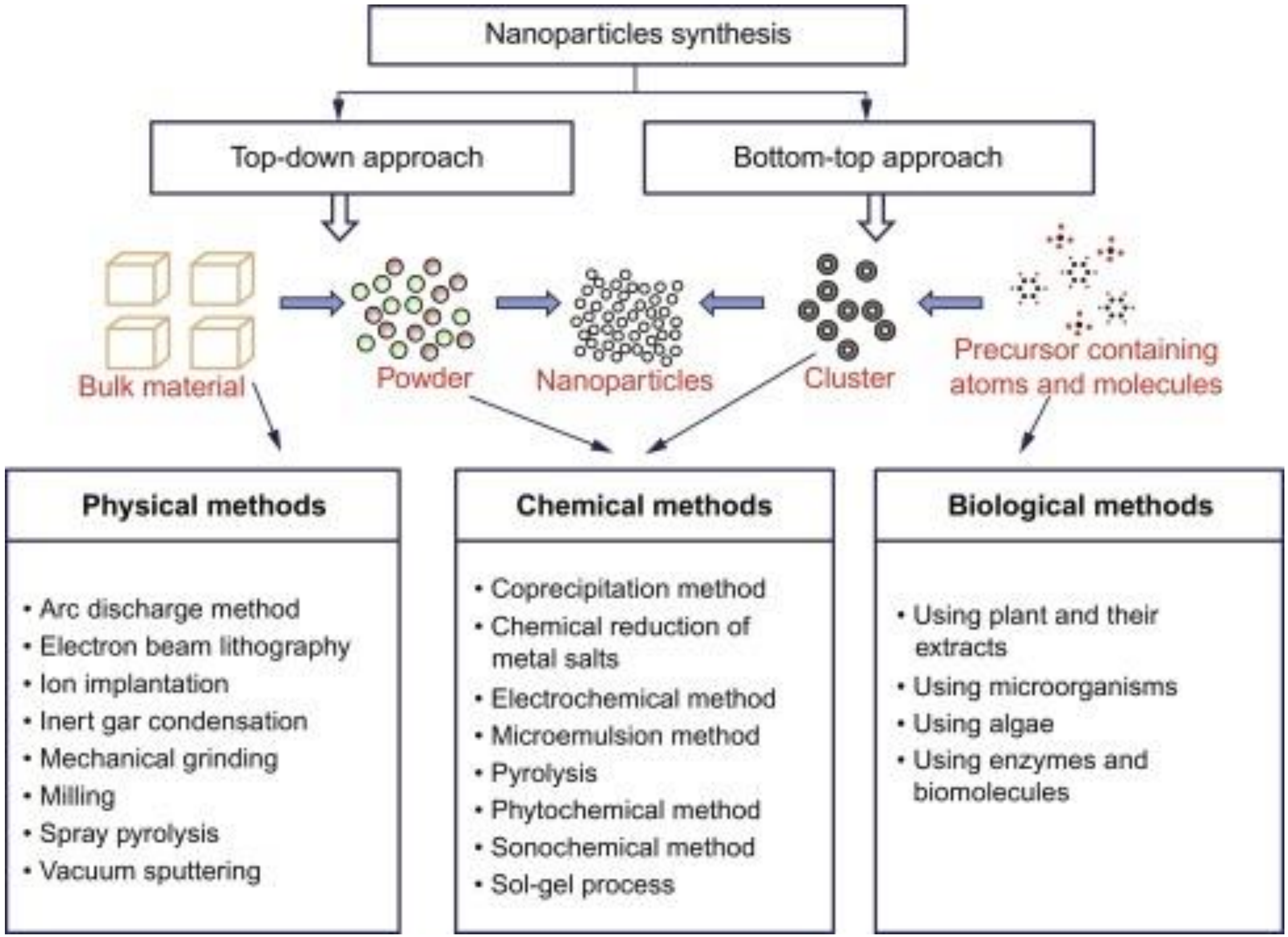
나노소재의 이해와 응용

2023-2

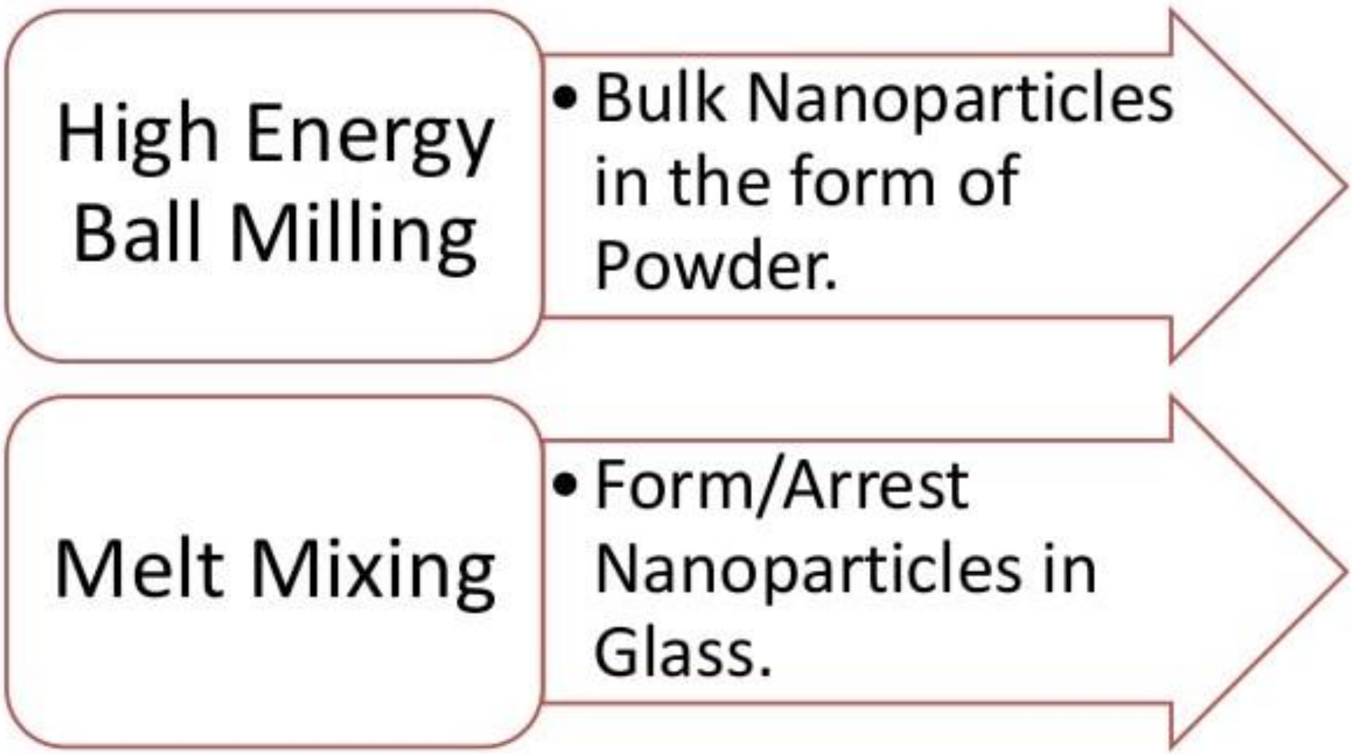
3. Synthesis of Nanomaterials - I
(Physical Methods)

3. Synthesis of Nanomaterials I (Physical Methods)



3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods



3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.1. High Energy Ball Milling

Some of the materials like Co, Cr, W, Ni, Ti, Al-Fe and Ag-Fe are made nanocrystalline using ball mill

Few milligrams to several kilograms of nanoparticles can be synthesized in a short time of a few minutes to a few hours

One of the simplest ways of making nanoparticles of some metals and alloys in the form of power

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.1. High Energy Ball Milling

