ENGINEERING MATERIALS

Unit 6 Engineering Materials

Nanomaterials: Introduction, Concept, properties, Synthesis of Nanomaterials by Physical Vapour transport method, Applications with concept of quantum computing

Shape Memory Alloy: Structure, properties and applications

Metallic glasses: Properties, Melt Spinning Technique, Applications

Biomaterials: Properties and Applications

Definiations:

Nanoscience: Nanoscience is the study of atoms, molecules and objects whose size is of the nanometer scale (1-100nm).

Nanotechnology: Nanotechnology is the technique of design, production of devices and systems by controlling the shape and size at the nanometer scale.

Nanoparticles: A particle size in the range of 1-100nm is called a nanoparticle.

Classification of nanomaterials:

The most popular mode of nanostructure classification is according to their dimensions on the nanoscale which is of the order of a few nanometers.

Nanostructures can be described as:

(1) ***Zero dimensional (0D) Nanostructures:*** In *0D* nanostructures, all of the three dimensions (x,y,z) are in the nanometric size range. Electrons confined in three dimensions. Ex: Nanoparticles , quantum dots.

(2) ***One dimensional (1D) nanostructures:*** In 1D nanostructures, two dimensions (x,y) are in the nanometric size range and the third dimension (z) remains large. Electrons confined in two dimensions. Ex.: Nanotubes, nanorods and quantum wires.

Two dimensional (2D) nanostructures: In *2D* Nano structures, one dimension(z) is reduced to the Nano metric size range and the other two dimension(x,y) remain large. Electrons confined in one dimension. Ex.: Nano thin films, Nano coatings and Nano layers.

(4) ***Three dimensional (3D) nanostructures:*** The *3D* nanostructures have all the three dimensions (x,y,z) outside of the Nano metric size range.

Quantum Effects:

When the particles are in nanoscale of about 1-100nm, the properties change significantly from those at larger scale. Thus when the particle is in nanoscale, the properties such as, melting point, fluorescence, electrical conductivity, chemical reactivity, magnetic permeability etc change as a function of the size of the particle.

Surface Area to Volume Ratio in Nanomaterials:

The surface area to volume ratio, also called the surface to volume ratio(SA : V)is the amount of surface area per unit volume of an object. Surface area to volume ratio is a great way to measure the efficiency of nanotechnology. Nanoparticles have a larger surface area compared to the same volume of the bulk material.

Let us assume that, the nanoparticles are spherical in shape. Let us consider the radius of the atom to be ‘r’. Then,

the surface area of the spherical atom = $4\pi r^2$.

The volume of the spherical atom = $4/3\pi r^3$.

Therefore, the surface area to the volume ratio is

$$SA:V = 3/r \qquad \text{.....(1)}$$

The above value of SA:V ratio shows that, surface area to volume ratio increases with the decrease in radius of the sphere and vice versa.

It can also be concluded that, when a given volume is divided into smaller pieces, the surface area increases. Therefore, smaller grains have more surface area with respect to their volume. More surface area to volume ratios are favorable for chemical reactions.

Electron Confinement (Quantum Confinement:

Quantum confinement describes how the electronic and optical properties change when the material size is at nanoscale.

One of the most direct effect of reducing the size of materials to nanoscale is the appearance of quantization effects due to the confinement of the movement of electrons.

This leads to the discrete energy levels depending on the size of the structure.

The electrons in a bulk material can be described by energy bands or electron energy levels.

These energy levels are described as continuous, because of the difference in energy levels. In this case, the electrons behaves as if it were free in which case the confinement dimensions are large compared to the wavelength of the particle.

However when the material size is decreased towards nanoscale, the confinement dimensions also naturally decrease. In other words, the energy spectrum becomes discrete measured as quanta rather than continuous as in bulk materials. ***This situation of discrete energy levels is called quantum confinement***.

Properties of Nanomaterials:

Nanomaterials have the structural features.

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, resulting in more "surface" dependent material properties.

The nanoscale also has spatial confinement effect on the materials which bring the quantum effects. The quantum effects in nanomaterials modify the electronic and optical properties of the materials.

The most important properties are listed below:

1. The nanomaterials have high strength, hardness, formability and toughness.
2. These materials are more brittle.
3. These materials exhibit super plasticity even at lower temperatures.
4. Magnetic moment or nanomaterials can be increased by decreasing the particle size.
5. Optical density of these materials can be varied with the diameter.
6. Size of the grains; controls the mechanical, electrical, optical, chemical, semiconducting and magnetic properties.
7. The melting point of nanomaterials gets reduced.
8. The magnetization and coercively are higher.

Applications of Nanomaterials:

1. Nanomaterials are used for the fabrication of signal processing elements such as filters delay lines switches.
2. Using these materials soft and permanent magnets can be manufactured which have a wider applications.
3. Nano crystalline materials like tungsten carbide, tantalum carbide and titanium carbide are used in making cutting tools. These tools are much harder and lasts longer than their conventional counter parts.
4. These materials are used make semiconductor lasers, Nano transistors, memory devices such as recording heads and magnetic storage devices etc.
5. Hydrogen based sensors made by nanomaterials are used in power generations.

6. Nanomaterials are used for the manufacturing of small size, light weight micro strip patch antennas. These miniaturized antennas are said to have large bandwidth, tunability and mechanical flexibility.
7. These materials are used in enzyme removal of CO_2 from air and waste water treatment.
8. Nano crystalline ZnO thermistors are used in current controlling devices.
9. SiC nanocrystalline is used in making artificial heart valves due to its low weight, high strength, inertness, extreme hardness and wear resistance.
10. When nanocrystalline ceramics such as zirconium, alumina are used as liners in automobile engine cylinders, they help in retaining heat much more efficiently and result in complete and efficient combustion of the fuel.

