Ceramics Manufacturing Processes

Although the term “ceramic” relates to a wide range of compounds as well as very different applications (building, cooking, sanitary, electric, magnetic, optical, mechanical, thermal, etc.), these materials have common properties because of their primarily ionic-covalent bonds as high melting point; high hardness; absence of the ductility at low temperatures; brittleness and low toughness.

These properties reveal that conventional methods of manufacturing metallic parts are not adapted to ceramics. The absence of ductility precludes shaping by the plastic deformation. The high hardness and brittleness limit possibilities of machining to cutting and grinding by means of expensive diamonds tools. With exception of glasses, the high melting points and possible decompositions make procedure of fusion difficult. Ceramic objects are therefore generally obtained by high temperature consolidation (sintering) of a granular structure in the form of powders by applying a ceramic process. (See fig.1).

The physical (size and shape of particles, grain size distribution) and chemical (surface of particles) characteristics of the powders will have to be adapted beforehand to process. The choice of shaping process depends on several parameters related to ceramic piece, such as the size, shape, surface quality, dimensional tolerances microstructural characteristics and economic considerations like productivity and the cost of the equipment.

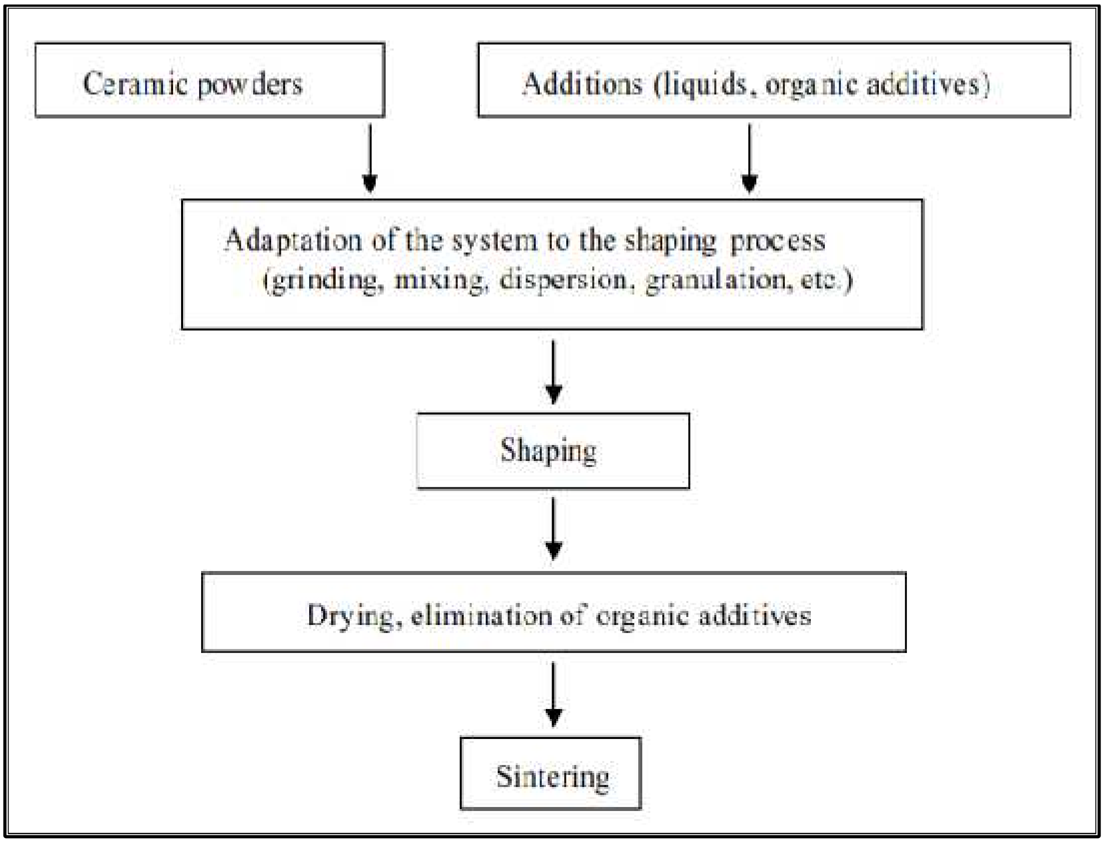

Fig (1): Flow chart of manufacturing of a ceramic piece.

1st. Ceramics Powders

Powders represent the starting form of ceramics for different types of ceramics manufacturing processes; a large variety of powders is available today in ceramic industry. Powders for traditional ceramics (clay, feldspar, kaolin, silica, talc, etc.) and powders for technical ceramics (alumina, zirconia, nitrides, carbides, titanates, etc.) exhibit very diverse chemical and physical characteristics, which must be controlled to manufacture the parts with the desired properties in a reproducible manner. Powder preparation is therefore an important stage in the shaping processes of ceramics.

