Metallic glasses

Metallic glasses were discovered in 1970. Metals are solids with crystalline property, malleability, ductility etc. Glasses are amorphous materials which are transparent and brittle in nature. Metallic glasses are the newly developed engineering materials which share the properties of both metals and glasses. They have high strength, good magnetic properties and better corrosion resistance.

Ex: Alloys of Fe, Ni, Al and Cu mixed with metalloids such as Si, Ge, As and C.

Types of metallic glasses

Metal- metalloid metallic glasses, Eg: Fe, Co, Ni: Bi, Si, P

Metal-metal metallic glasses Eg: Ni, Nb

Properties

- They do not have any crystal defects
- They have tetrahedral close packed structure
- They have high elasticity
- They are highly ductile
- Electrical resistivity is high and it does not vary much with temperature.
- Due to high resistivity, the eddy current loss is very small.
- They possess low magnetic losses, high permeability, high saturation magnetization and extreme mechanical hardness.
- They can act as catalyst.

Applications

- They are used as reinforcing elements in concrete, plastic or rubber.
- They are used to make razor blades and different kinds of springs.
- They are used to construct large fly wheels for energy storage.

They are used in transformers and magnetic shields since they possess low magnetic losses, high permeability, high saturation magnetization and extreme mechanical hardness.

- Used to produce high magnetic fields and magnetic levitation effect
- Used in preparing containers for nuclear waste disposal and magnets for fusion reactors
- Ideal materials for cutting tools and making surgical instruments.

Synthesis of Metallic glasses

Metallic glasses are prepared based on the principle of rapid cooling technique called quenching. Metals are taken to glassy state by increasing the rate of cooling [2×10^6 °C/second] and hence atoms won't be able to arrange orderly. This results in amorphous state leading to a new type of material.

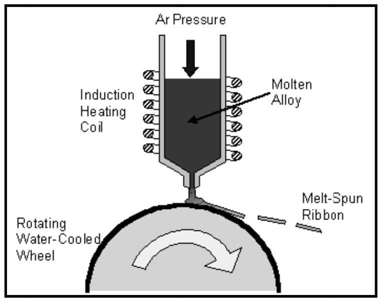
Melt spinning system

Principle

The cooled molten alloys are fed into highly conducting massive rollers at high speeds to give ribbons of metallic glasses.

Experimental setup

A melt spinner consists of refractory tube with fine nozzle and induction heater coil, spinning copper disc. This disc is rotated at a high speed to generate a high velocity of more than ~ 50 ms^{-1}. The alloy is melted by induction heating under inert helium or argon atmosphere. Ejection rate can be increased by increasing the pressure inside the refractory tube. A properly superheated molten alloy is ejected under pressure through the nozzle onto the spinning disc. The dynamic melt puddle impinging on the moving substrate is solidified and it is thrown out of the wheel by centrifugal force after travelling with it over a short distance. Thus, a continuous ribbon is obtained due to rapid quenching and it is wound on a spool.



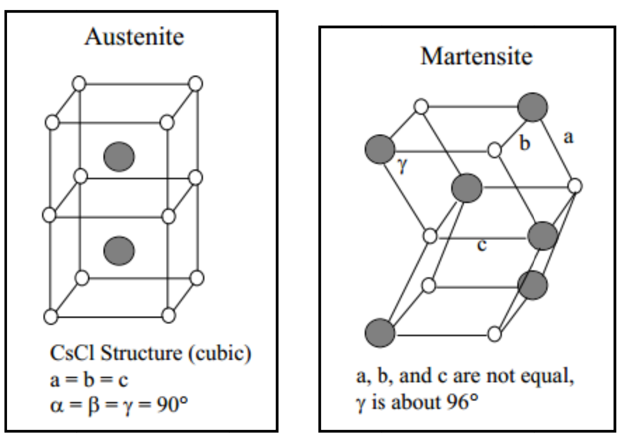
Shape memory alloys

Shape memory alloys (SMA) are smart/intelligent materials which show the ability to return to their original shape or size when they are subjected to appropriate thermal procedure. The range of temperature at which SMA switches back to its original shape is called transformation temperature.

Phases of SMA

Martensite and **Austenite** are the two solid phases which occur in SMA as shown in Fig.

i. Martensite is relatively soft and it is easily deformable phase which exists at low temperature (monoclinic).