Synthesis

- **The methods used for the synthesis of nanoparticles**

- **Physical methods**
- **Chemical methods**

The most commonly used techniques are

- **Mechanical alloying**
- **Inert gas condensation**
- **Sol gel technique**

- **Thin Film Deposition**
- **Physical Vapor Deposition (PVD)**
- – Direct impingement of particles on the hot substrate surface
- – Thermal evaporation, electron-beam evaporation, sputtering

- **Chemical Vapor Deposition (CVD)**
- Convective heat and mass transfer as well as diffusion with
- chemical reactions at the substrate surfaces
- More complex process than PVD
- More effective in terms of the rate of growth and the quality of
- deposition
- LP/AP CVD, Thermal/PE/Ph/LC CVD

Deposition

- Applying a thin film on a surface ranges from nanometers to micrometers
- Thin film is deposited on substrates.
- Different techniques are used for deposition PVD, CVD, sputtering electroplating & coating.

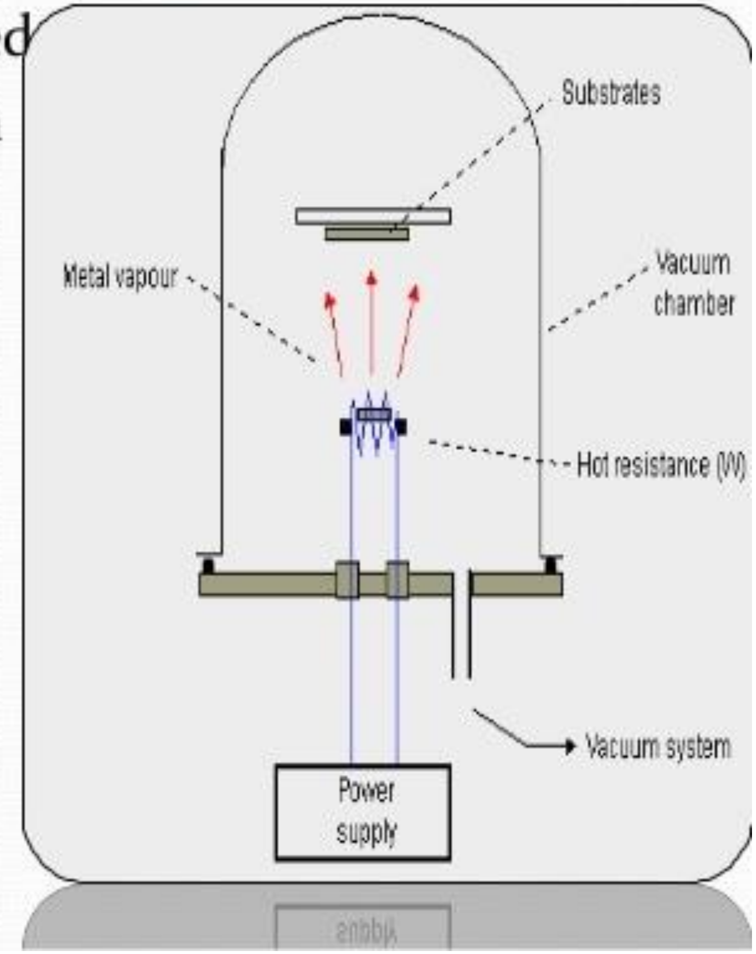
- PHYSICAL VAPOUR DEPOSITION
- Physical coating process involve condensation & evaporation of material.
- PVD is carried out at high temperature to vaporized the material and vacuum of different ranges is used which depends on the mean free path required in the system.

PVD Techniques

- Evaporative deposition
  - Electron beam vapor deposition
  - Pulsed laser deposition
- Sputter deposition
- Ion induced deposition
- Cathode Arc Deposition

Evaporative deposition

- Resistive heating method is used
- deposition is performed at high temperature & low vacuum
- Vacuum decreases the content of Contamination
- Voltage & current is manually controlled.
- Material is kept in boats.



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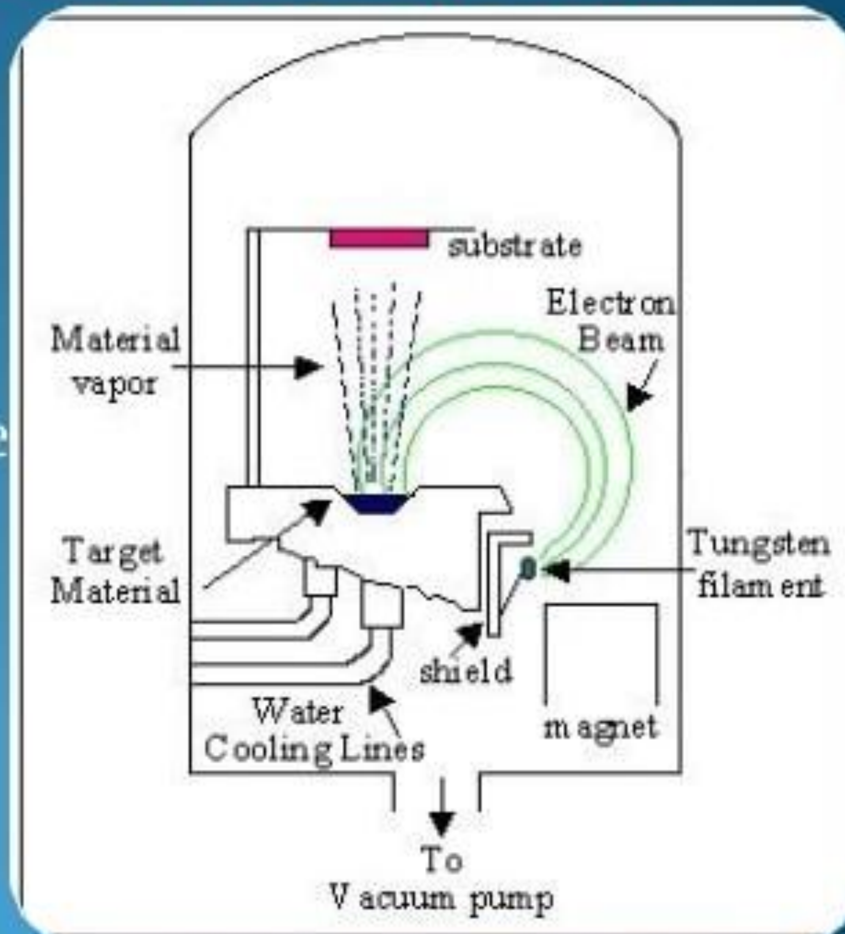
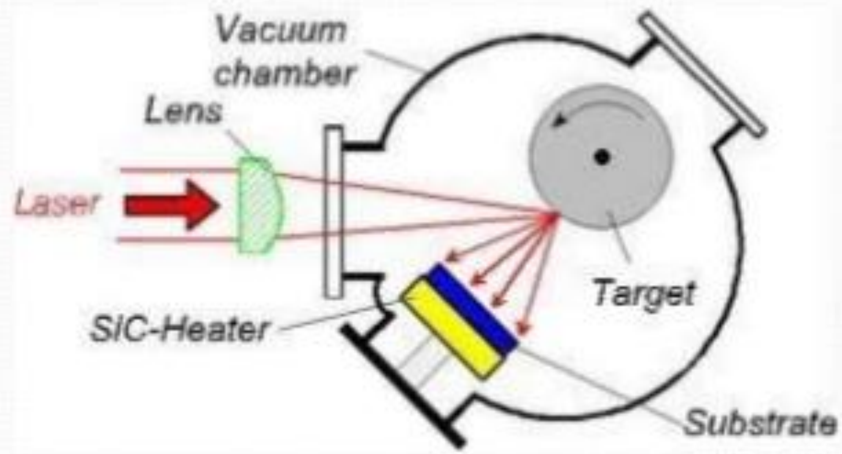
Electron beam vaporization system

