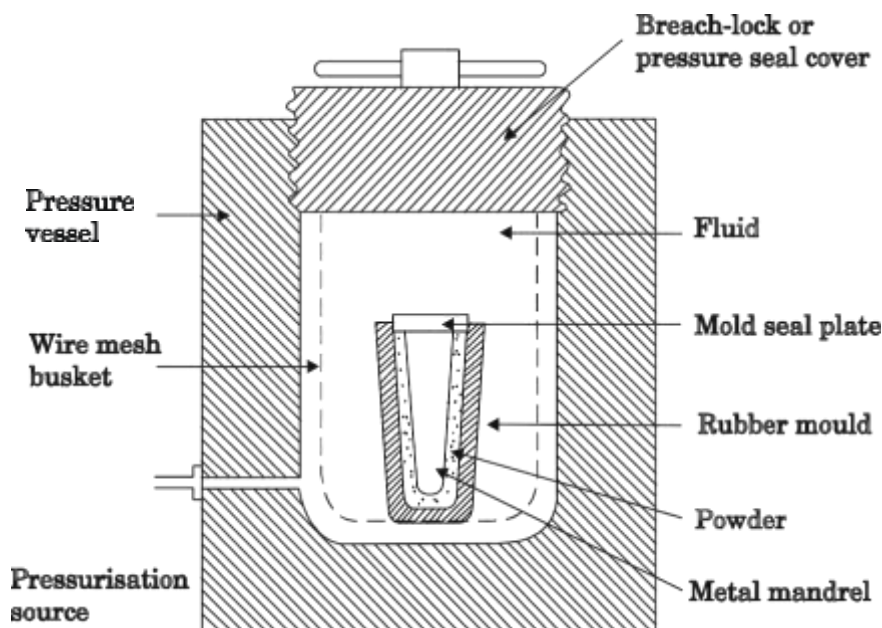


Fig. 4.5.2: Wet-bag isostatic pressing system

By removing the pressure, the rubber mould is taken out. The compacted material is removed by removing the mould sealed plate and metal mandrel.

The compacted materials are then subjected to densification resulting in more uniform shrinkage with less warping and cracking.

There are two different methods of isostatic pressing process

- (i) **wet-bag and**
- (ii) **dry-bag processing.**

In wet-bag processing method, raw material is filled in flexible rubber mold, sealed and then poured isostatically. The experimental set-up is shown in Fig. 4.22. The pressure applied in laboratory experiment process ranges from 35 to 1380 MPa.

However, in industry, the production units normally operate at a pressure of 400 MPa or even less.

This method is widely used for production of variety of products and sizes. The main disadvantages of this method are long cycle time, high labour requirements and low production rates.

## **GAS PRESSURE BONDING:**

### **Hot isostatic pressure :**

**The hot isostatic press (HIP) uses the simultaneous application of heat and pressure. We refer to this process as HIPing and the product as being HIPed. A furnace is constructed within a high-pressure vessel and the objects to be pressed are placed inside. Figure 4.5.3 shows a typical HIP arrangement.**

Temperatures can be up to 2000°C, and pressures are typically in the range 30-100 MPa. A gas is used as the pressure medium — unlike in the CIP where a liquid is often used. Argon is the most common gas used for HIPing, but oxidizing and reactive gases can be used. Note that the high-pressure vessel is not inside the furnace

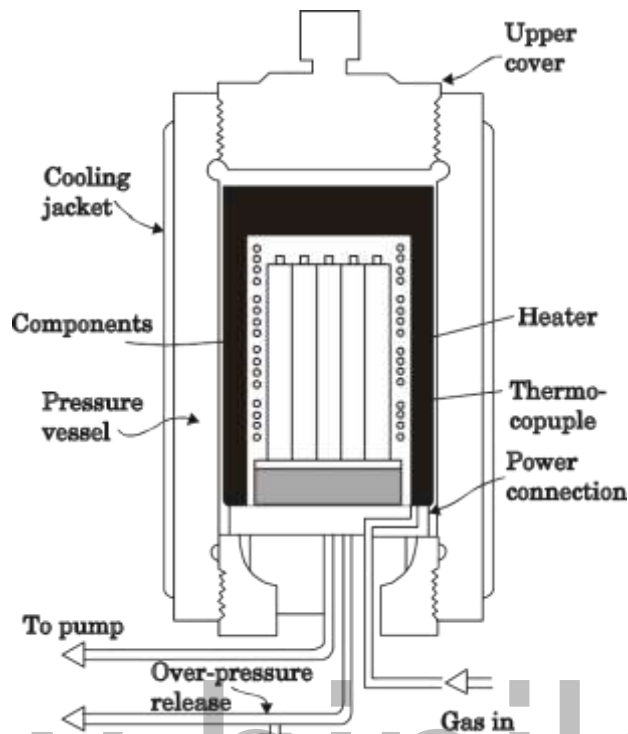


Fig. 4.5.3- Hot isostatic pressing apparatus

There are two variants of HIPing.

- Encapsulated: using a deformable container
- Not encapsulated: shape and sinter first, then HIPed
- Now HIPing is used for a wide variety of ceramic (and metallic) components, such as alumina-based tool bits and the silicon nitride nozzles used in flue-gas desulfurization plants by the utility industry.

The advantages of the HIPing process are becoming more important as interest in structural ceramics (e.g.,  $\text{Si}_3\text{N}_4$ ) grows.

- Nonoxide ceramics can be HIPed to full density while keeping the grain size small and not using additives. Very high densities combined with grain sizes (because of the relatively low temperatures) leads to products with special mechanical properties.

HIPing has also been applied to the formation of piezoelectric ceramics.

## 4.4 Ceramic materials

"Ceramic materials" are defined as those containing phases that are compounds of metallic and nonmetallic elements.

### 1. Functional Classification

- (i) Abrasives : Alumina, carborundum
- (ii) Pure oxide ceramics : MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>
- (iii) Fire-clay products : Bricks, tiles, porcelain etc.
- (iv) Inorganic glasses : Window glass, lead glass etc.
- (v) Cementing materials : Portland cement, lime etc.
- (vi) Rocks : Granites, sandstone etc
- (vii) Minerals : Quartz, calcite, etc.
- (viii) Refractories : Silica bricks, magnesite, etc.

### 2. Structural Classification

- (i) Crystalline ceramics: Single-phase like MgO or multi-phase form the MgO and Al<sub>2</sub>O<sub>3</sub> binary system.
- (ii) Non-crystalline ceramics: Natural and synthetic inorganic glasses.
- (iii) "Glass-bonded" ceramics: Fire clay products-crystalline phases are held in glassy matrix.
- (iv) Cements: Crystalline and non-Crystalline

## Properties of ceramic materials

### Mechanical properties

- (i) The compressive strength is several times more than the tensile strength.
- (ii) Non-ductile/brittle. Stress concentration has little or no effect on compressive strength
- (iii) The ceramic materials possess high modulus of elasticity due to ionic and covalent bonds.

### Electrical properties

(i) Ceramic exhibits low dielectric constant contributes to low power loss and low loss factor.

(ii) Porcelain has large positive temperature coefficient.

(iii) Rutile bodies have large negative coefficients,

(iv) The specific values of dielectric strength vary from 100 V per mil for low -tension electrical porcelain to 500 V per mil for some special ceramics.

(iv) At high temperature, rigidity is high.

(v) Rutile bodies show higher breakdown strength at higher frequencies.

### **Thermal properties**

Since the ceramic materials contain relatively few electrons, and ceramic phases are transparent to radiant type energy, their thermal properties differ from that of metals. The following are the most important thermal properties of ceramic materials.