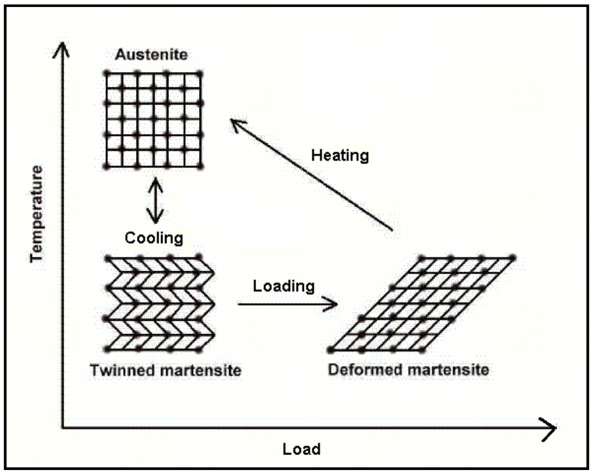
ii. Austenite – is a phase that occurs at high temperature having a crystal structure and high degree of symmetry (cubic).

iii. The mechanism involved in SMA is reversible (austenite to martensite and vice versa).

Characteristics of SMA

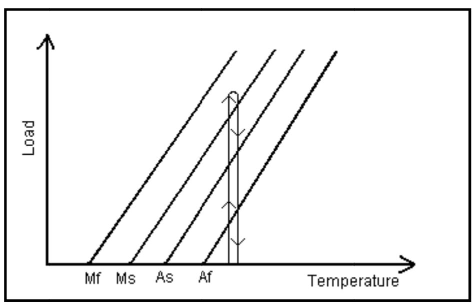
a. Shape memory effect

The Change of shape of a material at low temperature by loading and regaining of original shape by heating it is called shape memory effect. The original shape is recovered due to two different solid phases of the material namely martensite and austenite. On heating, martensite deformed and becomes austenite and upon cooling gets transformed to twinned martensite.



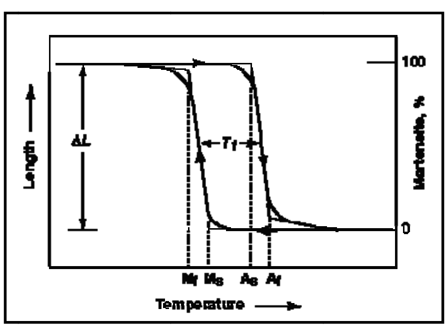
b. Pseudo-elasticity/ Super-elasticity

The phenomenon by which the change in shape occurs in SMA even without change in temperature is called Pseudoelasticity. This takes place at temperature greater than the austenite formation temperature. The load on the SMA is increased and austenite becomes transformed into martensite simply due to loading.



c. Hysteresis

The difference between the transition temperature upon heating and cooling is called hysteresis.



d. SMA’s exhibit changes in elec. resistance, volume and length during transformation with temperature

<u>Applications of SMA</u>

i. One of the most common applications of SMAs is Microvalves (Actuators)
ii. Shape memory alloys are use to make toys and ornamental goods.
iii. They are used in blood clot filters, artificial hearts and dental applications.
iv. SMAs are used a thermostat to open and close the valves at required temperature.

<u>Advantages of SMA</u>

i. They are very compact in nature
ii. They are safe and smart
iii. They are flexible in nature.
iv. They have non-corrosive nature.

<u>Disadvantages of SMA</u>

i. They are expensive (high cost)
ii. They have low efficiency
iii. Transformation of shape occurs over a range of temperatures
iv. Structural arrangements may sometime get deformed

<u>Nanomaterials</u>

Nanophase materials are newly developed materials with grain size at the nanometre range i.e. in the order of 1-100 nm. The particle size in nanomaterials is 1 nm. They are simply called as nanomaterials. They exist in different forms like nanodots, nanorods, nanoparticles and nanotubes etc.

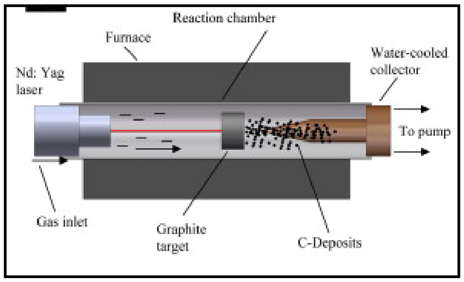
<u>Preparation of nanomaterials</u>

Top down approach – Bulk materials are broken into nano sized particle
Bottom up approach – Nano materials are produced by building of atom by an atom

Pulsed laser deposition

Principle

The laser pulse of high intensity and energy is used to evaporate carbon from graphite. These evaporated carbon atoms are condensed to from nanotubes.