- Electron beam is generated by tungsten filament.
- Material is placed in Graphite or tungsten crucible
- Deposition mechanism is same
- deposition is carried out under high vacuum.
- Deposition is controlled, and Uniform



Pulsed laser deposition

- High power laser is used for deposition.
- Argon or neon is used for inert atmosphere.
- High vacuum is formed
- laser is focused by lens, target decides the position of the deposition .



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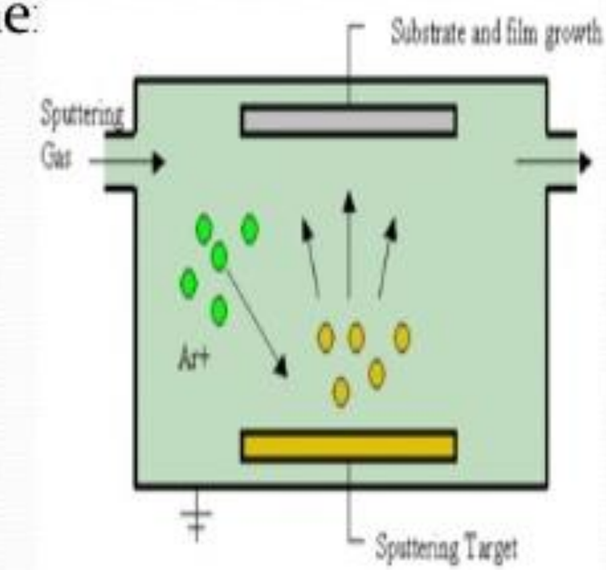
Sputter deposition

- Sputtering works on the bases of momentum principle, formed by the collision of the atoms and molecules.
- Plasma glow, ion accelerator or radioactive emitting is used to evaporate material.
- argon gas is used for inert atmosphe



- Types of sputtering
- Chemical and etching sputtering
- Electronic sputtering
- Potential sputtering

PVD advantages & Disadvantages

• Environment friendly then paint & electroplating. • more than one PVD technique can be used for coating. • Usually topcoats are not required. • Good strength and durability.	• Cooling systems are required. • Mostly high temperature and vacuum control needs skill & experience. • PVD coated materials has no chemical interaction with the surface that

Metallic Glasses

- It is the newly developed engineering materials. It share the properties of both metals and alloys.
- Most metals and alloys are crystalline. In contrast, a glass is an amorphous (non crystalline) brittle and transparent solid.
- Thus, metallic glasses are the metal alloys that are amorphous. That is, they do not have a long range atomic order.
- Advantages:

  1. homogeneous composition

  2. strong and

  3. superior corrosion resistance.

- To have this particular property, the metallic glasses are to be made by cooling a molten metal so rapidly at a rate of 2 x 10^{6}°Cs^{-1}. during this process of solidification, the atoms do not have enough time or energy to rearrange for crystal nucleation. Thus, the liquid upon reaching the glass transition temperature T_g solidifies as a metallic glass. Again, upon heating metallic glasses show a reversible glass-liquid transition at T_g.

Types of Metallic Glasses

- Metallic glasses are of two types based on their base material used for the preparation.

1. ***Metal-metal glasses***, Ni-Nb, Mg-Zn and Cu-Zr

2. ***Metal- Metalloid glasses.*** Transition metal like Fe, Co, Ni and metalloid like B, Si, C and P are used.

Preparation

- Various rapid cooling techniques such as spraying, spinning and laser deposition are used for the production of metallic glasses.