The objective from this stage is to obtain powder which yields desired microstructure, generally dense and homogenous, during shaping process and ensures a satisfactory densification during sintering. In this context, size and size distribution of particles, their shape and state of agglomeration, their specific surface area, degree of purity and chemical nature of their surface exert a critical influence. Many methods are available for preparation of ceramic powders. These can be divided into just three basic types: Mechanical, Chemical and Vapor phase.

A. Mechanical Methods

Mechanical methods use coarse-grained materials that have generally derived from naturally occurring minerals. They are subjected to a series of processes, collectively referred to as **comminution**, in which particle size is gradually reduced. The final step is known as **milling**, which produces particles of the desired size. Mechanical methods of powder production are used widely in production of the traditional ceramic products where high purity powders are not required and cost is one of the most important requirements.

B. Chemical Methods

Such as sol-gel processing, offer several advantages over mechanical methods because they allow exceptional control over the particles morphology and the purity. Chemical processes are used widely in the production of advanced ceramic materials.

C. Vapor Phase Processes

These processes can be used to produce ceramic powders. They tend to be very expensive, but offer many advantages, such as ability to produce particles of non-oxides and also ceramics nanoparticles. For most processing methods, we want a small particle size. The small size helps form the product and allows higher density bodies at lower sintering temperatures.

Types of Powders

Powders can have a complex structure; to describe this structure it is necessary to follow a consistent terminology. The terminology we use follows that used in ceramic processing industry.

- **Primary particles** are the smallest clearly identifiable unit in the powder. The primary particles may be crystalline or amorphous and cannot easily be broken down into smaller units.
- **Agglomerates** are clusters of the bonded primary particles. Soft agglomerates are easily broken up; hard agglomerates, because of stronger interparticle bonds, are more difficult to break up. Hard agglomerates should be avoided in ceramic powder processing as much as possible.

- **Particles** is a general term applied to both the primary particles and agglomerates.
- **Granules** are large agglomerates, usually (0.1–1) mm in diameter that are formed by addition of a granulating agent (e.g., a polymer binder).
- **Flocs** are clusters of particles in a liquid suspension held together electrostatically.
- **Colloids** are very fine particles (they can be as small as (1) nm in diameter) held in fluid suspension.
- **Aggregates** are coarse constituents, (>1mm), in a mixture. The important example is the addition of gravel to the cement to make concrete.

Ceramics Powders Making

A. Mechanical Milling

For traditional raw materials like clay and oxides produced from ores, it is often necessary to eliminate the aggregates and to reduce particle size. Compound formation during sintering process require diffusion process between the neighboring particles. Diffusional processes are proportional to square of the particle size.

The most common method for reducing the particle size is ball milling. A ball mill is a barrel that rotates on its axis and is partially filled with a grinding medium (called media) in the form of spheres, cylinders, or rods. **Fig.2** shows a cross section of a ball mill. The media creating both shearing and crushing actions on powder. The media should have a high density (ρ) in order to provide the most effective collisions.

The choice of media is also based on cost, wear resistance, and the possibility of introducing contamination into powder. Depending on the amount of powder to be milled, size of the mill, and final particle size required, the media could range from more than 8 cm to 0.6 cm in diameter, which used for fine grinding. The powder is often milled in a liquid with a binder. Ball milling eliminates aggregates and can typically reduce particle size down to (1 μm). The minimum particle size possible by ball milling is (~0.1 μm).

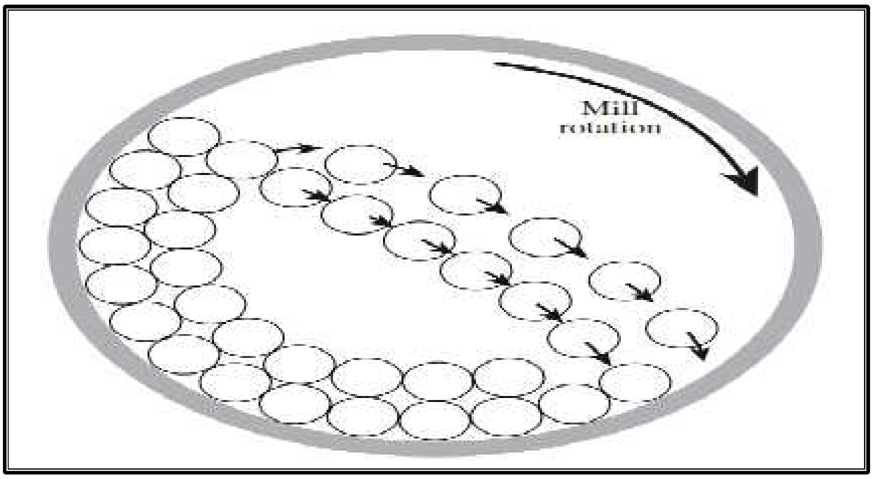

Fig (2): Cross section of a ball mill showing the movement of media as the mill rotates about its axis.