Construction

A quartz tube which contains the graphite target is kept inside the high temperature muffle furnace. This quartz tube is filled with argon gas and it is heated to 1473 K. A water cooled copper collector is fitted at the other end of the tube. The target material graphite contains small amount of nickel and cobalt as a catalyst to nucleate the formation of nanotubes.

Working

When an intense pulse of laser beam is incident on the target, it evaporates the carbon from the graphite. The evaporated carbon atoms are swept from the higher temperature, argon gas to the colder collector. When the carbon atoms reach the colder copper collector they condense into nanotubes.

Chemical vapour deposition

The deposition of nano films from gaseous phase by chemical reaction on high temperature is known as chemical vapour deposition. This method is used to prepare nanopowder.

In this technique, initially the material is heated to gaseous state and then it is deposited on a solid surface under vacuum condition to form nanopowder by chemical reaction with the substrate. It involves the flow of a gas with diffused reactants over a hot substrate surface. The gas that carriers the reactants is called the carrier gas. While the gas flows over the hot solid surface, the heat energy increases chemical reactions of the reactants that form film during and after the reactions.

The byproduct of the chemical reactions is then removed. The thin film of desired composition can thus be formed over the surface of the substrate.

<u>Properties of nanophase particles</u>

a) Mechanical properties

a. In nanophase materials, the elastic strength is low however; its plastic behavior is high.
b. In some nanophase materials, it is noted that there is decrease in hardness when the grain size is less than 10 nm.
c. Higher hardness and mechanical strength when grain size reduces to nano range.
d. It has very high ductility and superplastic behavior at low temperatures.

b) Magnetic properties

Nanoparticles of non-magnetic solids also exhibit new type of magnetic properties.

a. Bulk magnetic moment increases with decrease in coordination number. This means that small particles are more magnetic then the bulk material.
b. The nanomaterials show variation in their magnetic property when they change from bulk state to cluster (nanoparticles) state.
c. Non-magnetic materials become magnetic when the cluster size reduces to 80 atoms.

c) Chemical properties

The large surface to volume ratio, the variations in geometry and the electronic structure have a strong effect on catalytic properties. The reactivity of small clusters has been found to vary by higher orders of magnitude when the cluster size is changed by only a few atoms.

d) Variation of physical parameters with geometry

Starting from the bulk, the first effect of reducing the particle size is to create more surface sites. This in turn changes surface pressure and Interparticle spacing.

i) Interparticle spacing decreases with decrease in grain size for metal clusters. For example in copper, it decreases from 2.52 to 2.23 Å. The change in interparticle spacing and large surface to volume ratio in particles has a combined effect on material properties. Therefore, the nanophase materials have very high strength and super hardness.

ii) Melting point reduces with decrease in cluster size

iii) Ionization potential changes with cluster size of the nanograins

iv) The large surface to volume ratio, the variations in geometry and the electronic structure have a strong effect on catalytic properties. The reactivity of small clusters has been found to vary by higher orders of magnitude when the cluster size is changed by only a few atoms.

Applications of nano materials in various fields

a) Materials technology

- Harder metals having hardness 5 times higher than the normal metals can be produced
- Unusual color paints can be produced
- Smart magnetic fluids are used as vacuum seals, cooling fluids etc.
- Used in nanoelectronics devices such as nanotransistors, ceramic capacitors for energy storage etc.
- ZnO thermistors are used in thermal-protection and current-controlling devices

b) Information technology

- Nanoparticles are used for data storage
- Quantum electronic devices have started replacing bulk conventional devices
- Magnetic devices made of Cu-Fe alloy are used in RAM, READ/WRITE heads and sensors
- Nano dimensioanl photonic crystals are used in chemical/optical computers

c) Biomedicals

- Biosensitive nanoparticles are used for tagging of DNA and DNA chips
- Controlled drug delivery is possible
- Finds applications as an implant material

d) Energy storage

- Useful in magnetic refrigeration
- Metal nanoparticles are very useful in fabrication of ionic batteries

e) Optical devices

- Nanomaterials are used in making efficient semiconductor laser and CD's
- Nano Zinc Oxide is used to manufacture effective sunscreens
- Used in the coatings for eye glasses to protect from scratch or breakage

NLO materials

The field of study concerned with the interaction of light radiation and matter in which the matter responds in a non linear manner to the incident radiation fields is called **non linear optics**. This behavior is known as **non linear effect** and the materials which exhibit this effect are called **non linear materials**.