#### **1. Thermal capacity**

- The specific heats of fine clay bricks are 0.25 and 0.297 at 1000°C and 1400°C respectively.
- Carbon bricks possess specific heats of about 0.812 at 200°C and 0.412 at 1000°C

## 2. Thermal conductivity

- The ceramic material possesses a very low thermal conductivity since they do not have enough free electrons.
- The impurity content, porosity and temperature decrease the thermal conductivity.
- In order to have maximum thermal conductivity, it is imperative to have maximum density which most of the ceramic materials do not possess.

## 3. Thermal shock

- "Thermal shock resistance" is the ability of a material to resist cracking or disintegration of the material under abrupt or sudden changes in temperature.
- Lithium compounds are used in many ceramic compounds to reduce thermal expansion and to provide excellent thermal shock resistance.
- Common ceramic materials graded in order of decreasing thermal shock resistance are given below:

1. Silicon nitride
2. Fused silica
3. Cordierite
4. Zircon
5. Silicon carbide
6. Beryllia
7. Alumina
8. Porcelain
9. Steatite

## Chemical properties

1. Several ceramic products are highly resistant to all chemicals except hydrofluoric acid and to some extent, hot caustic solutions. They are not affected by the organic solvents.
2. Oxidic ceramics are completely resistant to oxidation, even at very high temperatures.
3. Zirconia, magnesia, alumina, graphite etc., are resistant to certain molten metal and are thus employed for making crucibles and furnace linings.
4. Where resistant to attack from acids, bases and salt solutions is required, ceramics like glass are employed.

### **Optical properties**

1. Several types of glasses have been employed for the production of windows, subjected to high temperatures and optical lenses.
2. Special glasses used for selective transmission or absorption of particular wavelength such as infrared and ultra violet.

### **Nuclear properties**

As ceramics are refractory, chemically resistant and its different compositions offer a wide range of neutron capture and scattering characteristics. They are finding nuclear applications such as fuel elements, moderators, and controls and shielding.

### **Classification of Ceramic Products**

A general classification of 'ceramic products' is difficult to make because of the great versatility of these materials, but the following list includes the major groups.

1. Whitewares
2. Bricks and tiles
3. Chemical stonewares
4. Cements and concretes
5. Abrasives
6. Glass
7. Insulators
8. Porcelain enamel
9. Refractories
10. Electrical porcelain
11. Mineral ores
12. Slags and fluxes

### **Advantages of Ceramic Materials**

The ceramic materials have the following advantages



1. The ceramic are hard, strong and dense.
2. They have high resistance to the reaction of chemicals and to the weathering.
3. Possess a high compression strength compared with tension.
4. They have high fusion points.
5. They offer excellent dielectric properties.
6. They are good thermal insulators.
7. They are resistant to high temperature creep.
8. Cheaply available.

### Applications of Ceramics

The applications of ceramics are listed below

1. **Whitewares (older ceramics):** are largely used as:

- Tiles
- Sanitary wares
- Low and high voltage insulators
- High frequency applications
- Chemical industry - as crucibles, jars and components of chemical reactors;
- Heat resistant applications as pyrometers, burners, burner tips, and radiant heater supports.

2. **Newer ceramics:** (e.g., borides, carbides, nitrides, single oxides, mixed oxides, silicates, metalloid and intermetallic compounds) which have the high hardness values and heat and oxidation values are largely used in the following applications.

- Refractories for industrial furnaces
- Electrical and electronic industries as inductors, semiconductors, dielectrics, ferro-electric crystals, piezo-electric crystals, glass, porcelain alumina, quartz and mica etc.

- Nuclear applications - as fuel elements, fuel containers, moderators, control rods and structural parts. Ceramics such as  $UO_2$ ,  $UC$ ,  $UC_2$  are employed for all these purposes.
- Ceramic metal cutting tools-made from glass free  $Al_2O_3$
- Optical applications- ceramic material are useful as window glass and can resist very high temperature

### 3. **Advanced ceramics:** (e.g., $ZrO_2$ , $B_4C$ , $SiC$ , $TiB_2$ etc)

The advanced ceramics are used in the following areas.

- Internal combustion engines and turbines, as armor plate
- Electronic packaging
- Cutting tools
- Energy conversion, storage and generation

### **Structure of crystalline ceramics**

Most ceramic phases, like metals, have crystalline structure. Ceramic crystals are formed by the pure ionic bond, a pure covalent bond or both the ionic and covalent bonds.

- Ionic bonds give ceramic materials of relatively high stability. They are also harder and more resistant to chemical reactions.
- Covalent bond usually gives high hardness, high melting point and low electrical conductivity at room temperature.
- The ceramic crystals structures are, however, invariably more complex as compared to those of metals, since atoms of different sizes and electronic configurations are assembled together

Common crystal structure found in crystalline ceramics particularly those of oxide type are:

#### **1. Rock salt structure**

#### **2. Cerium chloride structure**

#### **3. Zinc blend structure**

#### **4. Wurzite structure**

#### **5. Spinal structure**

## 6. Fluorite structure

## 7. Ilmenite structure

### Classification of ceramics

Ceramics can also be classified into three categories as

- (i) **Crystalline ceramics**
- (ii) **Non-crystalline (Amorphous) ceramics**
- (iii) **Bonded ceramic**

### CRYSTALLINE CERAMICS

These have simple crystal structure, such as aluminium oxide (corundum), magnesium oxide, silicon carbide. Most of the oxides can be considered packing of oxygen ions with the cations occupying the tetrahedral and / or octahedral sites in the structure.

Magnesium oxide is used in refractory furnace lining for steel making. Silicon carbide is used for cutting tools.

The crystal structure of ceramic is, more complex, since atom of different size and electronic configuration are assembled together.

Common crystal structures found in crystalline ceramics particularly those of the oxide type are briefly described below:

#### **Cesium Chloride Structure**

It is possible for ceramic compounds to have simple cubic structure that are not found among metals. Cesium chloride is a prototype for this case.

In this structure, chlorine ions are arranged in a simple cubic structure and all interstices are occupied by cesium ions. The co-ordination number is eight (Fig. 4.4.1).

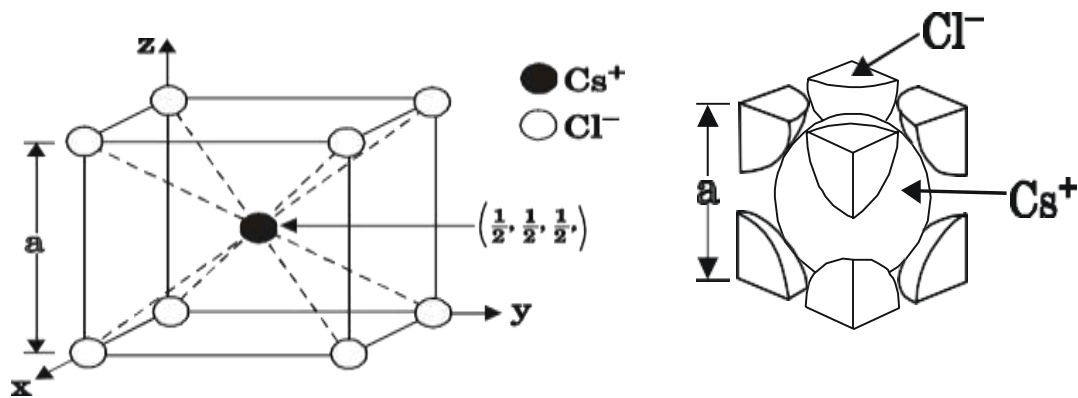


Fig. 4.4.1 A unit cell for the cesium chloride (CsCl) crystal structure

### Rock Salt Structure

Most of the oxides and halides crystallize in the closed packed cubic structure similar to that of a rock salt (sodium chloride). The structure can be considered as consisting of the fcc anions with smaller cations filling all available interstitial positions.

Here, each metal atom is surrounded by six non-metallic atoms and vice versa (Fig. 4.15). Thus, atomic coordination (CN) is the 6. Other examples include this

are MgO, CaO, BaO, CdO, MnO, FeO, CeO and NiO.