Type of milling

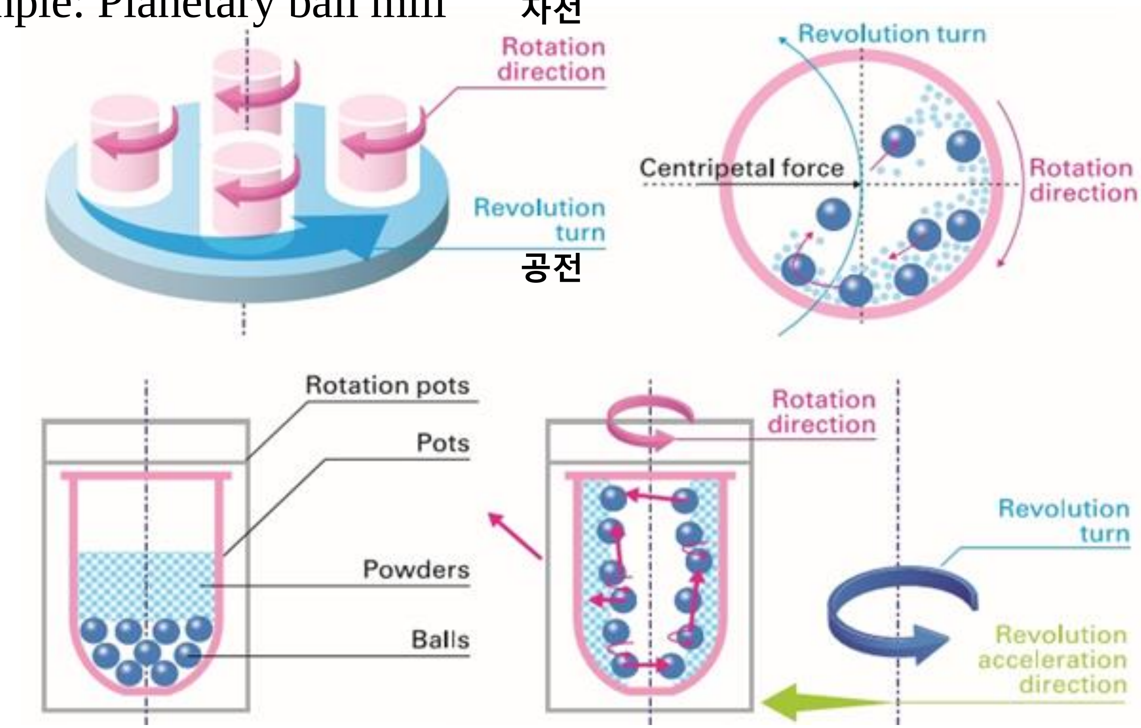
Planetary	Vibratory
Rod	Tumbler

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.1. High Energy Ball Milling

Example: Planetary ball mill



유성볼밀 (Planetary Ball Mill)은 공전과 자전의 회전 원리를 이용한 분쇄기로 볼밀의 턴테이블이 공전하는 동시에 분쇄용기 (Pot)가 공전의 반대방향으로 회전하면서 분쇄용기 내부에 투입된 Media와 피분쇄물과의 상호 충돌에 의한 高충격력과 高효율의 전단력을 이용하여 미분쇄 효율을 얻을 수 있는 장비

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.1. High Energy Ball Milling

Usually one or more containers are used at a time to make large quantities of fine particles: the size of container depends upon the quantity of interest

Hardened steel or tungsten carbide ball are put in containers along with power of flakes (< 50 μm) of a material of interest

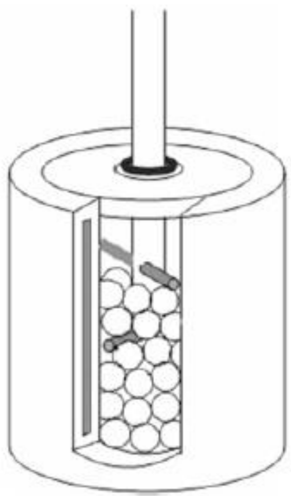


Fig. 3.1 A schematic diagram (*sectional*) of a ball mill vessel

- Usually 2:1 mass ratio of balls to materials is advisable
- If the container is more than half filled, the efficiency of milling is reduced
- Heavy milling balls increase the impact energy on collision

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.1. High Energy Ball Milling

- To avoid any impurities form balls, the container may be filled with air or inert gas. However this can be an additional source of impurity, if proper precaution to use high purity gases is not taken

- A temperature rise in the range of 100 ~ 1000˚C is expected to take place during the collusions.

- The gases like oxygen(O_2), nitrogen(N_2) etc. can be the source of impurities as constantly new, active surfaces are generated.

- Cryo-cooling is used sometimes to dissipate the heat generated.

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.1. High Energy Ball Milling

- The containers are rotated at high speed (a few hundred rpm) around their own axis. Additionally they may rotate around some central axis and are therefore called as ‘Planetary ball mill’

- When the containers are rotating around the central axis as well as their own axis, the material is forced to the wall and is pressed against the walls

- By controlling the speed of rotation of the central axis and container as well as duration of milling, it is possible to ground the material to fine powder (few nm to few tens of nm) whose size can be quite uniform.

