5.11 ADVANTAGES OF SHAPE MEMORY ALLOYS

- Simplicity, compactness and safety mechanism
- Bio - compatibility
- Diverse fields of application, clean, silent, spark free working condition
- Good mechanical properties. (strong, corrosion resistant)
- High power / weight ratios.

5.12 DISADVANTAGES OF SHAPE MEMORY ALLOYS

- Degradation poor fatigue properties.
- Expensive.
- Low energy efficiency.
- Complex control.
- Limited bandwidth due to heating and cooling restrictions.

5.13 NANOMATERIALS - INTRODUCTION

The word 'nano' is derived from a Greek word meaning dwarf or extremely small and means a billionth (10^{-9}) part of a unit. A nanometer or nm is one thousand millionth of a metre, (ie), 1nm = 10^{-9} m = 10^{-3} μm = 10 Å.

Nanoscience is the study of the fundamental principles of molecules and structures with atleast one dimensions in the range about 10^{-9} m to 10^{-7} m (1 to 100 nm).

All materials are composed of grains, which in turn comprise may atoms conventional materials have grain of size varying from hundreds of microns to centimeter. Nanomaterials when in powder form (called nanopowder) have grain sizes in the order of 1 - 100 nm. Hence nano phase materials are materials with the grain size in the order of 1 to 100 range. Such grain contain maximum of few hundreds of atoms each. ex : ZnO, Cu-Fe alloy, Ni, Pd, Pt, etc.,

In nanomaterials the majority of the atoms are located on the surface of the particles and hence the atoms are of a different environment. Nanomaterials have increased surface area substance with high surface areas have enhanced chemical, mechanical, optical and magnetic properties. Using a variety of synthesis methods, it is possible to produce nano structured materials in the form of nanoparticles, nano crystals clusters, nanowires, nanotubes, nano dots, etc.

Nanotechnology is a field of applied science focused on the design, synthesis, characterization and application of materials and devices on the nanoscale. Nanotechnology include nanoscale materials, powders, solutions and suspensions of nanoscale materials as well as composite materials and devices having a nanostructure.

In recent years nanotechnology has become one of the most important and existing forefront fields in Physics, Chemistry, Biology and Engineering and Technology. It is likely to provide many break through that will change the direction of technological advances.