Birefringence

The appearance of double refraction under the influence of an external agent is known as artificial double refraction or **induced birefringence**. The materials which experience a change in their optical behavior under the action of an electric field are called **electro-optic materials** and the resulting optical effects are known as **electro-optic effects**. Similarly the materials that get influences by a magnetic field are called **magneto-optic materials** and the resulting optic effects are known as **magneto-optic effects.**

Optical Kerr effect

Anisotropy induced in an isotropic medium under the influence of an electric field is known as Kerr effect. A sealed glass cell known as Kerr cell filled with a liquid comprising of asymmetric molecules is used to study the Kerr effect.

Two plane electrodes are placed in parallel to each other. When a voltage is applied to electrodes, a uniform electric field is produced in the cell. The Kerr cell is placed between a crossed polarizer systems. When the electric field is applied, the molecules of the liquid tend to align along the field direction.

As the molecules are asymmetric, the alignment causes anisotropy and the liquid becomes double refracting. The induced birefringence is proportional to the square of the applied electric field E and to the wavelength of incident light. Thus, the change in refractive influx is given by

$\Delta \mu = K\lambda E^2$, where K is known as the Kerr constant.

Non-linear properties

1. Second harmonic generation
2. Optical mixing
3. Optical phase conjugation
4. Soliton

Second harmonic generation

In a linear medium, polarization is directly proportional to electric field,E

$$P \propto E$$
$$P = \varepsilon_0 \chi E$$

Where ε_0 - permittivity of free space,

χ - electrical susceptibility.

In nonlinear medium for higher fields, the nonlinear effects are observed.

$$P = \varepsilon_0\left(\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \cdots\right) \qquad (1)$$

Where χ_1 is the linear susceptibility and χ_2 , χ_3 etc are higher order nonlinear susceptibilities.

The electric field passing through the medium with amplitude E_0 is

$$E = E_0 \cos \omega t \qquad (2)$$

Substituting the value of (2) in (1) we have

$$P = \varepsilon_0\left(\chi_1 E_0 cos\omega t + \chi_2 {E_0}^2 cos^2\omega t + \chi_3 {E_0}^3 cos^3\omega t + \cdots\right) \ (3)$$

We know that

$$\left.\begin{aligned} cos^2\omega t &= \frac{1 + \cos 2\omega t}{2} \\ cos^3\omega t &= \frac{cos 3\omega t + 3\cos \omega t}{4} \end{aligned}\right\} \qquad (4)$$

Substituting equation (4) in (3) we have

$$P = \varepsilon_0 \left(\chi_1 E_0 cos\omega t + \chi_2 {E_0}^2 \frac{1+\cos 2\omega t}{2} + \chi_3 {E_0}^3 \frac{cos3\omega t + 3\cos\omega t}{4} + \cdots \right)$$

$$P = \varepsilon_0 \left(\chi_1 E_0 cos\omega t + \chi_2 {E_0}^2 \left(\frac{1}{2}\right) + \chi_2 {E_0}^2 \left(\frac{\cos 2\omega t}{2}\right) + \chi_3 {E_0}^3 \left(\frac{cos3\omega t}{4}\right) + \chi_3 {E_0}^3 \left(\frac{3\cos\omega t}{4}\right) + \cdots \right)$$

$$P = \varepsilon_0 \left(\frac{1}{2}\chi_2 {E_0}^2 + \chi_1 E_0 cos\omega t + \frac{3}{4}\chi_3 {E_0}^3 cos\omega t + \chi_2 {E_0}^2 \left(\frac{\cos 2\omega t}{2}\right) + \chi_3 {E_0}^3 \left(\frac{cos3\omega t}{4}\right) + \cdots \right)$$

$$P = \varepsilon_0 \left(\frac{1}{2}\chi_2 {E_0}^2 + \left(\chi_1 + \frac{3}{4}\chi_3 {E_0}^2\right) E_0 cos\omega t + \frac{1}{2}\chi_2 {E_0}^2 \cos 2\omega t + \frac{1}{4}\chi_3 {E_0}^3 cos3\omega t + \cdots \right)$$

$$P = \frac{1}{2}\varepsilon_0\chi_2 {E_0}^2 + \varepsilon_0 \left(\chi_1 + \frac{3}{4}\chi_3 {E_0}^2\right) E_0 cos\omega t + \frac{1}{2}\varepsilon_0\chi_2 {E_0}^2 \cos 2\omega t + \frac{1}{4}\varepsilon_0\chi_3 {E_0}^3 cos3\omega t + \cdots \quad (5)$$