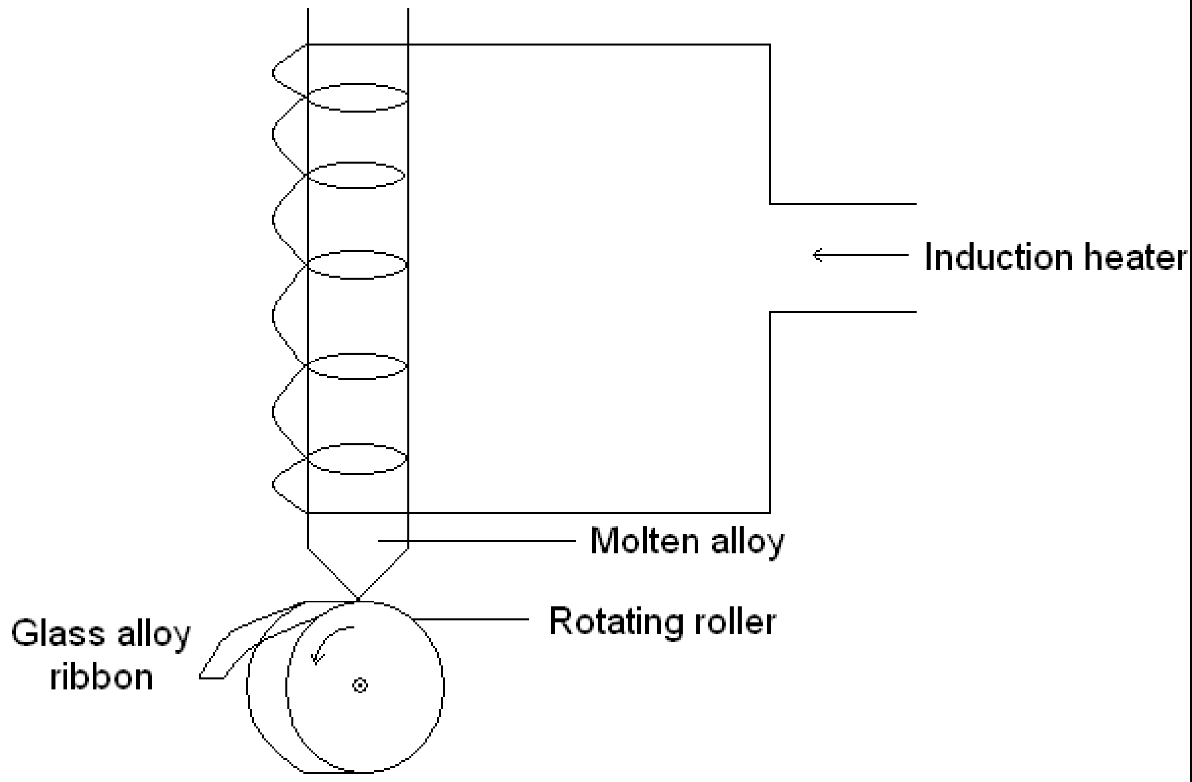


Fig. : Melt spinning process technique

- In this technique, there is spinning disc made of copper. In order to prepare a metallic glass of a particular type a suitable combination of metal-metal or metal-metalloid alloy in their stoichiometric ratio are taken in a refractory tube having a fine nozzle at its bottom. The nozzle side of the tube is placed just over the spinning disc.

- An induction heater attached to the refractory tube melts the alloy. This melt is kept above its melting point till it gets transformed into a homogeneous mixture. An inert gas such as helium is made to flow through the tube containing the homogeneous mixture. As a results, the melt gets ejected through the nozzle. The ejected melt is cooled at a faster rate with the help of spinning cooled copper disc. The ejection rate can be increased by increasing the pressure of the inert gas. Thus, a glassy alloy ribbon starts getting formed over the spinning disc.

- The thickness of the glassy ribbon may be varied by increasing or decreasing the speed of the spinning disc.

The other techniques

- The other techniques used for producing ribbons of metallic glasses include.

1. Twin roller system

In this technique a molten alloy is passed though two rollers rotating in opposite directions.

2. Melt extraction system

In this technique the fast moving roller sweeps off molten droplet into a strip from a solid rod.

Properties

- The strength of metallic glasses are very high (nearly twice that of stainless steel) but lighter in weight.
- They are ductile, malleable, brittle and opaque. The hardness is very high.
- The toughness is very high, i.e., the fracture resistance is very high (more than ceramics).
- They have high elasticity. i.e., the yield strength is very high.
- They have high corrosion resistance.
- They do not contain any crystalline defects like point defects, dislocation, stacking faults etc.
- They are soft magnetic materials. As a result, easy magnetization and demagnetization is possible.

- Magnetically soft metallic glasses have very narrow hysteresis loop as shown in figure. Thus, they have very low hysteresis energy losses.
- They have high electrical resistivity which leads to a low eddy current loss.

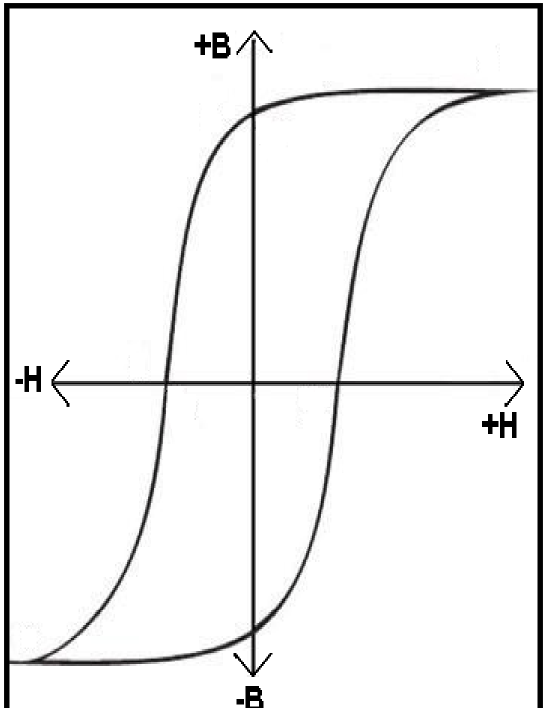


Fig:Hysteresis loop of ferromagnetic mettalic glass

Applications

- Metallic glasses are used as transformer core material in high power transformers.
- Because of their high electrical resistivity and nearly zero temperature coefficient of resistance, these materials are used in making cryothermometers, magneto-resistance sensors and computer memories.
- As the magnetic properties of the metallic glasses are not affected by irradiation they are used in making containers for nuclear waste disposal.
- These materials are used in the preparation of magnets for fusion reactors and magnets for levitated trains etc.

- Metallic glasses can also be used for making watch cases to replace Ni and other metals which can cause allergic reactions.

- The excellent corrosion resistance property makes these materials to be ideal for cutting and in making surgical instruments. They can be used as a prosthetic material for implantation in the human body.

- In future, the usage of metallic glasses in the electronic field can yield, stronger, lighter and more easily molded castings for personal electronics products.

- Metallic glasses are used in tap recorder as heads, in manufacturing of springs and standard resistances.