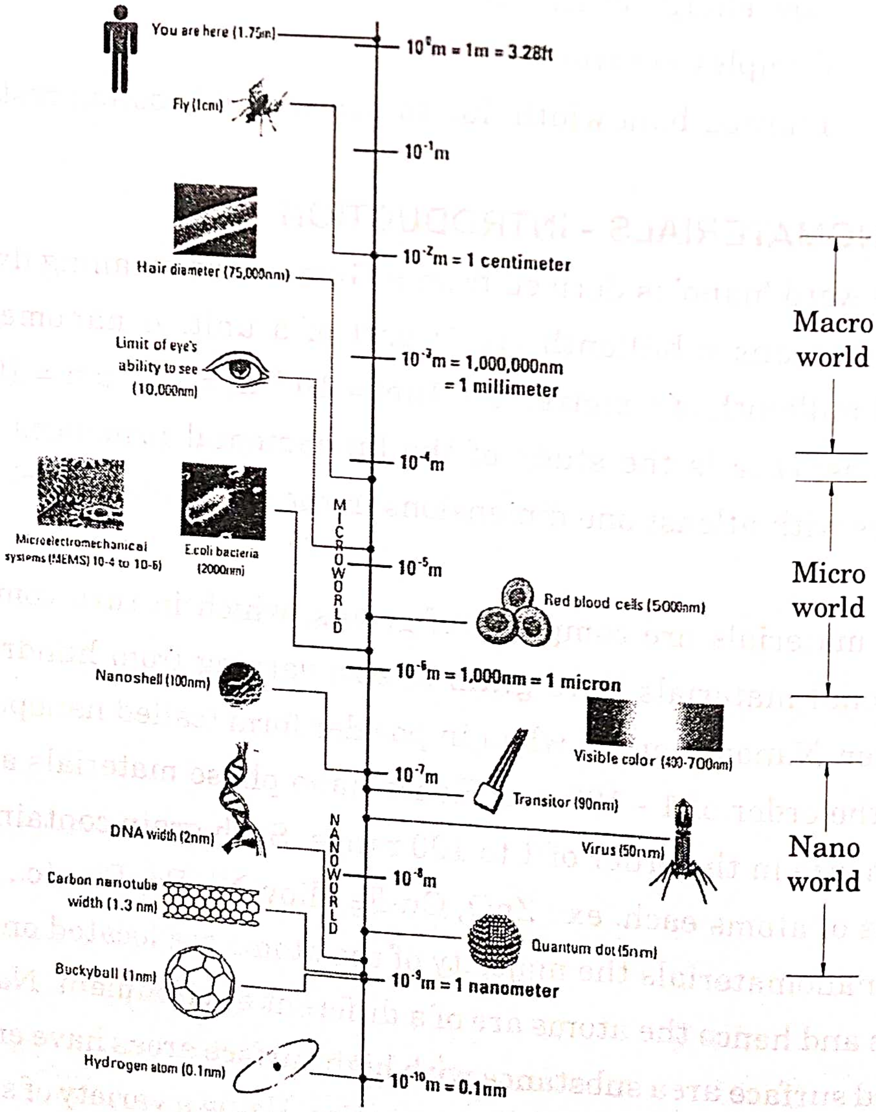


Fig. 5.11 Scale of lengths

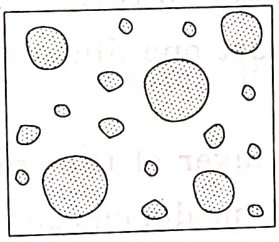
5.14 CLASSIFICATION OF NANOSTRUCTURED MATERIALS

There are different types of nanostructured materials, which is depends on the number of dimensions lie within the nanometer range. The classification are as follows:

i. Zero dimensional nano structure (0D)
ii. One dimensional nano structure (1D)
iii. Two dimensional nano structure (2D)
iv. Three dimensional nano structure (3D)

i. Zero dimensional nano structure (0D)

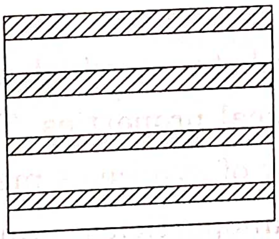
Ex : atoms



ii. One dimensional nano structure (1D)

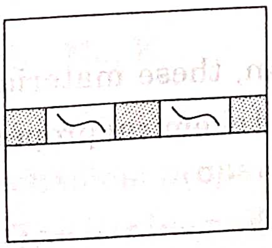
Ex : atom clusters

Ex : Fullereness



iii. Two dimensional nano structure (2D)

Multilayer material with nano thickness Ex : Nano tube.



iv. Three dimensional nano structure (3D)

Ex : Material with three dimensional equiaxed with three dimensional equiaxed nano size grain - Quantum well.

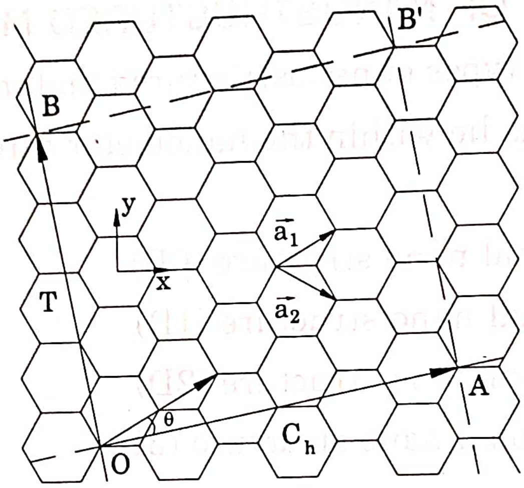


Fig. 5.12 An illustration showing chiral vector

These ranges from zero dimensional atom cluster to three dimensional equiaxed grain structure. Each class has got at least one dimension in the nanometer range.

- Any classical multilayered material with layer of thickness in the nanometer range is classified as a system of one dimension.
- Layers in the nanometer thickness range consisting at range of nanometer are two dimensional system.
- Finally, the last class in the system that consists of 3D microstructures (or) nano particles.

Nanomaterials have increased surface area substance which are having enhanced chemical, mechanical, optical and mechanical properties. This can be exploited for a variety of application. Using a variety of synthesis methods it is possible to produce nanomaterials in the form of nanoparticles, nano crystals, clusters, nano wires, nanotubes, nanodots etc.,

5.15 PROPERTIES OF NANO PARTICLES

The size of the nano particles are very very thin, these materials exhibits peculiar physical, electronic, magnetic, mechanical and chemical properties. Some of them are discussed below.