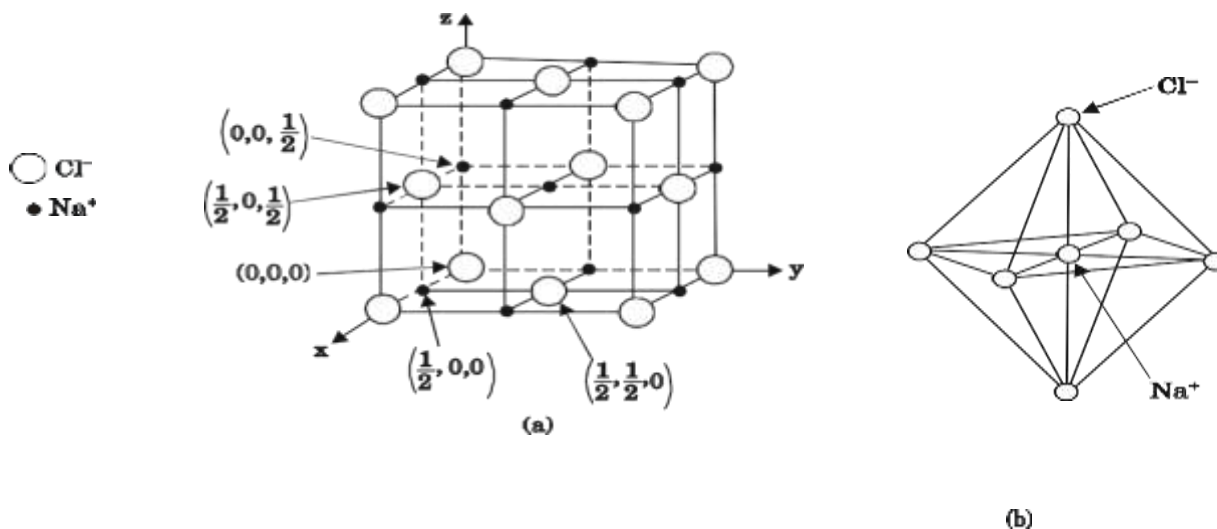


Fig. 4.4.2- A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure

## Zinc Blende Structure

Two of the more cubic ceramic compounds which have atoms in the 4-fold sites, are zinc blende (ZnS), silicon carbide ( $\beta$ -SiC). The atomic coordination is 4.

(Fig. 4.4.3)

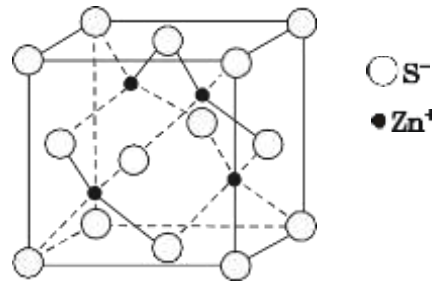


Fig. 4.4.3- A unit cell for the zinc blende (ZnS) crystal structure.

- Each type of atom form an fcc structure of its own.
- Only half of the available tetrahedral interstices are filled with the small cations.
- The structure is the same as the diamond cubic except that alternate atoms are of different elements.

This structure also includes cadmium sulphide (CdS) and aluminium phosphide (AlP).

## Perovskite Crystal Structure

It is also possible for ceramic compounds to have more than one type of cation. For example Barium titanate (BaTiO<sub>3</sub>),

having both Ba<sup>2+</sup> and Ti<sup>4+</sup> cations, falls into this classification.

This material has a *perovskite crystal structure*. A unit cell of this structure is shown in fig. 4.17. Ba<sup>2+</sup> ions are situated at all eight corners of the cube and a single Ti<sup>4+</sup> is at the cube

center. The  $O^{2-}$  ions located at the center of each of the six faces of the unit cell.

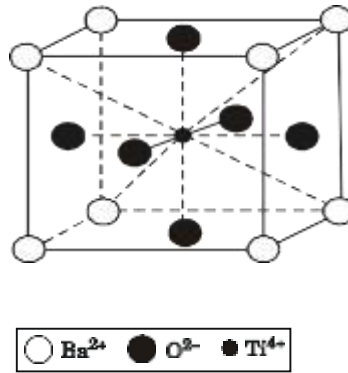


Fig. 4.4.4- A unit cell for the perovskite crystal structure

## NON - CRYSTALLINE CERAMICS

These are usually regarded super, cooled liquids. Their molecules are not arranged in regular geometric shapes. *e.g.* amorphous or fused  $SiO_2$  has each Si bonded to four O and each O is bonded to two Si.

This type of ceramics is used for mirrors, optical lenses, reinforcement fibres for GRP and optical fibres for data transmission.

### Silicates and Silica

Silicates are composed of silicon and oxygen, which are abundantly available in the Earth's crust. For example, rocks, soils and clay come under the classification of silicates.

A unit cell of silicate is a tetrahedron on which each atom of silicon is bounded to four atoms of oxygen as shown in figure 4.4.5.

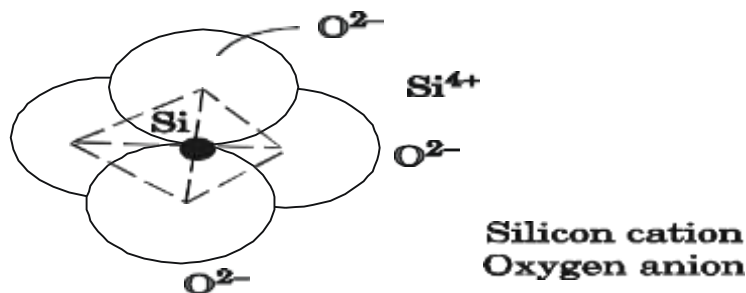


Fig. 4.4.5- Silicate Structure

Oxygen atoms are located on the edges of a tetrahedron structure and silicon atoms are located at the centre.

This basic unit of silicate is treated as negatively charged.

There is a covalent bond between Si and O, i.e. Si-O.

## Silica

Silica ( $\text{SiO}_2$ ) is the simple form of silicate. This is a three-dimensional network of tetrahedron where every corner oxygen atom is shared by adjacent tetrahedra. This material becomes electrically neutral but electronically stable.

Under this arrangement, the ratio of Si to O becomes 1:2 as given by chemical formula,  $\text{SiO}_2$ .

There are three polymorphic forms of silica: (1) quartz, (2) cristobalite and (3) tridymite. Silica is used in the manufacture of different varieties of glasses.

## Structure of glasses

Generally, solids have three-dimensional periodic structures as shown in figure 4.4.6. This is a crystalline structure.

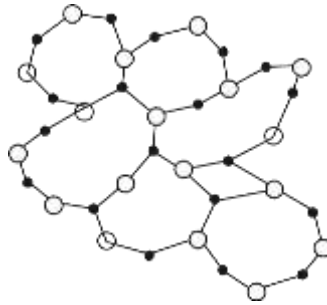


*Fig. 4.4.6- Crystalline Structure (Orderly Repeated)*

The materials, which do not have three-dimensional structures, but random structure as shown in figure 4.4.6 are said to be amorphous or glassy.

Many metal alloys, oxide compounds and non-oxide compounds form glassy structure. Fused silica or vitreous silica has high degree of atomic randomness.

Similarly, oxide as  $B_2O_3$  and  $GeO_2$  may also form glassy structure.



*Fig. 4.4.7- Random Structure (Amorphous)*

The glasses that are used containers and windows are silica glasses in which oxides such as  $CaO$  and  $Na_2O$  are added.

## **BONDED CERAMICS**

These ceramics contain both crystalline and non-crystalline materials which are bound together by a glassy matrix after firing. This group includes the lining and clay products.

Bonded ceramics are used as electrical insulators, refractory for furnace, spark plugs etc.



## 4.1 Fibre reinforced plastics

It is a composite material. We know that the composite materials have been developed to get improved or desired properties in them. Nowadays fiber reinforced plastics (FRP) plays an important role in the machine parts where we require high strength, high modulus, heat resistance and light weight.