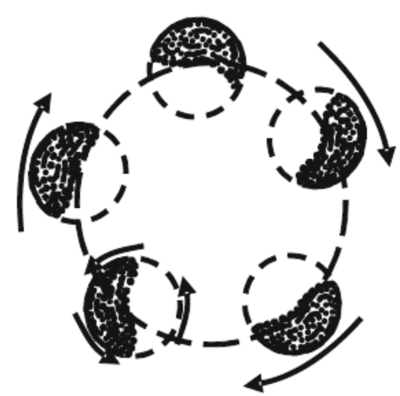


Fig. 3.2 Ball mill in planetary motion (schematic). Sketch shows that the material is thrown against the wall during the course of rotation of a single container. Dark regions are illustrating the powder material, while the rest is empty

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.2. Melt Mixing

- It is possible to trap or arrest nanoparticles in a Glass.

- Glass is an amorphous solid which lacks large range periodic arrangement of atoms/molecules

- When a liquid is cooled below certain temperature (T_m), it forms either a crystalline or amorphous solid(Glass)

- Beside temperature, rate of cooling and tendency to nucleate decide whether the melt can be cooled as a glass or crystalline sold with long range order.

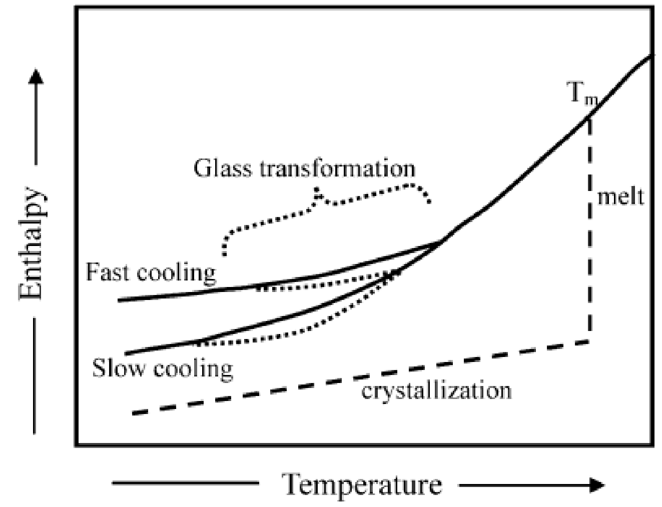


Fig. 3.3 Cooling pattern of glass forming melt

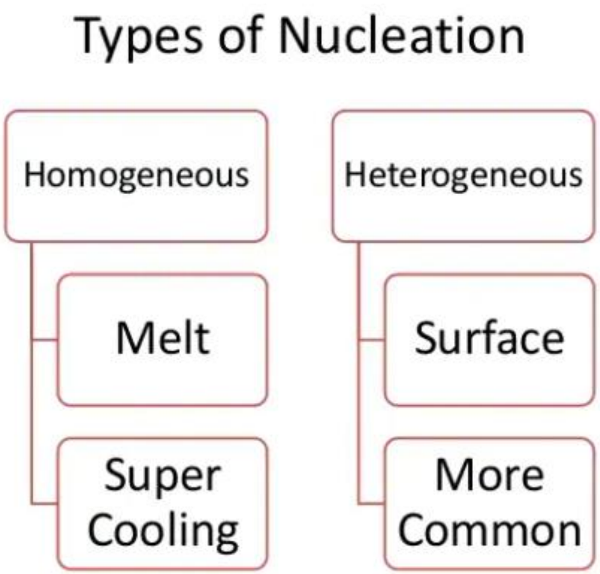
3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.2. Melt Mixing

What is Nucleation?

- Nucleation is the initial process that occurs in the formation of a crystal form a solution (a liquid or a vapour) in which a small number of ion, atoms, or molecules become arranged in a pattern characteristics of a crystalline solid, forming a site upon which additional particles are deposited as the crystal grow.



- Metals usually form crystalline solids but if cooled at very high rate they can form amorphous solid. Such solids are known as Metallic glasses.
- Even in such cases the atoms try to reorganize themselves into crystalline solids
- Addition of element like B, P, Si etc. helps to keep the metallic glasses in amorphous state.

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.2. Melt Mixing

Formation of Nanocrystals within metallic glasses

- Silicates(Germanates) have a central silicon atom in a pyramidal structure with oxygen atoms at the corners.
- Such silicate units, not sharing the edges, but connected only through the corners are randomly distributed in 3-D to form glassy structure.