The advantages of ball milling are that the equipment is simple and Inexpensive. The disadvantages of ball milling are that it cannot produce ultrafine particles, can add impurities to powder from the media and the inside of the mill and it is inefficient due to loss of the energy. There are many other mechanical methods that can be used to achieve comminution.

Fluid-energy milling, also called the jet milling, achieves particle size reduction by particle–particle impact in a high-velocity fluid, usually either compressed air or superheated steam. The powder is added to fluid and injected into the grinding chamber at sonic or near sonic velocity, producing controlled particle size down to (**1 µm**) with a narrow size distribution.

In **Vibratory milling**, the drum containing the media and powder is vigorously shaken. The collisions between the media are much more violent than ball milling and this can shorten milling times.

Attrition milling, or agitated ball milling, differs from conventional ball milling in that the milling chamber does not rotate. Instead, a slurry containing the particles and media is stirred continuously at frequencies of (**1–10**) Hz. The grinding chamber is aligned either vertically or horizontally, with the stirrer located in the center of the chamber. The media consists of small spheres of (**0.2–5 mm**), which provide rapid milling time with more energy efficient than other methods and helps reduce contamination.

B. Spray Drying

Spray drying is an example of powder production from solution. It is widely used for preparing electrical ceramics. In this technique, an atomizer in the form of spray rotary disk used to disperse the liquid or slurry into a controlled drop size spray with broad particle size distribution. The fine droplets that produced by an atomizer are sprayed into a drying chamber and the powder is collected. Droplet sizes in range of 10 µm to over 100 µm can be produced. In drying chamber, the flow pattern of the hot air determines the completeness of moisture removal and the maximum temperature that the particles experience. Finally, the particles are carried out of the chamber in the air stream and captured in a bag or another form of collector as shown in **fig.3**.

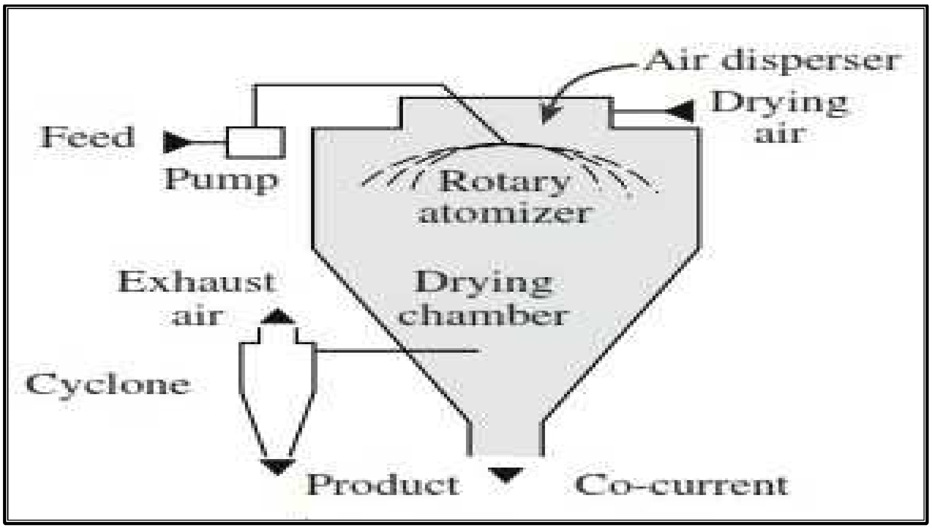

Fig (3): Spray drying scheme.

C. Sol-Gel Processing

The term "Sol" refer to colloidal particles or molecules are suspended in a liquid or solution and "gel" refer to the sol when mixed with another liquid, which causes the formation of a continuous three-dimensional network. Sol-gel processing is the most important topics in this field because, although expensive, it can produce the powders with high surface area, which allows sintering to nearly full density of particles at much lower temperatures compared with the other techniques. In addition, the process gives us excellent control of product purity, homogeneity and the composition.