Shape memory alloys

- Shape memory alloys (SMA's) are metals which exhibit two very unique properties, shape memory effect and pseudo elasticity or super elasticity (SE).

- These alloys are a unique class of materials, which remember their shape even after severe deformation. i.e., when a SMA is ones deformed in the cold shape (martensite) these materials will stay deformed until heated; where, upon heating they will spontaneously return to their original pre-determined hot shape (austenite).

- It is observed that, the structural changes at the atomic level contributes to this unique properties of the materials.

Types of shape memory alloys

There are two types of Shape memory alloys (SMA’s)

1. The one way shape memory alloy
2. The two way shape memory alloy

- The materials which exhibit shape memory effect (i.e., taking their own shape) only upon heating are said to have one way shape memory.

- In contrast, some of the materials exhibit shape memory effect both during heating and cooling. Hence, these materials are said to have two shape memory

Crystal structure of shape memory alloy

- The shape memory alloys are said to have two distinct crystal structure or phases. The effect of temperature and internal stresses determines the crystal structure or the phase that the SMA will have at particular instant.
- The phase which exists at high temperature is called the austenite phase (microscopically they possess small platelets structure).
- The other phase which is found to exists at low temperature is called the martensite phase (microscopically they possess needle like structure). The material remain in solid form in both the cases.
- In austenite phase it possesses a highly symmetric structure such as the one in cubic system. But, in the martensitic phase the structure is of low symmetry such as monoclinic. The basis for the shape memory effect is that, these material can easily transform to and from martensite.

Classification of shape memory alloys

- The shape memory materials could be broadly classified into three types

1. Temperature induced shape memory

2. Stress induced shape memory

3.Ferro-magnetic shape memory materials.

Temperature Induced Transformation

- The phase transformation takes place in SMA's not at a particular temperature but over a range of temperature. This transformation is called the temperature transformation.

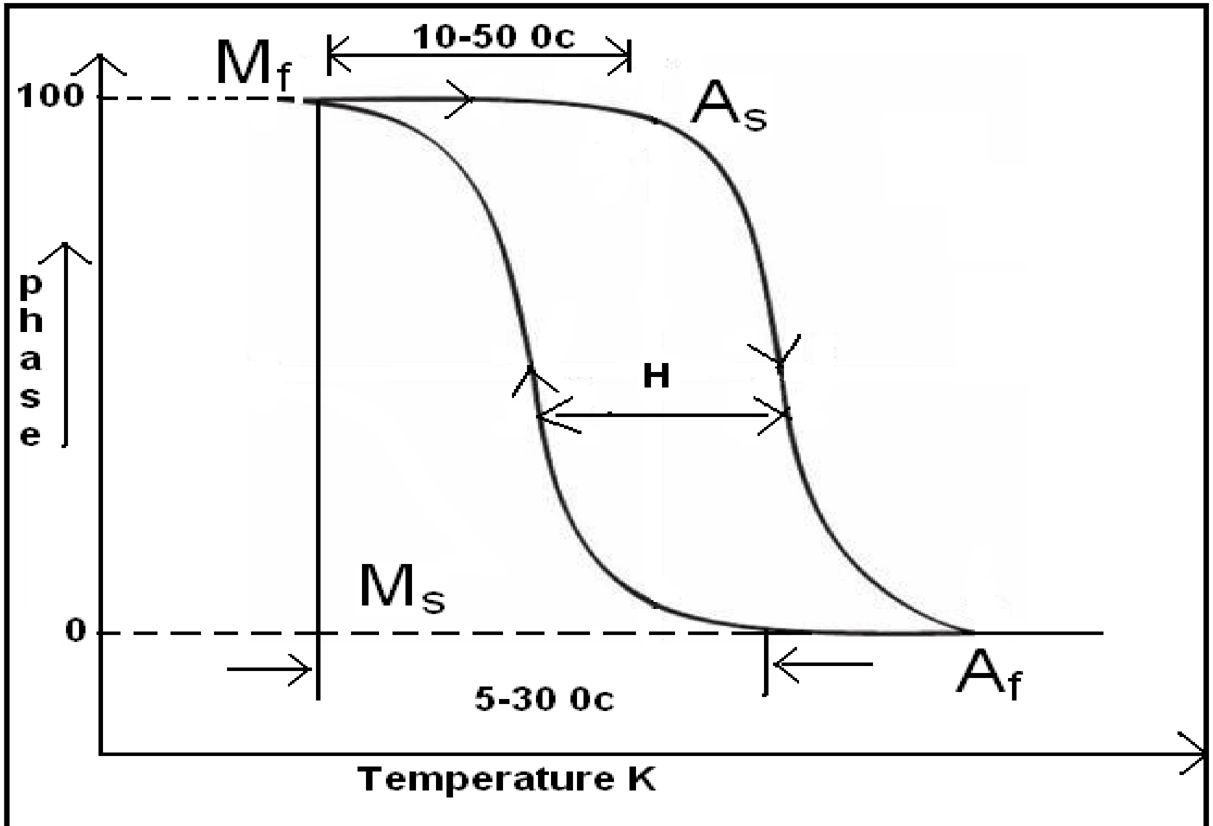


Fig:Temperature induced transformation

- The temperature induced transformation is characterized by four temperatures, M_s and M_f during cooling and A_s and A_f during heating.

- M_s And M_f indicate the temperature at which the transformation from the parent phase austenite into martensite starts and finishes respectively.

- Similarly A_s and A_f indicate the temperature at which the reverse transformation from martensite to austenite starts and finishes upon heating.

- Thus, it is observed that, the overall transformation has a temperature range of 10-15°C depending on the chemical composition of the alloy. This overall transformation is found to exhibit hysteresis in which, the transformations on heating and cooling do not overlap. This hysteresis H is found to depend on the composition of the alloy system.

Stress Induced Transformation

- The stress induced transformation takes place at a constant temperature. At a temperature above the A_f temperature, the martensite phase can be induced by applying stress over the austenite phase.