5.15.1 Physical properties

i. Since the size of the particle is very less, particles are very close to each other. Hence the inter particle spacing is very less in nanomaterials.

ii. Because of its very less size, these nano materials cannot be further divided into small particles and it does not have any dislocation in it. Thus we can say that they have high strength and super hardness.

iii. The melting point of nanomaterials will be very less.

5.15.2 Electrical properties

i. The energy bands in these materials will be very narrow.

ii. The ionization potential is found to be higher for nano-materials.

iii. When the nanomaterials are prepared from bulk materials, they have more localized molecular bands.

iv. Nano-materials are capable of storing hydrogen atoms.

5.15.3 Magnetic properties

i. In nano-materials a large number of atoms will be present at the surface. These atoms will have less-co-ordination number and hence posses local magnetic moment with in themselves.

ii. Due to large magnetic moment these nano-materials exhibits spontaneous magnetisation at smaller sizes.

iii. Ferro-magnetic and anti ferro magnetic multilayer nano-materials has GMR (Gaint Magneto Resistance) effect.

iv. The nanomaterials shows variation in their magnetic property, when they change from bulk state to cluster (nano particle) state. Some by the examples are

Materials	Bulk state	Nano phase state
a. Iron, Ni, Cobalt →	Ferromagnetic →	Super paramagnetic
b. Na, K →	Ferromagnetic →	Ferromagnetic
c. Cr →	Antiferromagnetic →	Frustrated Paramagnetic.

5.15.4 Mechanical properties

i. The hardness of nano phase materials varies from material to material. This may be due to the phase transformation, stress relief, density and grain boundaries.

ii. They exhibit super plastic behaviour.

5.16 QUANTUM WELLS, QUANTUM WIRES AND QUANTUM DOTS

When the size of a material is continuously reduced from a bulk or macroscopic size such as a meter or a centimetre to a very small size, the properties remain same at first, then small changes begin to occur until finally when the size drops below 100 nm, dramatic changes in properties can occur.

If one dimension is reduced to the nanorange while the other two dimensions remain large, then we obtain a structure known as a *quantum well.*

If two dimensions are reduced to the nanorange and one remains large the resulting structure is called as a *quantum wire.*

The process of size reduction in which all three dimensions leads to low nanometer range is referred as a *quantum dot.*

The word quantum is associated with these three types of nanostructures because the changes in properties arise from quantum physics in the domain of nanorange. Fig. 5.13 shows the size reductions in both rectangular and spherical geometry.

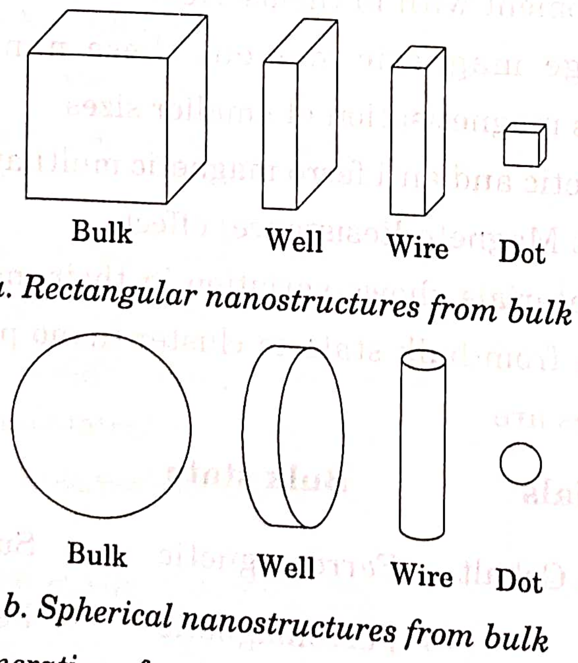


Fig. 5.13 Progressive generation of rectangular and spherical nanostructures from bulk