The fibrous glass is used in reinforced plastics in the form of ravings, chopped strands, milled fibers, yarns, mats and woven fabrics. Most commonly used reinforcements are

- (i) Random chopped strand mat, bonded together with a resinous binder (polyester).
- (ii) Mat from continuous strands, deposited in a swirl pattern and loosely bonded together with a resinous binder.
- (iii) Filament type thin mats.
- (iv) Performs
- (v) Woven fibrous glass clothes.
- (vi) Parallel stranded glass fibers
- (vii) Short stranded

The glass fibers having a vinyl silane-epoxy surface treatment on the fibers are used. This treatment gives best dry and wet strength. E type glass is one of the important glass fiber materials which use boric acid rather than soda ash as one of the component of the melt. Mostly polyester resin is used as plastic. Epoxy and phenolic resins are also used.

The fibers are made from synthetic textile fibers treated in such a way that the side groups are entirely removed. The carbon fiber reinforced plastics are used in aeroengines, high pressure rotor and stator blades since they can withstand higher thrusts. Silica and boron fiber reinforced plastics have high strength and low density. But these are all costlier than glass or carbon fiber reinforced plastics.

### Advantages

1. It has high strength to weight ratio
2. It has low cost tooling.
3. Large shapes are possible in one piece. Since it can be fashioned more easily than a metal it is used in making complicated machine parts.
4. Excellent environment exposure resistance can be obtainable.

5. It has excellent electrical properties.
6. It has higher heat resistance.

### Disadvantages

1. The material cost is so high.
2. The strengths perpendicular to fiber orientations are low.
3. It has low rate of heat transfer and dissipation.
4. It has lower flexural modulus than steel and requires higher thickness .

### Fiber reinforced metal

Fiber reinforced metals (FRM) are composites, which are made up of inorganic fibers fabricate with metal.

FRM are composed of fibers (reinforcement phase) and metals (matrix phase). The following diagram exhibits the FRMs (silicon fiber reinforced in metals).

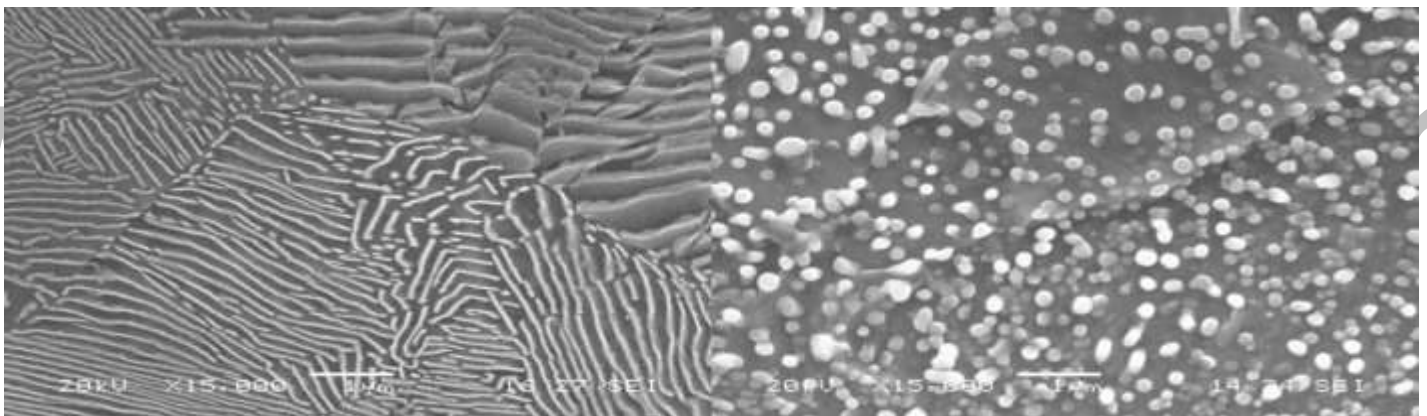


Fig:4.1.1- Fiber reinforced metal

### Fabrication of FRM

The fabrication of FRM consists of joining the interfaces of both phases. Before doing the fabrication of FRM, the reinforcement fibers and the matrix materials should be chosen carefully with light weight and high strength materials.

The reinforcement fibers and the corresponding matrix metals used for fabricating FRM are given below.

S. No	Reinforcement Fibers	Matrix metals	Composite System
1.	Boron	Al and Mg	Boron System
2.	Carborundum	Al and Ti	Corborundum System
3.	Carbon	Al, Mg and Cu	Carbon System
4.	Alumina	Al and Mg	Alumina System

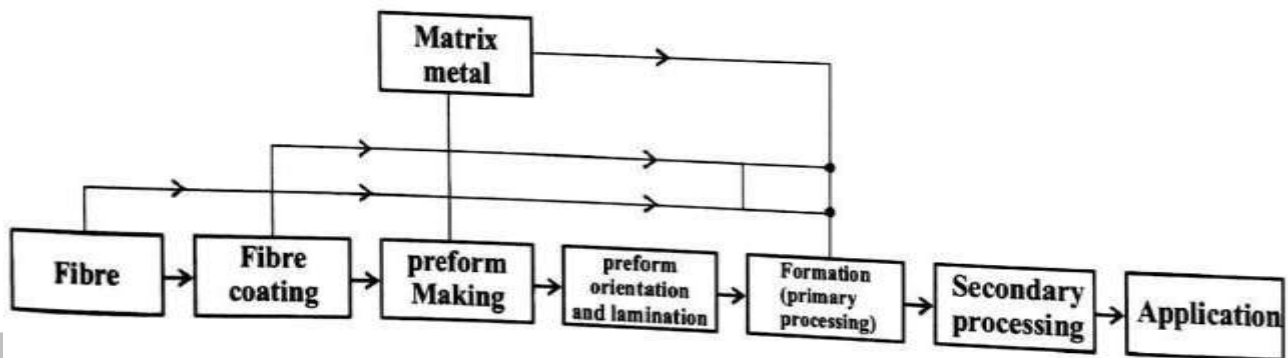


Fig:4.1.2-Matrix Process

1. Depending upon requirements, fibers are given pre-treatment such as fibre coating to improve wetting and joining ability with matrix metals and to prevent failure caused by reaction between different surfaces.
2. Then, performs are made, which are cut to the required dimensions.
3. These performs are oriented and laminated according to the design specifications of the components.
4. The next process is called forming (primary processing) in which composition and shaping is carried out.
5. At this stage the matrix metal and the reinforcement fibers are primarily processed together to form the FRM composite.
6. After forming the FRM, the secondary processing such as cutting, trimming and joining is done.

Thus the fabrication is complete and shall be used for further applications.

## Properties of FRM

- i) FRM is light weight
- ii) FRM has a high stiffness
- iii) FRM possess high strength at high temperatures [i.e. 200 to 400 °C].
- iv) FRM are high in inter-lamina strength and stress transmissibility between filaments and highly resistant to polyaxial and complex stress.
- v) FRM are resistant to impact and superior in extreme low temperature characteristics.
- vi) FRM are infiltrated by water and are not corroded by rain.
- vii) They do not require any measures against lightning strike or static, nor any coating for electromagnetic shielding

## Applications of FRM

- i) FRM are used in constructing space machines and satellite body structures. The material system used for this are B/Al, B/Mg, C/Al, C/Mg.
- ii) FRM are to make pylons, frames, beams, fans, compressor blades, fairings, wing boxes, access-doors in air crafts. The material systems used here are B/ Al, SiC/ Al.
- iii) FRM are used to make truss structures in helicopters. The promising material systems used are B/ Al, SiC/ Al, Al<sub>2</sub>O<sub>3</sub>/ Al.
- iv) FRM are used to make engine electric components such as motor brushes, cables, etc., C/Cu is the material systems used for these products.
- v) FRM are used to make sports goods such as tennis rackets, Golf clubs, etc., the materials systems used for these are B/ Al, SiC/ Al, C/Al, Al<sub>2</sub>O<sub>3</sub>/ Al.