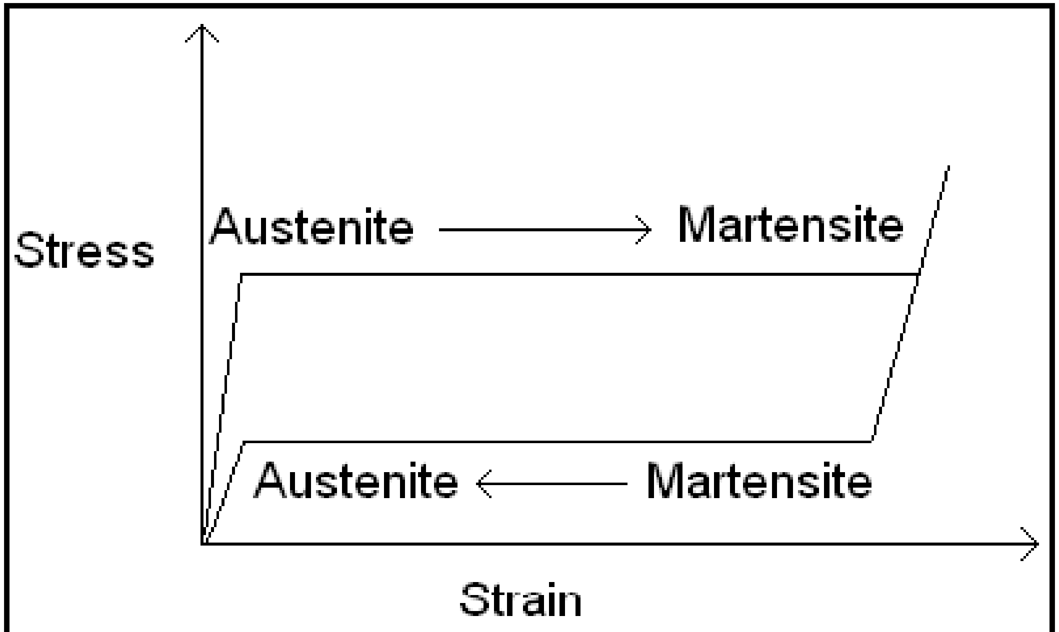


Fig. : Stress induced transformation

- When stressed above a certain value the austenite phase undergoes a large elastic deformation. Stressing beyond the elastic limit will result in permanent plastic strains. On the removal of the stress, the material almost completely recovers to the parent austenite phase at a much lower value of stress.

Functional Properties

- The SMA's are characterized by two important properties.

  1. Shape Memory Effect (SME)
  2. Super Elasticity (pseudoelasticity).

1. Shape memory effect

The SME is the phenomena in which a specimen apparently deformed at lower temperature reverts to its undeformed original shape when heated to higher temperature.

This SME is a consequence of a crystallographically reversible martensitic phase transformation occurring in the solid state. Schematically, the crystallographic formation of martensite and reversion to austenite on heating.