In most sol-gel processes, the reactants are solutions of metal alkoxy compounds. Alkoxides result from reaction of the metals (M) with alcohols. The general reaction is[[$nROH+M \rightarrow M(OR)_n+(n/2)H_2$]], where (R) is an organic group. In some cases, nonmetal such as (Si) is also used. There are several advantages to using metal alkoxides as precursors for ceramic powders.

Most of alkoxides can be easily prepared, commercially available and can be readily purified prior to use. Also interaction of the alkoxides with the water yields the precipitates of particles. Precipitate particles usually range in size from (0.01 to 1 μm); depending on hydrolysis conditions, we can easily produce nanoparticles. This method has been successful in preparing a range of advanced ceramics.

This technique used for forming powders, fibers and also allows us to deposit films and coatings on a range of different surfaces. Sol-gel process consists of two steps, first we form a sol and then we transform this into a gel. In ceramic synthesis, two different sol-gel routes have been identified and depend on the gel structure.

- **Particulate gel**—using a network of colloidal particles.
- **Polymeric gel**—using an array of polymeric chains.

The process that occurs depends on the form of the sol, i.e., whether it is a solution or a suspension of fine particles. A flow diagram indicating each of the processes shown in Fig.4.

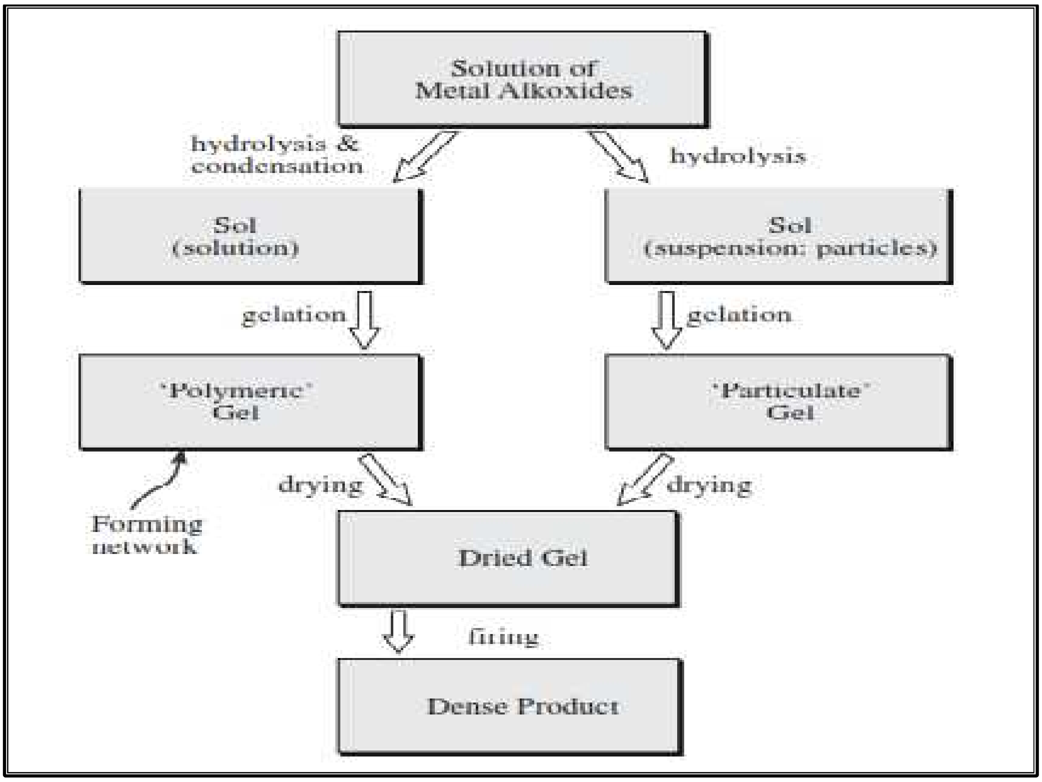

Fig (4): Flow chart comparing sol-gel processing using a solution and a suspension of fine particles.

Sol-Gel Mechanism using Metal Alkoxides

The three basic steps in sol-gel process are summarized in **fig.5**. The conversion of the sol to a gel occurs by hydrolysis and condensation reactions. The gel is converted into oxide by drying and firing. We will now look at each of these steps in a little more detail.