## 4.8 HIGH ALUMINA CERAMICS

High alumina ceramics contains 85% or more by weight of  $\text{Al}_2\text{O}_3$ .

- Alumina is nothing but an aluminium oxide ( $\text{Al}_2\text{O}_3$ ), which is the oldest engineering ceramic.
- Alumina is produced from bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ).

### *Characteristics of alumina:*

1. Aluminas have excellent hardness, wear resistance and chemical inertness properties.
2. They are more stiffer than steels.
3. They are more stronger in compression than many hardened tool steels.
4. They retain 50% of their room temperature strength at elevated temperature (about  $1093^\circ\text{C}$ ).
5. They possess very good environmental resistance.
6. These are mechanically strong, dense materials, unlike refractories which are usually porous.
7. They have ability to resist high temperature because they are poor thermal conductors.
8. They possess low neutron absorption cross-section. This property enables them to find application in nuclear equipment.
9. Alumina is blended with other ceramics such as zirconia to improve its tensile and toughness properties.
10. They have high corrosion resistance.
11. They have high dimensional stability.

## Applications & uses

- (i) Alumina is used as a refractory material for high temperature applications.
- (ii) Alumina makes an excellent high voltage insulator. Classical applications are for insulators in spark plugs and in insulating substrates to support integrated circuits.
- (iii) Alumina based ceramic tools have very high abrasion resistance, hot hardness and are chemically stable than high speed steels. So they are used in cutting cast irons, and steels to obtain good surface finish.
- (iv) Because of its high hardness, it is often used as an abrasive material in grinding wheels.
- (v) It is used for pump liners, pump impellers, check valves and nozzles subjected to erosion.

Some unique applications found in medical use that include restoration of teeth, bone filter and orthopaedic implants

## 4.2 Metallic glasses

**Definition:** *Metallic glasses* are the amorphous metallic solids which have high strength, good magnetic properties and better corrosion resistance and will possess both the properties of metals and glasses.

*Examples: Alloys of Fe, Ni, Al, Mn, Cu, Cr and Co mixed with metalloids such as Si, Ge, As, B, C, P and N.*

### CONCEPT BEHIND THE FORMATION OF METALLIC GLASSES

Generally, liquids can be made into glassy state by increasing the rate of cooling. In a similar manner the metals can also be made into glassy state by increasing the rate to cooling to a very high level [ $2 \times 10^6$  °C per second]. At that state the atoms will not be able to arrange orderly because of its rapid cooling rate.

Thus, the atoms will not be allowed to go to crystalline state, rather it goes to amorphous state and it will form a new type of material. These new types of materials which are made by rapid cooling technique (i.e., the temperature decreases suddenly with respect to time) are called *metallic glasses*.

The cooling rate for the formation of metallic glasses varies from material to material. **Glass Transition Temperature**

*The temperature at which the metals [alloys] in the molten form transforms into glasses i.e., liquids to solids is known as **glass transition temperature (T<sub>g</sub>)**.*

It was found that the glass transition temperature for metallic alloys varies from 20°C to 300°C.

### PREPERATION OF METALLIC GLASSES

#### Principle

*“Quenching” is a technique used to form metallic glasses, Quenching means rapid cooling. Actually, atoms of any materials move freely in a liquid state. Atoms can be arranged *regularly* when a liquid is cooled *slowly*. Instead, when a liquid is *quenched*, there will be an *irregular pattern*, which results in the formation of metallic glasses.*

## Technique

The process involved in the formation of metallic glasses is melt spinning technique. This technique is illustrated in Fig.

## Experimental Setup

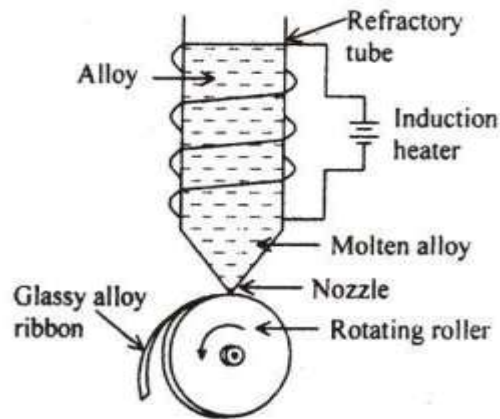


Fig:4.2.1- Melt spinning technique

The setup consists of a refractory tube with fine nozzle at the bottom. The refractory tube is placed over the rotating roller made up of copper. An induction heater is wound over the refractory tube in order to heat the alloy inside the refractory tube as shown in fig 4.2.1

## Preparation

The alloy is put into the refractory tube and the induction heater is switched ON. This heats the alloy and hence the super-heated molten alloy is ejected through the nozzle of the refractory tube onto the rotating roller and is made to cool suddenly. The ejection rate may be increased by increasing the gas pressure inside the refractory tube. Thus due to rapid quenching a glassy alloy ribbon called metallic glass is formed over the rotating roller.

Metallic glasses of various thicknesses can be formed by increasing (or) decreasing the diameter and speed of the roller.

## TYPES OF METALLIC GLASSES

Metallic glasses are of two types viz,

### (i) Metal-metalloid glasses

Examples: Metals : Metalloids

Fe, Co, Ni: Ge, Si, B, C



## (ii) Metal – Metal glasses

Examples: Metals : Metals

Ni : Niobium

Mg : Zn

Cu : Zr

## PROPERTIES OF METALLIC GLASSES

Since the atoms in the metallic glasses are disordered, they have some peculiar properties as follows:

### (i) Structural Properties

- a. Metallic glasses have tetrahedral closely packed (TCP) structure rather than hexagonal closely packed (HCP) structure.
- b. They do not have any crystal defects such as grain boundaries, dislocations etc.

### (ii) Mechanical Properties

- a. The metallic glasses are very strong in nature.
- b. They have high corrosion resistance.
- c. They possess malleability, ductility etc.

### (iii) Magnetic Properties

- a. Metallic glasses can be easily magnetized and demagnetized.
- b. They have very narrow hysteresis loop as shown in fig. In Fig the hysteresis loop of the metal alloy in crystalline phase is also given for reference.
- c. They exhibit very low hysteresis loss and hence transformer core loss is very less.

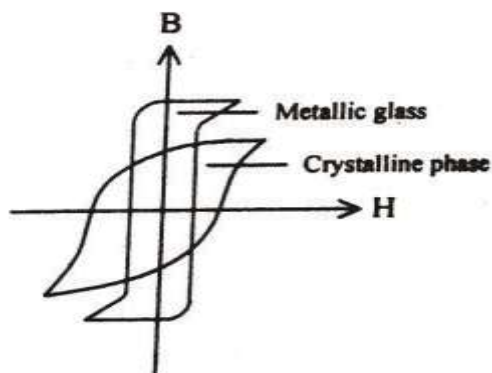


Fig:4.2.2- Hysteresis loop

#### (iv) Electrical Properties

- a. Metallic glasses have high electrical resistance .
- b. The electrical resistance for metal glasses will not vary with temperature.
- c. They possess very low eddy current losses.

#### APPLICATIONS OF METALLIC GLASSES

- \* Since the metallic glasses possess low magnetic loss, high permeability, saturation magnetization and low coercivity, *these materials are used in cores of high power transformers.*
- \* As the metallic glasses are malleable and ductile, it can be used in simple filament winding to reinforce pressure vessels.
- \* Since the metallic glasses are very strong/hard they are used to make different kinds of springs.
- \* As the metallic glasses are similar to the soft magnetic alloys, they are used in leads of tape recorder, cores of transformers and magnetic shields.
- \* Because of their high resistivity, they are used to make computer memories, magneto-resistance sensors etc.
- \* Since they have high corrosion resistance, they are used in reactor vessels, surgical clips, marine cables etc.
- \* Since some metallic glasses can behave as super conductors, they are used in the production of high magnetic fields.
- \* Since the metallic glasses are not affected by irradiation, they are used in nuclear reactors.