5.17 FABRICATION METHODS

Methods employed to produce nanostructured materials are numerous, with each method having its own advantages and disadvantages depending on the desired properties or applications. The different methods used to produce nanostructures are broadly classified under two groups namely

a) bottom-up approach and

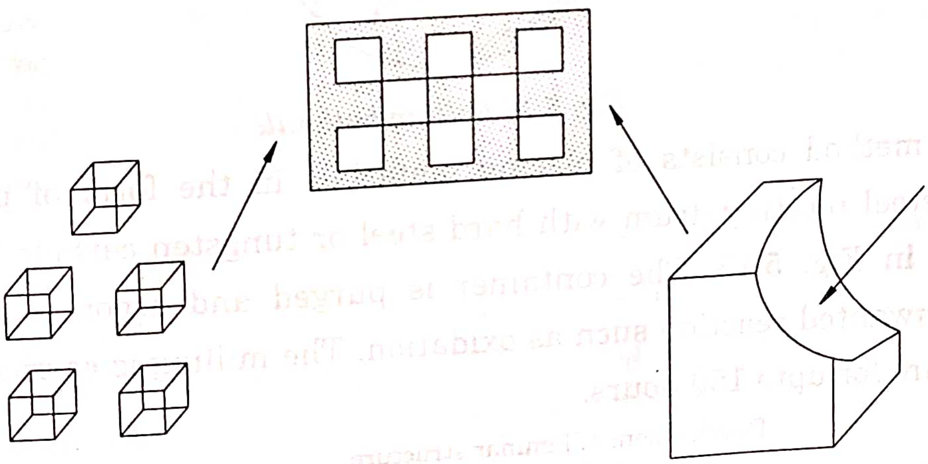
b) top-down approach.

The two approaches are shown schematically in Fig. 5.14.

The *bottom-up* approach first forms the nanostructured building blocks such as atoms and molecules and *assemble them* into larger nanostructured material. This is a powerful approach of creating identical structures with atomic precision.

The *top-down* approach involves the *breaking down* of large pieces of bulk material to generate the required nanostructured material from them. Both approaches can be done in gas, liquid, solid state or in vacuum.

Nanostructured material



Assemble from
Nano-building Blocks

Bottom - up approach

"Sculpt" from Bulk

Top-down approach

Fig. 5.14 Schematic representation of the bottom - up and top-down approach for nanostructure fabrication

5.18 TOP DOWN PROCESSES

The top-down processes starts with large scale object and gradually reduces its dimensions. The top-down approaches are simpler. Methods used to produce nanostructured materials under top-down approach are given below.

a. Milling

b. Lithographics

c. Machining

5.18.1 Milling

One nano fabrication technique of major industrial importance is high energy ball milling. This technique is also known as mechanical alloying or mechanical attrition. It is a solid state process used for the manufacture of a wide range of nanopowders. High energy ball milling can induce structural changes and chemical reactions at room temperature.

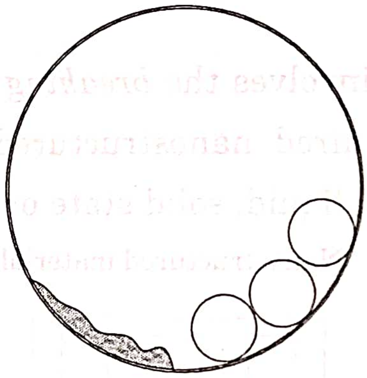


Fig. 5.15 Rolling ball mill

The method consists of placing materials in the form of powder into a stainless steel rotating drum with hard steel or tungsten carbide balls inside it as shown in Fig. 5.15. The container is purged and argon is introduced to prevent unwanted reaction such as oxidation. The milling is carried out at room temperature for upto 150 hours.