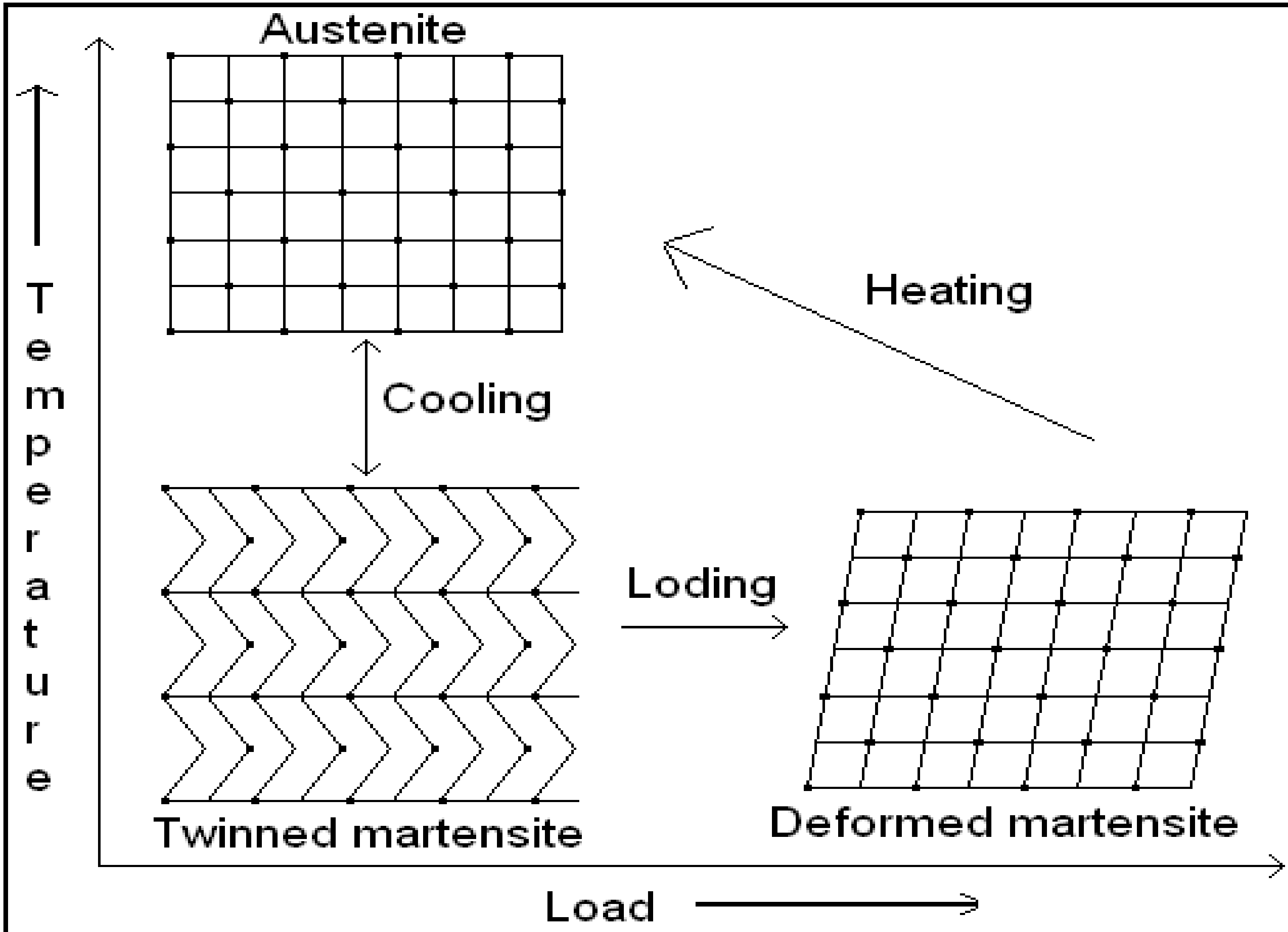


Fig. : Shape memory effect

- From the figure it is seen that, the high temperature austenitic structure undergoes twinning as the temperature is lowered, this twinned structure having microscopically needle like structure is called martensite. This phase is relatively soft and easily deformed phase of SMA which exists at lower temperatures.

- This phase upon deformation (i.e., on applying external stress) takes on a particular shape called the deformed (de-twinned) martensite, and in the process undergoes a large elastic strain. If heated in this condition, the deformed martensite returns to the stable austenite structure and in the process recovers the elastic strain. Thus, the shape memory phenomenon is seen.

- This SME is being implemented in making coffee pots, thermostats, vascular stents and hydraulic fitting for air planes.

2. Super elasticity (Pseudoelasticity)

Super elasticity (Pseudoelasticity) refers to the ability of SMA to return to its original shape upon unloading after a substantial deformation. This SE based on stress induced martensitic (SIM) transformation. This SE in SMA's occurs at a constant temperature when the alloy is completely compose of austenite phase (temperature is grater than A_f).

The stress on the SMA is increased until the austenite phase becomes transformed in to a martensite phase simply due to loading. But, as soon as the loading is decreased the martensite begins to transform back to austenite since, the temperature is still above A_f. As a result, it comes back to its original shape.

This effect, which causes the material to be extremely elastic is known as pseudoelasticity or superelasticity. This SE is non linear and moreover it is temperature and strain dependent. This SE is a mechanical type of behavior of SMA's.

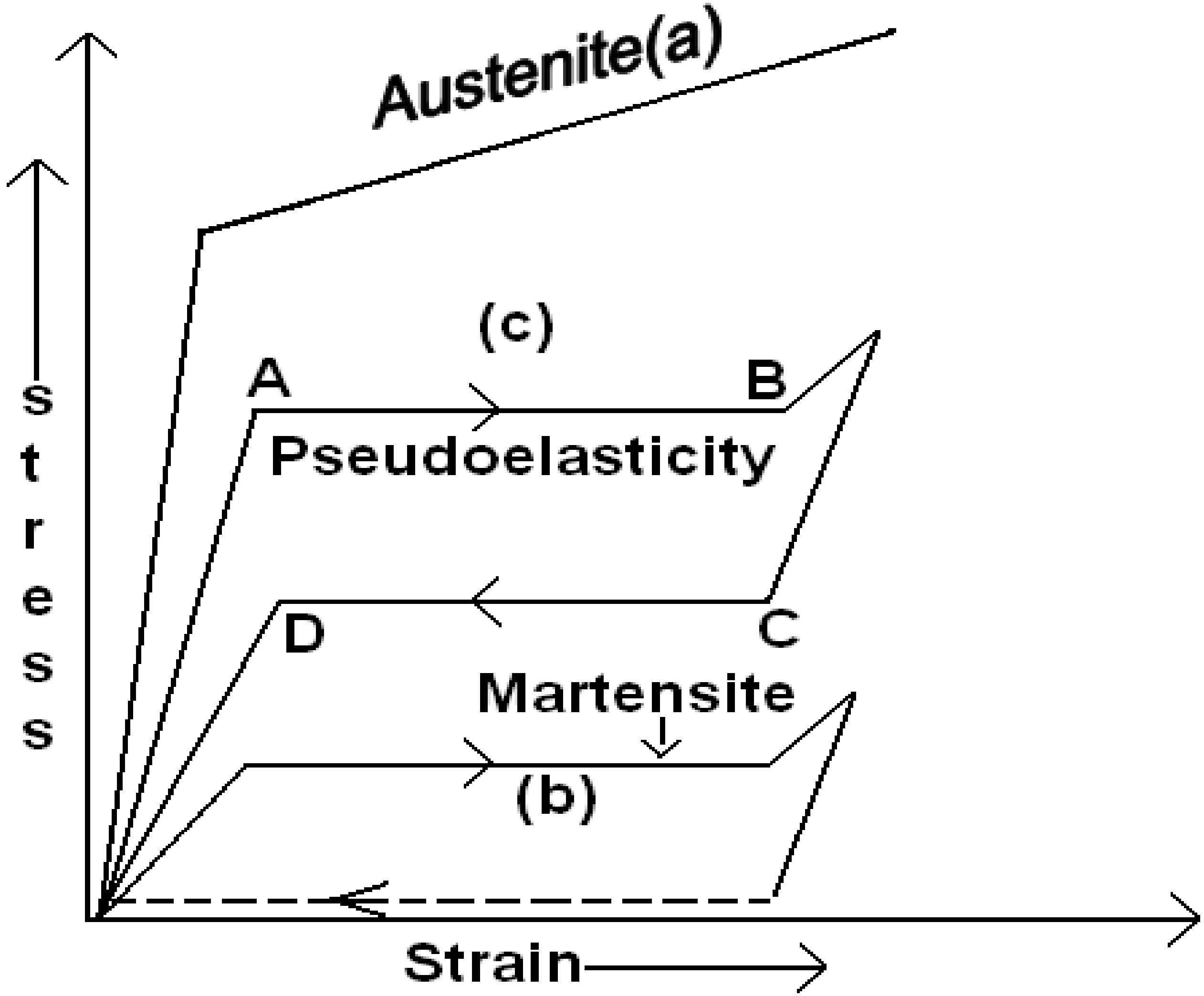


Fig: stress -strain behaviour of different shapes of SMA's at constant temperature.