## 4.7 PIEZO AND FERROELECTRIC CERAMICS

We know that the piezoelectric crystals undergo a change in polarisation when they are subjected to a stress. The application of compressive stress results in the displacement of charge in one direction while tensile stress leads to the displacement of charge in opposite direction.

*Pyroelectric crystal* is one which produces spontaneous polarisation due to application of electric field. Further in these crystals, a change in temperature also produces a change in spontaneous polarisation.

On the other hand, if one changes the direction of electric field, the direction of spontaneous polarisation also changes. The crystals exhibiting this additional property are known as *ferroelectrics*.

Therefore, ferroelectric crystal exhibit spontaneous and reversible polarisation. Most of the properties of ferroelectricity and ferromagnetism are common.

The ferroelectric properties disappear at certain temperature  $T_C$  (curie temperature). The crystal will be in paraelectric state above  $T_C$ , which is analogous to paramagnetism.

The crystal in the paraelectric state obeys Curie-Weiss law. Therefore, the spontaneous polarisation takes place, below  $T_C$ .

Examples for the ferroelectric ceramics are Rochelle salt,  $\text{BaTiO}_3$ ,  $\text{SiTO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{LiNbO}_3$ ,  $\text{NaNbO}_3$ ,  $\text{KNbO}_3$ ,  $\text{PbTa}_2\text{O}_3$ , etc.

The structure, Curie temperature and Curie constants of ferroelectric ceramics are shown in Table.

## Hysteresis

Ferroelectric ceramic materials exhibit the hysteresis behaviour. The hysteresis behaviour exhibited by a single crystal and polycrystalline material is shown in fig. 4.24 and fig. 4.25 respectively.

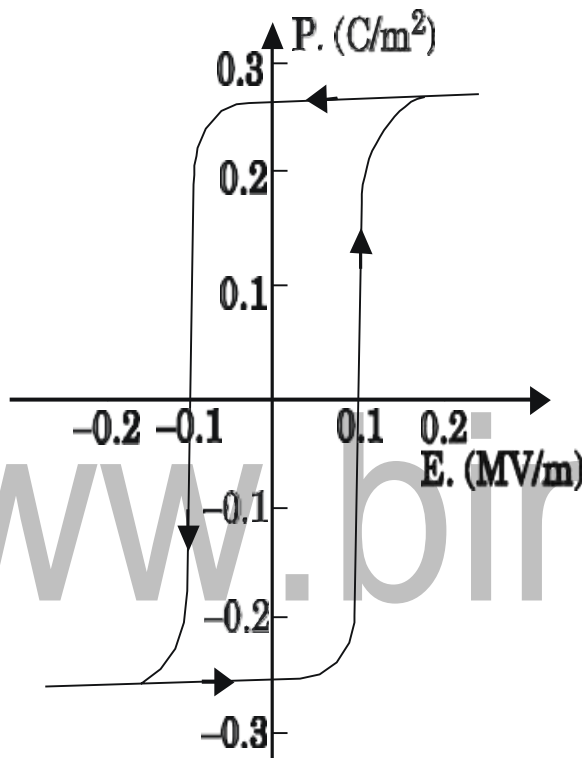


Fig. 4.7.1 Hysteresis loop - single crystal

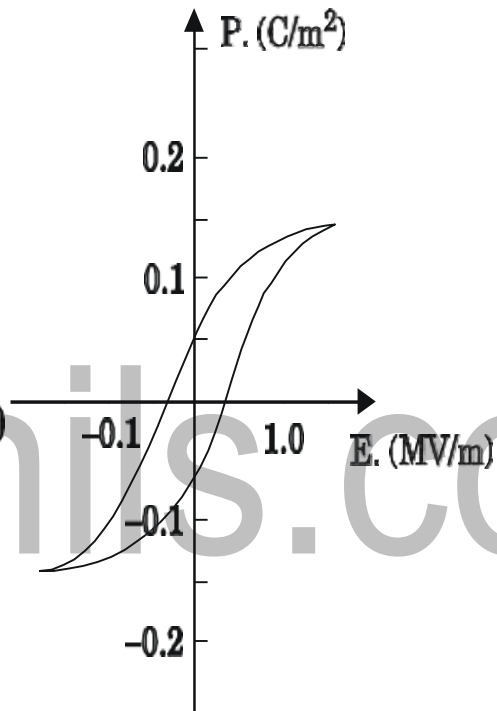


Fig. 4.7.2 Hysteresis loop - polycrystalline

## FERROMAGNETIC CERAMICS

We know that soft magnetic (ferro magnetic) materials are easy to magnetise with low value of magnetic field. On the other hand, the hard magnetic materials require larger magnetic field for magnetisation as well as demagnetisation.

Therefore, the coercive field is very high and hence, used to make hard magnets for applications such as recording media and permanent magnet. The soft magnetic ceramics, exhibits similar properties as that of soft magnetic materials (metal counter parts).

However, soft magnetic ceramics are good electrical insulators. The eddy current losses of the soft magnetic ceramics are very low. Therefore, the magnetic ceramic materials are used whenever there is a requirement of reduction in the eddy current losses. The magnetic ceramic materials are classified into three types namely,

- **spinel,**
- **garnets and**
- **hexagonal ferrites.**

### *Hexagonal Ferrites*

Hexagonal ferrites are ferromagnetic materials. The general formula for hexagonal ferrites is  $BaO \cdot 6Fe_2O_3$ . The structure of ferrites is in line with magneto plumbite and hence, it is called *magneto ferrites*.

In this structure, all magnetic spins are parallel. Based on the arrangement of grains, hexagonal ferrites are classified as *isotropic* and *anisotropic ferrites*.

The grains are arranged in random manner in isotropic ferrites, while in anisotropy crystals they are aligned in a regular manner. One can obtain the anisotropy by the influence of magnetic field.

Thus, hexagonal ferrites have high anisotropy constants and hence, are used to fabricate hard magnets with high coercive fields.

In view of its low conductivity, high coercive fields, easy manufacturing, etc., hexagonal ferrites is one of the important permanent magnets. It finds wide application like loudspeaker and compact dc motors, where a large field is required.

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### 4.3 Shape memory alloys

*Shape memory alloys (SMA) are the alloys which change its shape from its original shape to new shape and while heating /cooling it will return to its original shape.*

#### Transformation temperature

In SMA, the shape recovery process occurs not at a single temperature rather it occurs over a range of temperature [may be few degrees].

*Thus, the range of temperature at which the SMA switches from new shape to its original shape is called **transformation temperature (or) memory transfer temperature.***

Below the transformation temperature the SMA can be bent into various shapes. Above the transformation temperature the SMA returns to its original shape. This change in shape was mainly caused due to the change in crystal structure (phase) within the materials, due to the rearrangement of atoms within itself.

#### PHASES (STRUCTURES) OF SMA

In general the SMA has two phases (crystal structures) viz.,

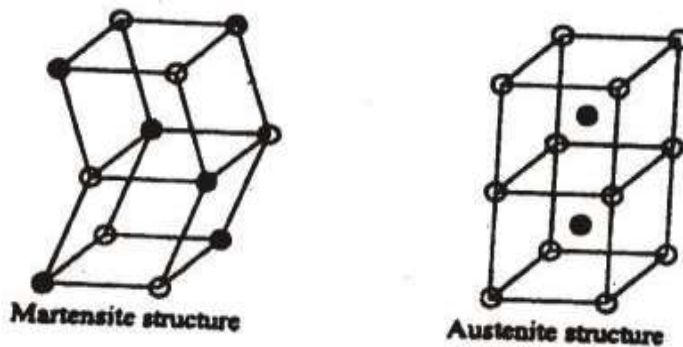


Fig:4.3.1- Two phases of SMA

#### (i) Martensite

Martensite is an interstitial super solution of carbon in  $\gamma$ -iron and it crystallizes into **twinned structure** as shown in fig. 4.3.1. The SMA will have this structure generally at lower temperatures and it is soft in this phase.