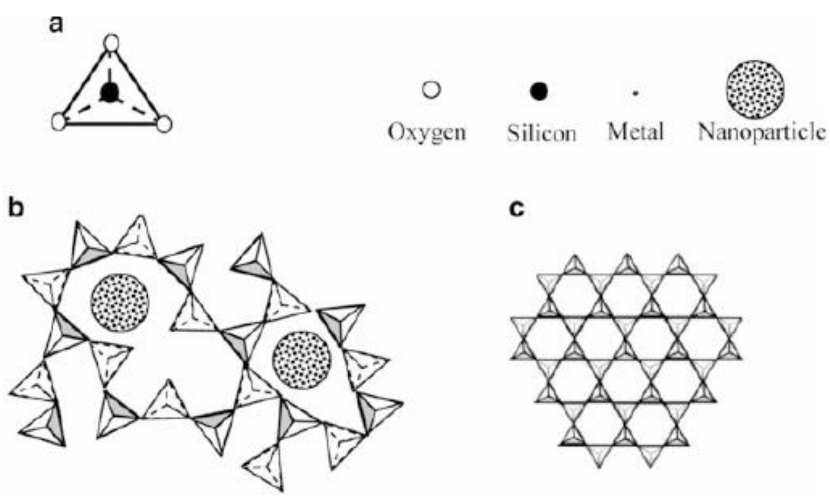


Fig. 3.4 Structure of silicates
(**a**) Tetrahedral (pyramidal) building block of typical silicates or germanets
(**b**) Disordered arrangement of tetrahedral units to form a 'glassy' substance. This entraps
nanoparticles inside appropriate voids
(**c**) Tetrahedron can also form crystalline regular arrangement

3. Synthesis of Nanomaterials I (Physical Methods)

3.1 Mechanical Methods

3.1.2. Melt Mixing

Formation of Nanocrystals within metallic glasses

- A window glass has in addition to SiO_2 (~ 72 %), oxides of sodium (~ 14.5 %), calcium (~ 8.5 %), magnesium (~ 3.5 %) and aluminium (~ 1.5 %) as its constituents.

- Laboratory glassware has silica (80 %), boron oxide (10 %), sodium oxide (5 %), alumina (3 %), magnesium oxide (1 %) and calcium oxide (1 %)

- Beautiful colours in glasses like red, yellow, blue, orange, green and their shades are a result of addition of some elements like gold, cobalt, nickel, iron etc. These colours are attributed to the formation of nanoparticles of these elements

- The melt of glass forming materials and desired nanoparticle material is well homogenized before the cooling begins. The nanoparticles are usually well separated and immobilized by glassy matrix.

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

- Evaporation methods help synthesizing nanostructures by evaporating the materials on certain substrates

- The nanostructured materials can be in the form of thin film, multilayer films or nanoparticulate thin film (thin film composed of nanoparticles).

- Material of interest is brought in the gaseous phase (atoms or molecules) which can form clusters and then deposit on appropriate substrates.

- It is also possible to obtain very thin (even atomic layers, known as monolayers) layers or multilayers (multilayers are layers of two or more materials stacked over each other) forming nanomaterials of wide interest.

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

Evaporation

- Evaporation can be achieved by various methods like resistive heating, electron beam heating, laser heating, sputtering.
- All the synthesis processes need to be carried out in a properly designed vacuum system (see Appendix IV for vacuum techniques), so as to avoid uncontrolled oxidation of source materials and final product as well as that of components
- Materials to be evaporated are usually heated from some suitable filament, crucible, boat (collectively called as ‘evaporation source’ or ‘crucible’)

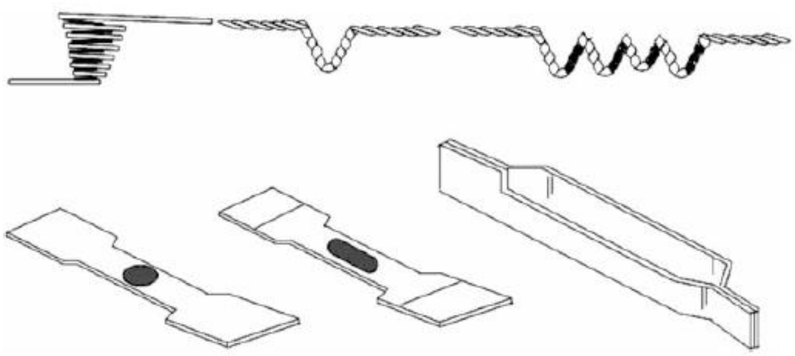


Fig. 3.5 Different shapes of filaments, canoe and baskets used for holding the materials for evaporation