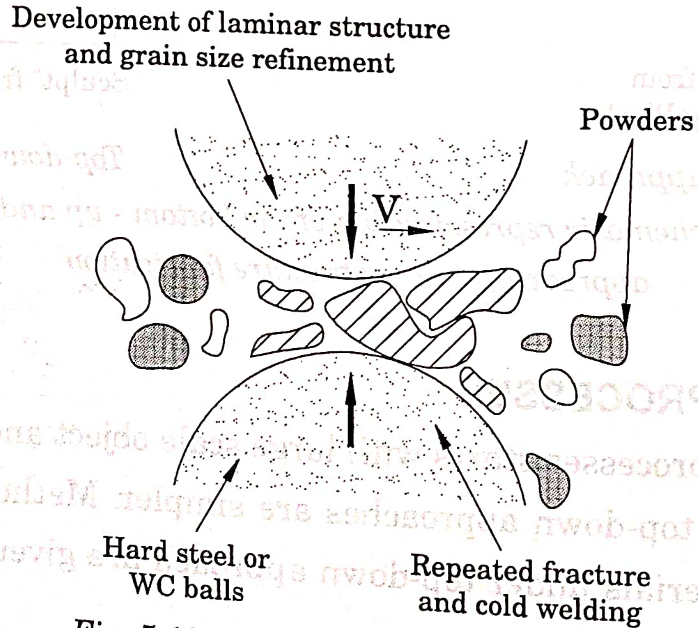
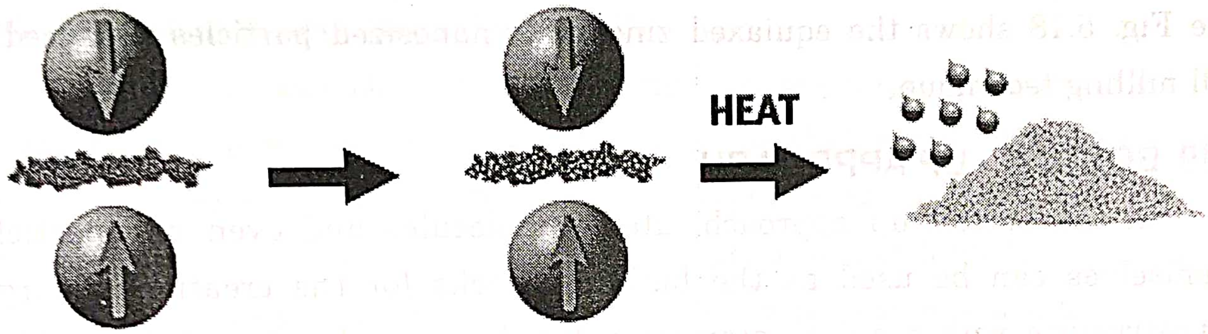


Fig. 5.16 Mechanical alloying process

As shown in Fig. 5.16 the powder materials are crushed mechanically in the rotating drum by the hard balls. This repeated deformation can cause large reductions in grain size in the powder particles. The size of the nanostructured grains induced in the powder particles is determined by the chemistry of the powder particles, milling and heat treatment conditions.

The process steps in the formation of nanoparticles by milling is shown in Fig. 5.17.



Ball mill acts as a low temperature chemical reactor, reaction process results from local heat and pressure at contact surface.

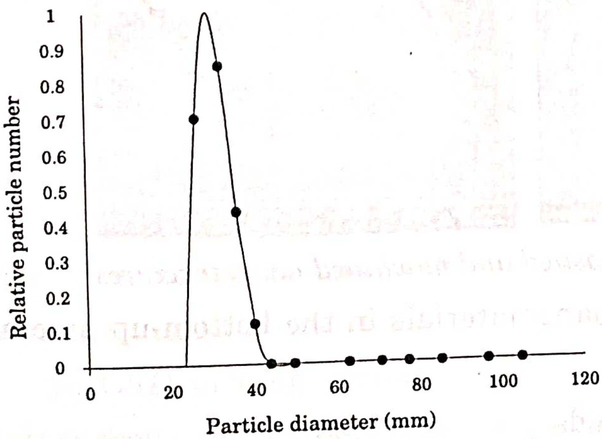
Chemical reactions occur at nanoscale. Low temperature enables controlled nano particle formation.

Reaction product is heat treated. Solid phase chemistry prevents particles from agglomeration.

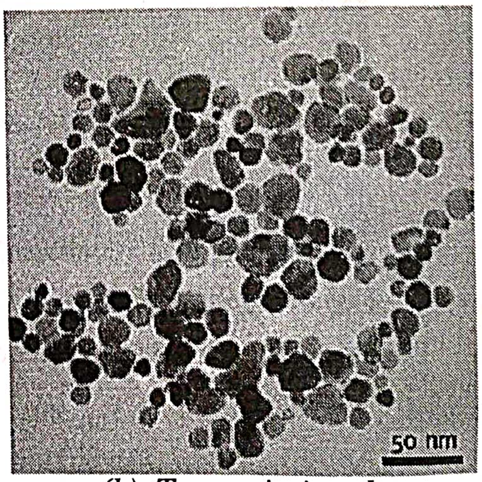
Fig. 5.17 Schematic representation of process steps in the nanoparticle formation is milling

High energy ball milling is used for the production of

a. nanocrystalline materials
b. nanoparticles
c. nanocomposites
d. nanotubes
e. nanorods and
f. nanowires



(a) Particle size distribution curve for MCP ~ 30 nm zinc oxide nanopowder showing a mean particle size of 30 nm measured by Photon correlation spectroscopy



(b) Transmission electron micrograph of ~ 30 nm zinc oxide showing an equiaxed shape and mono dispersed suspension

Fig. 5.18 Zinc oxide nanosize particles prepared using high energy ball milling

- The deposition rate can be easily controlled by varying the current with time.
- Multilayered nanostructures can be prepared by this method.