#### (ii) Austenite

Austenite is the solid solution of carbon and other alloying elements in  $\gamma$ -iron and it crystallizes into **cubic structure** as shown in fig4.3.1. The SMA will attain this structure at higher temperatures and it is hard in this phase

## PROCESSING OF SMA

### Shape memory effect

*It is very clear that at lower temperature the SMA will be in martensite structure and when it is heated then it will change its shape to austenite structure and while cooling it will again return to martensite form. This effect is called **shape memory effect**.*

Let us consider a shape memory alloy, for which the temperature decreased. Due to decrease in temperature, phase transformation take place from austenite to twinned martensite as shown in fig 4.3.3 [Process 1] i.e., a micro constituent transformation takes place from the platelet structure (Austenite) to needle like structure (martensite).

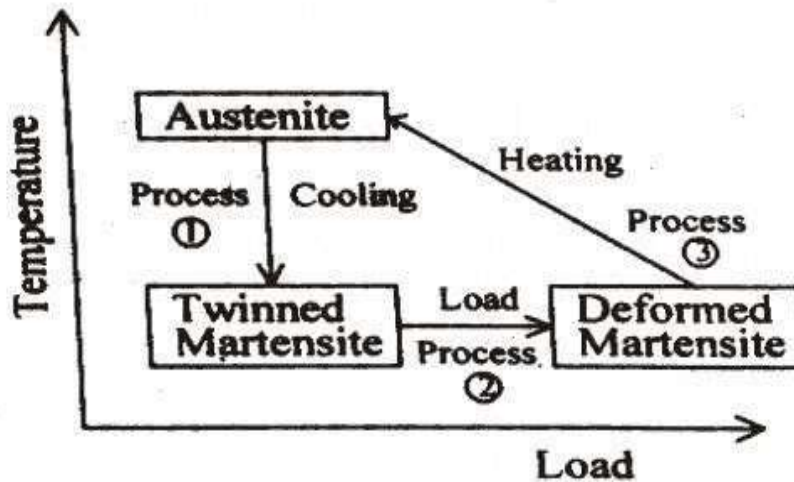


Fig:4.3.3- Phase transformation

During this state the twinned martensite phase will have same size as that of austenite phase as shown (Macroscopic view). Hence macroscopically if we see, no change in size (or) shape is visible between the Austenite phase and twinned Martensite phase of the SMA. It is found that the transformation from austenite to martensite takes place not only at a single temperature, but over a range of temperatures.



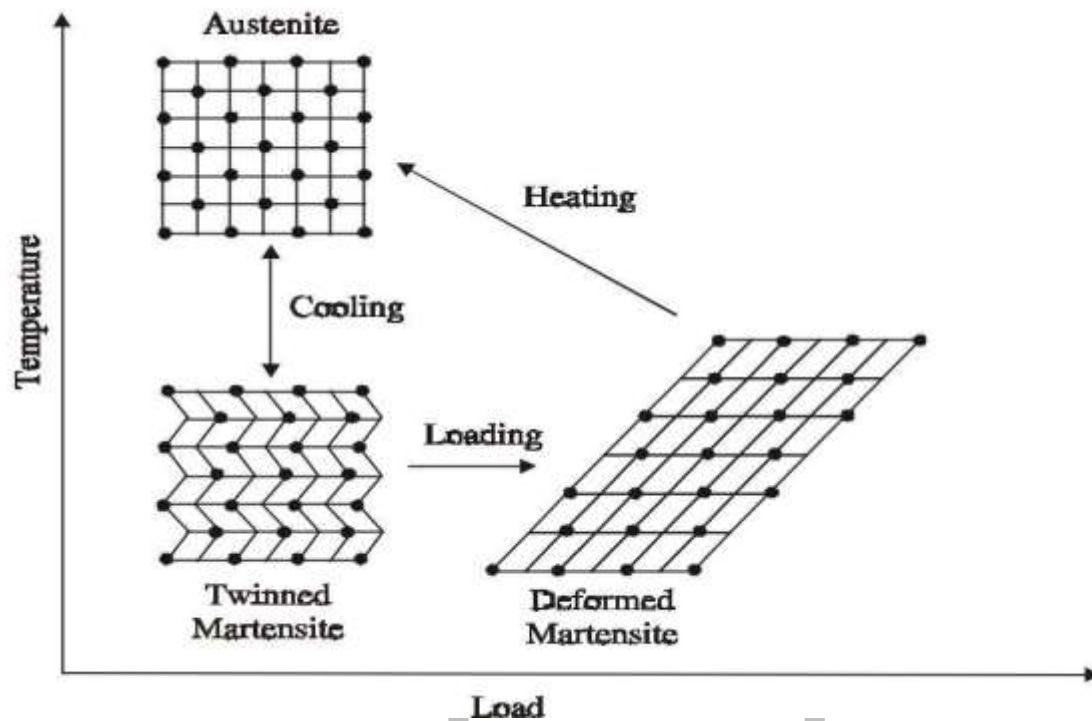


Fig:4.3.4- Transformation from austenite to martensite

Both austenite and twinned martensite is suitable in a particular range of temperature. Now when the twinned martensite is applied a load, it goes to deformed martensite phase as indicated in fig (Process 2). During the transformation from twinned martensite to deformed martensite the change in shape and size occur both microscopically and macroscopically as shown in fig 4.3.4

Now when the material is further heated it will go from deformed martensite to austenite form (Process 3) and the cycle continues as shown in fig 4.3.4

### CHARACTERISTICS OF SMA

- (i) The transformation occurs not only at a single temperature rather they occur over a range of temperatures.
- (ii) **Pseudo – elasticity:** *Pseudo-elasticity occur in some type of SMA in which the change in its shape will occur even without change in its temperature*

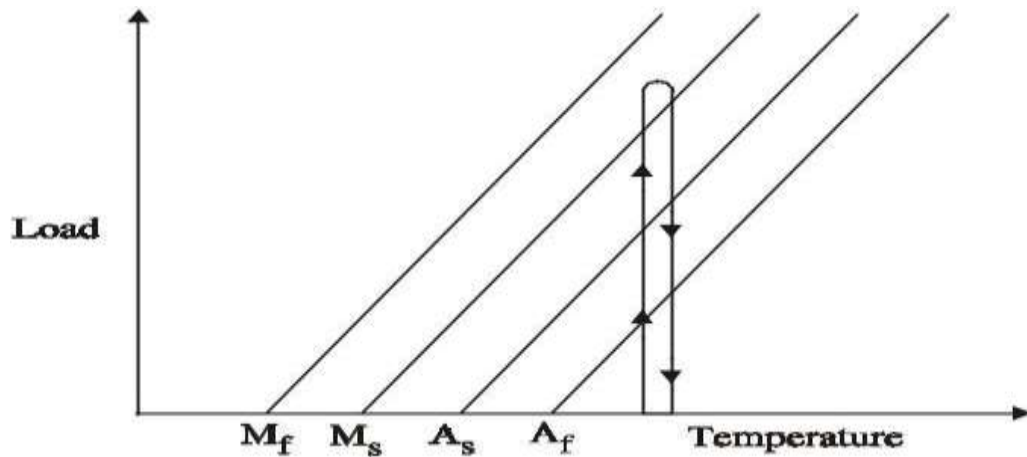


Fig:4.3.5- Transformation over a range of temperatures.

(i) **Super – elasticity:** *The shape memory alloys which have change in its shape at constant temperature are called **super-elastic SMAs** and that effect is known as super-elasticity.*

Here, at a single temperature, when the load is applied the SMA will have a new shape(deformed Martensite) and if the load is removed it will regain its original shape (Twinned Martensite), similar to pressing a **rubber** (or) **a spring**.