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

Vacuum techniques

- Vacuum is the space devoid of any gas, liquid, solid or any particles. Vacuum is needed for various purposes such as packaging of food, materials deposition and processing, analysis equipment and many other applications
- Extent of vacuum is measured with reference to normal atmospheric pressure at sea level i.e. one atmosphere.
- This in turn is measured as the pressure exerted by air on unit area of a flat surface. Pressure is defined as force per unit area.
  -> The SI unit for pressure is Pascal (Pa) defined as N/m^2. At sea level mercury column height is 760 mm.

1 atmosphere = 760 torr = 1.013×10^5 Pa
1 torr = 1 mm of Hg = 10^{-3} mbar
1 bar = 750 torr
1 Pa = 7.5 mtorr

Low vacuum	10^5 Pa (750 torr) to 3.3×10^3 Pa (25 torr)
Medium vacuum	3.3×10^3 Pa (25 torr) to $\sim 10^{-1}$ Pa (7.5×10^{-4} torr)
High vacuum	10^{-1} Pa (7.5×10^{-4} torr) to 10^{-4} Pa (7.5×10^{-7} torr)
Very high vacuum	10^{-4} Pa (7.5×10^{-7} torr) to 10^{-6} Pa (7.5×10^{-9} torr)
Ultra high vacuum	10^{-6} Pa (7.5×10^{-9} torr) to 10^{-10} Pa (7.5×10^{-13} torr) or below

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

Evaporation

- Usually the sources are electrically heated so that enough vapours of the material to be deposited are generated
- If the material to be deposited wets the filament material without forming any alloy or compound, the filament is considered to be suitable.
- The materials which is melt in a basket has a disadvantage that the crucible itself and surrounding parts also get heated and become the source of unwanted contamination or impurities.

Electron beam evaporation

- Electron beam focuses on the material to be deposited, kept in the crucible as it is generated from a filament that is not in the proximity of the evaporating material.
- It melts only some central portion of the material in crucible avoiding any contamination from crucible. Thus high purity vapours of materials can be obtained.

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.3.1 Physical Vapour Deposition with Consolidation

Physical Vapour Deposition (PVD)

- Use of materials of interest as sources of evaporation
- An inert gas or reactive gas for collisions with material vapour
- A cold finger on which clusters or nanoparticles can condense
- A scraper to scrape the nanoparticles piston-anvil (an arrangement in which nanoparticle powder can be compacted)

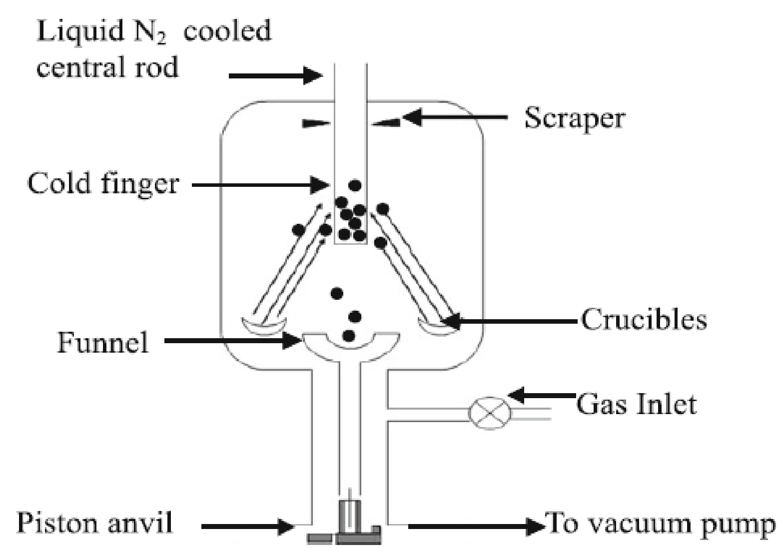


Fig. 3.6 Schematic diagram of synthesis of nanoparticles by physical vapour deposition. Particles condense on the central cooled rod, are scraped and consolidated using a piston-anvil system in vacuum to form a pellet

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.3.1 Physical Vapour Deposition with Consolidation

Physical Vapour Deposition (PVD)

- Usually metals or high vapour pressure metal oxides are evaporated or sublimated from filaments or boats of refractory metals like W, Ta and Mo in which the materials to be evaporated are held

- The density of the evaporated material close to the source is quite high and particle size is small (<5 nm)

- Such particles would prefer to acquire a stable lower surface energy state

- Due to small particle or clustercluster interaction bigger particles get formed. Therefore, they should be removed away as fast as possible from the source. This is done by forcing an inert gas near the source, which removes the particles from the vicinity of the source.