Disadvantages

The nucleation of nanostructures on the electrode substrate during electrodeposition is influenced by the following factors:

- Crystal structure of the substrate
- Specific free surface energy,
- Adhesion energy,
- Lattice orientation of the electrode surface, and crystallographic lattice mismatch at the nucleus-substrate interface boundary.

5.20 APPLICATIONS OF NANO - PARTICLES

Though nano - particles are very small, they are the important materials to built the future world. They have applications almost in all engineering fields as follows

(i) Mechanical Engineering

(i) Since they are stronger, lighter etc., they are used to make hard metals.

(ii) Smart magnetic fluids are used in vaccum seals, magnetic separators etc.

(iii) They are also used in Gaint Magneto Resistance (GMR) spin valves.

(iv) Nano-MEMS (Micro - Electro Mechanical Systems) are used in ICs, optical switches, pressure sensors, mass sensors etc.

(ii) Electrical, Electronics and Communication Engineering

(i) Orderly assembled nanomaterials are used as quantum electronic devices and photonic crystals.

(ii) Some of the nanomaterials are used as sensing elements. Especially the molecular nanomaterials are used to design the robots, assemblers etc.

(iii) They are used in energy storage devices such as hydrogen storage devices, magnetic refreigeration and in ionic batteries.

(iv) Dispersed nanomaterials are used in magnetic recording devices, rocket propellant, solar cells, fuel cells, etc.

(v) Recently nano-robots were designed, which are used to remove the damaged cancer cells and also to modify the neutron network in human body.

(iii) Computer Science Engineering and IT

(i) Nano-materials are used to make CD's and semiconductor laser.

(ii) These materials are used to store the informations in smaller chips.

(iii) They are used in mobiles, lap-tops etc.

(iv) Further they are used in chemical / Optical computers.

(v) Nano - dimensional photonic crystals and quantum electronic devices plays a vital role in the recently developed computers.

(iv) Bio-medical and chemical Engineering

(i) Consolidated state nanoparticles are used as catalyst, electrodes in solar and fuel cells.

(ii) Bio-sensitive nanoparticles are used in the production of DNA - chips, bio-sensors etc.

(iii) Nano-structured ceramic materials are used in synthetic bones.

(iv) Few nanomaterials are also used in adsorbents, self - cleaning glass, fuel additives, drugs, ferrofluids, paints etc.

(v) Nano - metallic colloids are used as film precursors.

5.21 CARBON NANOTUBES (CNT)

Carbon nanotubes were first observed by Sumio Iijima in 1991. So far we know only three forms of carbon, namely diamond, graphite and amorphous carbon. Now we come to know that there is a whole family of other forms of carbon known as Carbon nanotubes, which are related to graphite.

A promising group of nanostructures with large application potential are carbon nanotubes. The hexagonal lattice of carbon is simply graphite. A single sheet of graphite is called *Graphene* (Fig. 5.25).

Carbon nanotubes (CNTs) consists of a graphene sheet which has been rolled up into a cylindrical shape as shown in Fig. 5.26.

Physical Vapor Deposition Technique for Growing Nanostructures

by **Xudong Wang**

Thermal evaporation is one of the simplest and most popular synthesis methods, and it has been very successful and versatile in fabricating nanobelts and nanowires with various characteristics. The basic process of this method is sublimating source material(s) in powder form at high temperature, and a subsequent deposition of the vapor in a certain temperature region to form desired nanostructures.