(iv) **Hysterisis:** For an SMA, during cooling process, a martensite starts ( $m_s$ ) and ends( $m_e$ ) and during heating process, austenite starts ( $A_s$ ) and ends ( $A_e$ ).

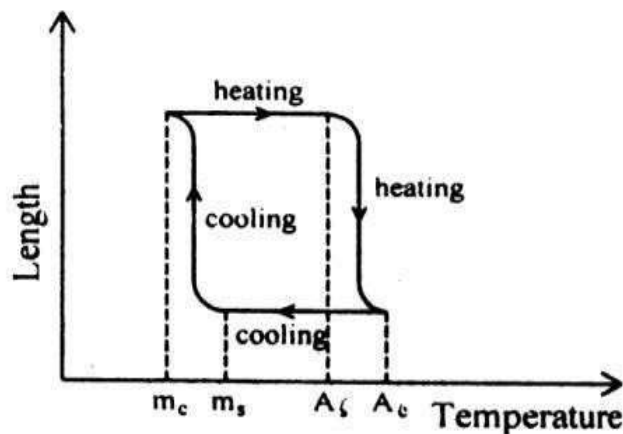


Fig:4.3.6- Cooling & Heating process

It is found that they do not overlap with each other and the transformation process exhibits the form of hysteresis curve as shown in fig.(4.3.6)

iii. Crystallographically the thermo-elastic martensites are reversible.

## APPLICATIONS OF SMA

Shape memory alloys have vast applications in our day-to-day life, as follows:

1. We know that the recently manufactured eye glass frames can be bent back and forth, and can retain its original shape within fraction of time. All these materials are made up of Ni-Ti alloys, which can withstand to maximum deformation.

2. We might have seen toys such as butterflies, snakes etc. which are movable and flexible. These materials are made using SMAs.

3. The life time of Helicopter blades depends on vibrations and their return to its original shape. Hence shape memory alloys are used in helicopter blades.

4. The SMA is cooled and sent into vein, due to body temperature it changes its shape and acts as a blood clot filter, by which it controls the blood flow rate.

5. The SMA is mainly used to control and prevent the fire and toxic gases (or) liquids to a large extent. For example, if an SMA is placed in a fire safety valve, when fire occurs, then due to change in temperature the SMA changes its shape and shuts off the fire. Similar principle has been used in the area of leakage in toxic gases (or) liquids.

6. The Ni-Ti spring is used to release the hot milk and the ingredients at certain temperature and to close it after particular time, thereby we can get coffee automatically [coffee makers].

7. SMA is used for cryofit hydraulic couplings i.e., to join the ends of tubes. Here, the SMA material is pasted in between the two tubes to be joint at a particular temperature when the temperature change the SMA expands and thus the two ends are joined.

8. Using SMA the circuit can be connected and disconnected, depending on the variation in temperature. Hence SMA is used as a circuit edge connector.

9. They are used in controlling and preventing cracks.

10. They are used in relays and activators.

11. They are used for steering the small tubes inserted into the human body.

12. They are used to correct the irregularities in teeth.

13. Ni-Ti SMA is also used in artificial hip-joints, bone-plates, pins for healing bones-fractures and also in connecting broken bones.

### **Advantages**

- i. SMA is very compact in nature.
- ii. It is safe and smart.
- iii. They are flexible.
- iv They are Non-Corrosive.

### **Disadvantages**

- i. Cost is high
- ii. Efficiency is low.
- iii. Transformation occurs over a range of temperatures.
- iv. Structural arrangements may sometime get deformed.

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## 4.6 THERMAL PROPERTIES

Since the ceramic materials contain relatively few electrons, their thermal properties differ from that of metals. The most important thermal properties of ceramic materials are.

- (i) **Thermal capacity**
- (ii) **Thermal conductivity**
- (iii) **Thermal shock resistance**

### (i) **Thermal capacity**

- The specific heats of fine clay bricks are 0.25 at 1000°C and 0.297 at 1400°C.
- Carbon bricks possess specific heats of about 0.812 at 200°C and 0.412 at 1000°C.

### (ii) **Thermal conductivity**

- The ceramic materials possess a very low thermal conductivity since they do not have enough free electrons.
- The impurity content, porosity and temperature decrease the thermal conductivity.
- The ceramic materials possess low thermal conductivity due to its low density.

### (iii) **Thermal Shock**

“*Thermal shock resistance*” is the ability of a material to resist cracking or disintegration of the material under sudden changes in temperature.

- *Lithium compounds* are in many ceramic compounds to *reduce thermal expansion* and *provide excellent thermal shock resistance*.

## MECHANICAL PROPERTIES OF CERAMICS

The mechanical behaviour of ceramic phases is determined in a number of ways depending upon how the force is applied: compressive, tensile, transverse, torsional shear or impact.

- **Compressive strength.** Compressive strength in ceramics in general is many times greater than tensile strength. Therefore, ceramics like brick, cement, and glass are always used in the compression and not in tension.
- **Shear strength.** High shear strengths and low fracture strengths are generally characteristics of ceramics. Therefore, they commonly fail nonductilely, *i.e.* in a brittle manner by fracture.
- **Tensile strength.** Tensile strength in ceramics are theoretically high, but in practice are usually quite low. Failures are often due to stress concentrations at the pores, grain corner or microcrack.
- **Transverse strength or modulus of rupture.** Transverse strength is difficult to ascertain in ceramic materials. Ceramics are, therefore not used in places where transverse strength of materials is an important criterion.
- **Torsional strength.** Torsional strength is seldom considered as a critical property of ceramics since tensile and cantilever requirements will show the torsional strength of material.
- **Modulus of elasticity.** Ceramic materials have high modulus of elasticity ranging from  $7 \times 10^{10}$  to  $42 \times 10^{10}$  N/m<sup>2</sup> which indicates the strength of the bond.
- **Plastic deformation.** Due to the restricted slip, most of materials does not permit plastic deformation. The ceramic materials have greater resistance to slip than do metals.

## **Toughness of Ceramic Materials**

Due to presence of covalent-ionic bonding, ceramics have low toughness.

## **ELECTRICAL PROPERTIES**

Electrical properties depends upon composition, texture, size and density of material and also on temperature and time. These factors greatly influence the electrical behavior of a ceramic material.

Ceramic materials are used as insulators, conductors, semiconductor and dielectrics. Ceramics are also used as ferroelectric and piezoelectric materials.

- Ceramics are generally poor conductors of electricity because the electrons associated with the atoms ceramics are shared covalent or ionic bonds. The electrical properties of ceramics mainly depend on the following factors.

(i) volume resistivity, (ii) dielectric strength,  
(iii) dielectric constant, and (iv) dissipation factor (or lossfactor).

### **Ceramic insulator**

Ceramic materials are used in an electrical circuit both as the electrical insulators and as its functional parts.

Porcelains are very commonly used as electrical insulators and resistors.

### **Dielectric ceramics**

Ceramic materials have good dielectric capacity.

Porcelain and high grade fire clays have high dielectric strength. The dielectric varies with temperature.

### **Ceramic semiconductor**

Although ceramic compounds are normally insulators, they become semiconductors if they contain multivalent transition elements.

## CHEMICAL PROPERTIES

### *Chemical resistance*

- The great majority of ceramic products, are highly resistant to all chemicals except hydrofluoric acid and to some extent, hot caustic solutions.
- Organic solvents do not affect the ceramics.
- Oxidic ceramics are completely resistant to oxidation, even at very high temperatures.
- Magnesia, zirconia, porcelain, graphite, alumina, etc., are resistant to certain molten metals. They are used for making crucibles and furnace linings.
- Ceramics like glass are employed where resistance to attack from acids, bases and salt solutions is required.