In the above equation, first term gives rise to dc field across the medium; the second term gives external polarization and is called first or fundamental harmonic polarizability. The third term which oscillates at a frequency 2ω is called second harmonic of polarization and the terms are referred as higher harmonic polarization. Both the first term and third term added together is called optical rectification.

The second harmonic generation is possible only to the crystals lacking inversion symmetry. SHG crystals are quartz, potassium dihydrogen phosphate, ammonium dihydrogen phosphate, barium titanate and lithium iodate.

When the fundamental radiation from Nd:YAG laser is sent through SHG crystal like KDP, conversion takes place to double the frequency i.e. half the wavelength takes place.

Biomaterials

The materials which are used for structural applications in the field of medicine are known as biomaterials. These materials are used to make devices to replace damaged or diseased body parts in human and animal bodies.

Biomaterials should have high compatibility, corrosion resistant and required property. Different materials possess different specific properties.

Classification of biomaterials

i) **Metals and alloys** are used as biomaterials due to their excellent electrical and thermal conductivity and mechanical properties. The types of biomaterials using metals and alloys are cobalt based alloys, titanium, stainless steel, protosal from cast alloy, conducting metals such as platinum.

Applications

a. Stainless steel is the predominant implant alloy. This is mainly due to its ease of fabrication and desirable mechanical properties and corrosion resistant.

b. Protosal from cast alloy of Co-Cr-Mo is use to make stem and used for implant help endoprosthesis.
c. Ni-Ti shape memory alloy is used in dental arch wires, micro surgical instruments, blood clot filters, guide wires etc.

ii) **Ceramics** are used as biomaterials due to their high mechanical strength and biocompatibility. Types of bio-ceramic materials include tricalcium phosphate, metal oxides, apatite ceramics, porous ceramics, carbon and alumina.

Applications

a. Ceramic implants like alumina with some SiO_2 and alkali metals are used to make femoral head.
b. Tricalcium phosphate is used in bone repairs.
c. Apatite ceramics are new bio active ceramics. They are regarded as synthetic bone, readily allows bone ingrowth, better than currently used alumina.
d. Carbon coatings find wide applications in heart valves, blood vessel grafts, percutaneous devices because of exceptional compatibility with soft tissues and blood.

iii) **Bio Polymers**

Biopolymers are macromolecules (protein, nucleic acid and polysachacides) formed in nature during the growth cycles of all organisms.

Applications

Biopolymers find variety of applications as biomaterials. The most prominent among them are collagens and its derivatives. Collagens which are major animal structural proteins are widely used in a variety of forms such as solution, gel, fibers, membranes, sponge and tubing for large number of biomedical applications including drug delivery system, vessels, valves corneal prosthesis, wound dressing, cartilage substitute and dental applications.

iv) **Composite materials** are also used as biomaterials. Sometimes, a single material mentioned above cannot fulfill the complete requirements imposed on specific applications. In such case, combinations of more than one material are required.

Biomaterials in Ophthalmology

Biomaterials are used to improve and maintain vision. Eye implants are used to restore functionality of cornea, lens etc. when they are damaged or diseased. The biomaterials include viscoelastic solutions intraocular lenses, contact lenses, eye shields, artificial tears, vitreous replacements, correction of corneal curvature.

Dental materials

Polymers, composites, ceramic materials and metal alloys are four main groups of materials used for dental applications. A large number of materials are tested for porous dental implants which includes stainless steel, Co-Cr-Mo alloy, PMMA, proplast and Daceon, velour coated metallic implants, porous calcium aluminate single crystal alumina, bioglass, vitreous and pyrolytic carbons. The dental applications include impressions materials, dentine base and ceorons, bridges, inlays and repair of cavities, artificial teeth, repair of alveolar bone, support for mandible.