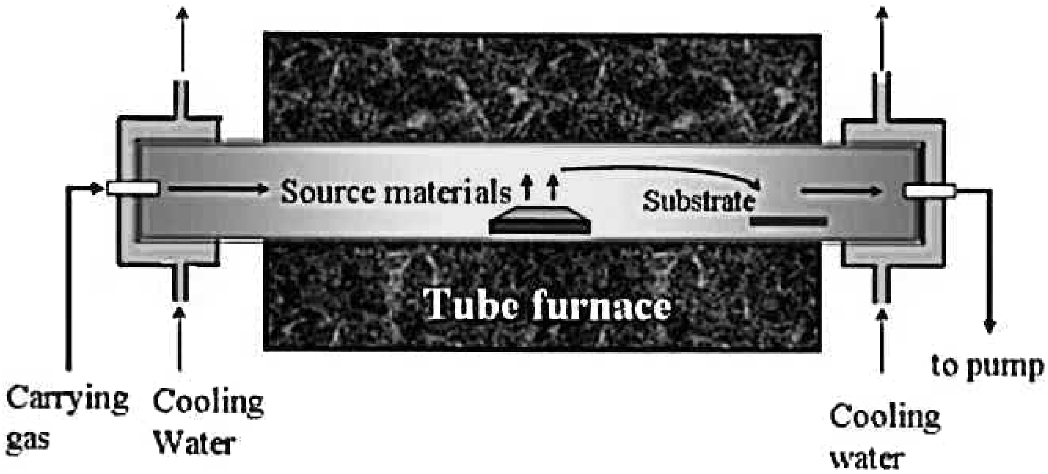


Figure 1. Thermal evaporate deposition system for synthesis of 1D nanostructures

A typical experimental system is shown in Figure 1. The synthesis is performed in an alumina or quartz tube, which is located in a horizontal tube furnace. High purity oxide powders contained in an alumina boat are loaded in the middle of the furnace, the highest temperature region. The substrates for collecting the desired nanostructures are usually placed down-stream following the carrier gas. The substrates can be silicon wafer, poly-crystalline alumina or single crystal alumina (sapphire). Both ends of the tube are covered by stainless steel caps and sealed with O-rings. Cooling water flows inside the cover caps to achieve a reasonable temperature gradient in the tube.

During the experiments, the system is first pumped down to around 10-2 Torr. Then the furnace is turned on to heat the tube to the reaction temperature at a specific heating rate. An inert carrying gas, such as argon or nitrogen, is then introduced into the system at a constant flow rate to bring the pressure in the tube back to 200-500 Torr (different pressures are required by different source materials and final deposited nanostructures). The reaction temperature and pressure are held for a certain period of time to vaporize the source material and achieve a reasonable amount of deposition.

Source materials can be vaporized at the high temperature and low presure condition. The vapor is then carried by the innert carrying gas down to the lower temperature region, where the vapor gradually becomes supersaturated. Once it reaches the substrate, nucleation and growth of nanostructures will occur. The growth is terminated when the furnace is turned off. The system is then cooled down to room temperature with flowing inert gas.

The thermal evaporation process is basically a physical vapor deposition process and has been successfully used for synthesizing a variety of oxide and non-oxide nanobelts and nanowires. Moreover, this system can also be used for chemical vapor deposition (CVD) by simply applying reaction gases instead of the carrier gas and placing substrates in the middle of the tube. For example, multi-wall and single-wall carbon nanotubes have been successfully fabricated in this system using hydrogen and methane/acetylene as reactants. Metal catalysts, such as gold, tin, copper, etc. have also been used to achieve size control and alignment.

- It is used as antenna wires in cell phones.

19. What is Nano Technology or Nano Science?

Nanotechnology is a field of applied science and technology which deals with the matter on the atomic and molecular scale, normally 1 to 100 nanometers, and the fabrication of devices with critical dimensions that lie within that size range.

20. What are Nanomaterials?

Nanomaterials are the materials with atoms arranged in nanosized clusters which become the building block of the material. Any Material with a size between 1 and 100 nm [10^{-9} m to 10^{-7} m] is called nanomaterial.

21. What is Top – down approach ? Give its Methods

Top – down approach

The removal or division of bulk material or the miniaturization of bulk fabrication processes to produce the desired nanostructure is known as top-down approach. It is the process of breaking down bulk material to Nanosize

Top – down Methods : Milling, Lithographics and Machining

22. What is Bottom–up approach? Give its Methods

Bottom–up approach

Molecules and even nanoparticles can be used as the building block for producing complex nanostructures. This is known as Bottom–up approach. The Nano particles are made by building atom by atom.