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.3.1 Physical Vapour Deposition with Consolidation

Physical Vapour Deposition (PVD)

- In general the rate of evaporation and the pressure of gases inside the chamber determine the particle size and their distribution.
- Distance of the source from the cold finger is also important.
- Evaporated atoms and clusters tend to collide with gas molecules and make bigger particles, which condense on cold finger. While moving away from the source to cold finger the clusters grow
- If clusters have been formed on inert gas molecules or atoms, on reaching the cold finger, gas atoms or molecules may leave the particles there and then escape to the gas phase.

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.3.1 Physical Vapour Deposition with Consolidation

Physical Vapour Deposition (PVD)

- If reactive gases like O_2, H_2 and NH_3 are used in the system, evaporated material can interact with these gases forming oxide, nitride or hydride particles.
- Alternatively one can first make metal nanoparticles and later make appropriate post-treatment to achieve desired metal compound etc.

- Size, shape and even the phase of the evaporated material can depend upon the gas pressure in deposition chamber. For example using gas pressure of H_2 more than 500 kPa, TiH_2 particles of ~12 nm size were produced.

- By annealing them in O_2 atmosphere, they could be converted into titania (TiO_2) having rutile phase. If titanium nanoparticles were produced in H_2 gas pressure less than 500 kPa, they could not be converted into any crystalline oxide phase of titanium but always remained amorphous.

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.3.2 Ionized Cluster Beam Deposition

- First developed by Takagi and Yamada around 1985
- Useful to obtain adherent and high quality single crystalline thin films
- The set up consists of a source of evaporation, a nozzle through which material can expand into the chamber, an electron beam to ionize the clusters, an arrangement to accelerate the clusters and a substrate on which nanoparticle film can be deposited, all housed in a suitable vacuum chamber.

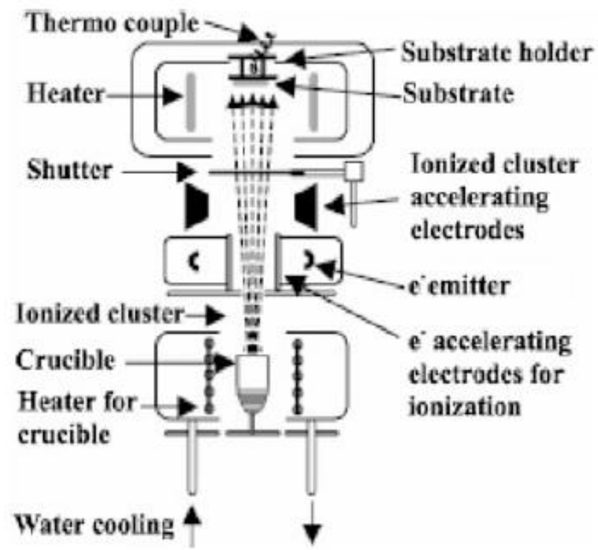


Fig. 3.7 Ionized cluster beam apparatus

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.3.2 Ionized Cluster Beam Deposition

- Small clusters from molten material are expanded through the fine nozzle. The vapour pressure ~ 1 Pa to 1 kPa needs to be created in the source
- The nozzle needs to have a diameter larger than the mean free path of atoms or molecules in vapour form in the source to form the clusters
- On collision with electron beam, clusters get ionized. Due to applied accelerating voltage, the clusters are directed towards the substrate.
- By controlling the accelerating voltage, it is possible to control the energy with which the clusters hit the substrate
- Stable clusters of some materials would require considerable energy to break their bonds and would rather prefer to remain as small clusters of particles.
- It is possible to obtain the films of nanocrystalline material using ionized cluster beam. However it is not unlikely that some neutral atoms also get incorporated in the film

Next

3. Synthesis of Nanomaterials - I (Physical Methods)