- At a temperature above Af, the austenite phase is found to have much higher yield and flow stresses. But, the martensite is easily deformed to several percent strain at quite a low stress.

- This martensite phase is found to come back to the austenite phase upon heating after removing the stress as shown by the dashed line. But, no such shape recovery is found in the austenite phase upon staining and heating, because no phase change occurs. The above two behaviors are called as thermo mechanical behaviors.

- The super elasticity behavior is applied in making eye glass frames, medical tools, cellular phone antennae’s and orthodontic arches.

Applications of shape memory alloys

1. Aircraft and space industry

In this areas the SMA's can be used as, fine-tuned helicopter blades and as lock ring electrical connectors. In addition, they are used in antenna opening, high-damping parts, hubble telescope and in triggering devices.

2. Automobile industry

In this industry the SMA's are used in making spring acuators, clutch systems, thermostats, oil pressure control unit and high pressure sealing plugs.

3. Medical field

The largest commercial application of SMA’s are in the field of bioengineering and medical applications.

- They are used as dental arch wires. These wires will make the misaligned teeth gradually to return to their original shape exerting a small and nearly constant force on the misaligned teeth.
- They are also used as blood clot filter.
- Nitinol needle wire localizers are used to locate and mark breast tumours so that subsequent surgery can be more exact and less invasive.
- They are used to make tweezers to remove foreign objects through small incisions.
- They are used as guide wires for catheters through blood vessels.
- They are also used in designing micro surgical instruments and micro grippers etc.

4. Consumer products

- SMA’s are used in making eye glass frames which offers improved comfort and flexibility and in cellular phone antenna.
- Nitinol is used in robotic actuators and micro manipulators to simulate human muscle motion.
- Ni-Ti springs in coffee pots can be trained to open a valve and release hot water at proper temperature.
- Shape memory based toys and ornamental goods have been fabricated.
- SMA’s can be used as couplers and fasteners.
- SMA based fixed safely valves have been developed for industrial facilities.
- Temperature sensitive SMA valves are used to instantly restrict water flow in shower or sinks.
- They can be used to design safely valves that provide emergency shutdown of process control lines that handle flammable and toxic fluid and gases.

- Advantages of SMA’s

  Advantages of SMA’s are biocompatibility, diverse fields of application and good mechanical properties.

- Disadvantages of SMA’s

  Disadvantage is that, they are highly expensive to manufacture and machine it.

Biomaterials

- A biomaterial is simply an engineering material of substances derived from living tissues.
- Biomaterial is also defined as an abstraction of various states of biology-based materials used in various stage of microarray experiment.
- A biomaterial can be a result of a chain of treatments, each treatment involving one or more biomaterials in equal amount.
- The biomaterials are defined as the materials with novel chemical, physical, mechanical or “intelligent” properties produced through processes that mimic biological phenomena.

Biomedical Compatibility of Ti-Al-Nb Alloys for Implant Applications

- Over the last 30 years, biocompatible Ti alloy have been made use of to replace human bones and teeth as these alloys are strong, lightweight and biocompatible.

- The material of choice used in implant is titanium-vanadium-aluminium (Ti-V-Al) alloys because of their excellent biocompatibility and their combination of high specific strength, corrosion resistance, low density, good ductility and elastic modulus.

- In perticular, Ti-6Al-4V which was initially developed as a high temperature aerospace alloy is commonly used as implant material due to its excellent properties and processability compared to other alloys.

- However, V is a potentially toxic element: therefore other alloying elements are currently being examined.

Types of Biomaterials:

- The biomaterials are in general classified into the following types:

1. Polymers
2. Ceramics
3. Composites
4. Natural biomaterials

Polymers:

- The polymers have physical properties that are most similar to the natural tissues.
- The polymers may undergo either ***unintentional degradation or controlled degradation.***
- An ***unintentional degradation*** in polymer may occur due to chemical reactions such as oxidation and hydrolysis. During a chemical reaction, chemicals may be released from polymers and can induce adverse local and systemic host reactions that cause clinical complications. Ex: PVC.
- In ***controlled degradation***, the materials degrade into smaller fragments as well as monomers and get eliminated by normal metabolic processes of the body.

- Polymers are generally not used in biomedical applications that bear load.
- Application of polymers include joint lining, wound dressings, intraocular lens replacement.

Material	Applications
Polyamides	Sutures
Polypropylene	Sutures
Polyethylene	Joint replacement
PTFE	Soft tissue augmentation
Polyesters	Vascular Prostheses, DDS
PMMA	Dental restoration, Intraocular lenses, Joint replacement(bone cement)

Ceramics:

- Ceramics are attractive biomaterials are widely used in several different fields such as dentistry, orthopedics and as medical sensors.
- These bioceramics can be either bioinert, bioactive or biodegradable.
- The ceramic materials are non metallic, inorganic compounds that exhibit great stiffness, high resistance to corrosion, excellent wear resistance and of low density.
- The major problem with ceramics is that they are brittle, have a low tensile strength and are relatively difficult to process.

Bioceramic materials with their applications:

Bioceramic	*Application*
Alumina	***Joint replacement, dental implants***
Apatite ceramics	***Synthetic bone***
Zirconia	***Joint replacement***
Bioactive glasses	***Bone replacement***
Carbons	***Heart valves, dental implants***
Porcelain	***Dental restorations***

Composites

- Composite biomaterials find their applications in the field of dentistry as restorative materials or as dental cement.
- These materials are extensively used for prosthetic limbs because of their low density and high strength property.
- BIS – GMA Quartz/ silica filter and PMMA – glass filter, these two composites are used in Dental restrorations (dental cement).

Natural Biomaterials:

- The biomaterials derived from the animals and plants are called natural biomaterials.
- The advantage of using natural biomaterial for implants is that, they are similar to materials familiar to the body and does not offer the problem of toxicity often faced by the synthetic materials.
- The Collagen is the most prevalent protein available in animal. This is used as a scaffold for neo-tissue growth.
- In cosmetic field, injectable collagen is widely used for augmentation.

Thank you