Bottom up Methods : Vapour phase deposition, Molecular Beam epitaxy, Plasma assisted deposition, Metal Organic vapour phase epitaxy (MOVPE) Liquid phase process [Colloidal method and Sol–Gel method]

23. Mention the methods used to fabricate nanostructures?

Top – down Methods

- Milling
- Lithographics
- Machining

Bottom up Methods

- Vapour phase deposition
- Molecular Beam epitaxy
- Plasma assisted deposition
- Metal Organic vapour phase epitaxy [MOVPE]
- Liquid phase process [Colloidal method and Sol – Gel method]

24. What is milling?

Large grained materials [metals, ceramics and polymers] in the form of powders are crushed mechanically in rotating drums by hard steel or

...gy, space, biosensors, drug delivery medicine., etc

43. What are carbon nanotubes?

A carbon nanotube is a thick sheet of graphite (called graphene) rolled up into a cylinder with diameter of the order of a nanometer.

Sumio Iijima of Japan in 1991 discovered the carbon nanotube. Carbon nanotubes (CNTs) are an allotrope [form] of carbon. The other allotropes of carbon are diamond and graphite. Nanotubes are composed entirely of sp^2 bonds

44. What is Buckyball or fullerence?

Nanotubes are members of the fullerene structural family, which also includes buckyballs (C_{50}), the Buckyballs are spherical in shape like a football contains only 50 carbon atoms.

45. What is chiral vectors?

The way in which the graphene sheet is wrapped and it is represented by a pair of indices (n,m) called the chiral vector.

45. What are the different kinds of Carbon nanotube structures?

The different kinds of structures in CNTs are Armchair structure, Zigzag Structure and Chiral structure. These structures are obtained by the different ways of wrapping the graphene sheet.

- If $m = 0$, the nanotubes are called "zigzag".
- If $n = m$, the nanotubes are called "armchair".
- If $m, n \neq 0$ and $m \neq n$ are called "chiral".

47. What are the types of Carbon nanotubes ?

There are two main types of nanotubes:

(i) single - walled nanotubes (SWNTs) and

(ii) multi - walled nanotubes (MWNTs).

Single - walled nanotubes (SWNTs)

- Single-walled nanotubes (SWNT) have a diameter of 2 nanometer with tube length of 100 μm.
- The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite into a seamless cylinder.

Multiwalled nanotubes (MWNTs)

- It consist of multiple layers of graphite rolled to form a tube shape with many concentric carbon cylinders.

48. Mention any four Properties of Carbon Nanotubes

- Single walled carbon nanotubes are metallic or semiconductors depending on the chirality and diameter.
- The nanotube has very low resistance
- These are very strong. SWNTs are 100 times stronger than steel.
- Carbon nanotubes are highly conductive both to electricity and heat.
- They exhibit an electrical conductivity as high as copper, and thermal conductivity as great as diamond.

49. What are the method of Synthesis or Carbon Nanotubes?

Carbon nanotubes are produced by three methods, they are

(i) Electric arc discharge method

(ii) Laser ablation method

(iii) Chemical vapor deposition (CVD) method

50. Mention the Applications of Carbon Nanotubes.

- Nanometer-sized semiconductor devices, probes, and interconnects
- Devices for energy storage and energy conversion
- Sensors, Fuel cells
- Lithium ion batteries, Field emission displays and radiation sources
- Flat panel displays, Hydrogen storage devices.
- Lubricants, coatings, catalysts, electro-optical devices, and medical applications.
- Tennis rackets containing carbon nanotubes
- Lightweight bullet-proof vests.
- Nanotube based Field effect transistors.

PART - B QUESTIONS

1. What are metallic glasses ? How it is prepared by melt spinning technique.
2. Explain the properties and applications of metallic glasses.
3. What is shape memory alloy ? Mention the properties of shape memory alloy.
4. Explain the characteristics and applications of shape memory alloy.
5. Discuss in detail the various properties and applications of nanomaterials.
6. Explain ball milling method to produce nanoparticles.
7. Explain chemical vapour deposition method to produce nanoparticles?
8. Explain with a neat diagram plasma arcing method to prepare nanoparticles.
9. Describe in detail sol-gel method to prepare nanoparticles.
10. Explain with a neat diagram electro deposition method to produce metallic nanomaterials. List out the specific advantages of this method.
11. Explain with the neat diagram of the various structures of carbon nanotubes.
12. Explain the various properties and applications of carbon nanotubes.
13. What is a carbon nanotube ? Describe the fabrication of carbon nanotube using pulsed laser deposition method.
14. Describe chemical vapour deposition techni...