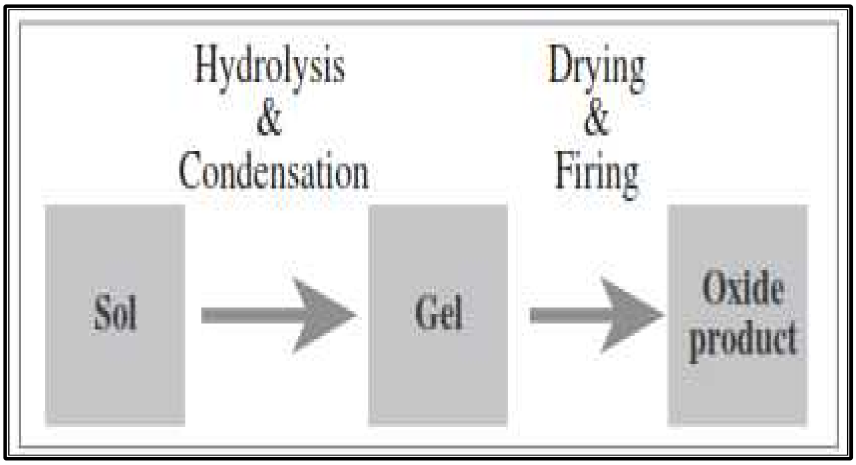

Fig (5): Basic steps in sol-gel process using metal alkoxides.

1. Sol formation by Hydrolysis and Condensation

Metal alkoxides undergo hydrolysis process very easily when react with water. In some cases, such as silicon alkoxides, is insoluble in water, but water is necessary for the hydrolysis reaction; hence we need to select a solvent for both the alkoxide and water. Ethanol is a suitable solvent for both components in this case. During initial stage of hydrolysis, an alcohol molecule, (ROH), is expelled.

$$\boxed{M(OR)_z + H_2O \rightarrow M(OH)(OR)_{z-1} + ROH}$$

This is an example of a condensation reaction involving elimination of an alcohol. The second stage involving the condensation process in which the (hydroxy metal alkoxide) product can react by a further condensation reaction to form polymerizable species. **See fig.6**.

$$M(OH)(OR)_{z-1} + M(OR)_z \rightarrow (RO)_{z-1}MOM(OR)_{z-1} + ROH$$

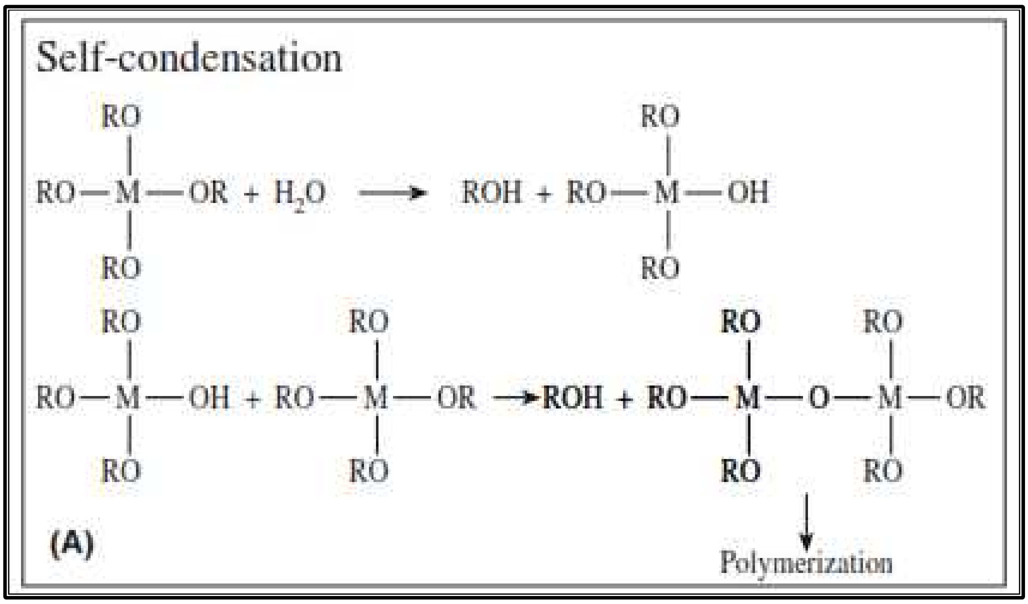

Fig (6): Condensation reactions in sol-gel technique.

As a result, hydrolysis and polycondensation reactions lead to form a colloid. The term colloid is used primarily to describe a broad range of solid-liquid mixtures, all of which contain distinct solid particles which are dispersed to various degrees in a liquid medium.

2. Sol-Gel Transition

Viscosity is a key parameter that is used to determine when sol-gel transition occurs. At the transition, there is an abrupt increase in the viscosity, so that at the end of the hydrolysis and polycondensation reactions, the sol evolves gradually towards the formation of a gel like polymer network chains containing both a liquid phase and a solid phase. **See fig.7**.

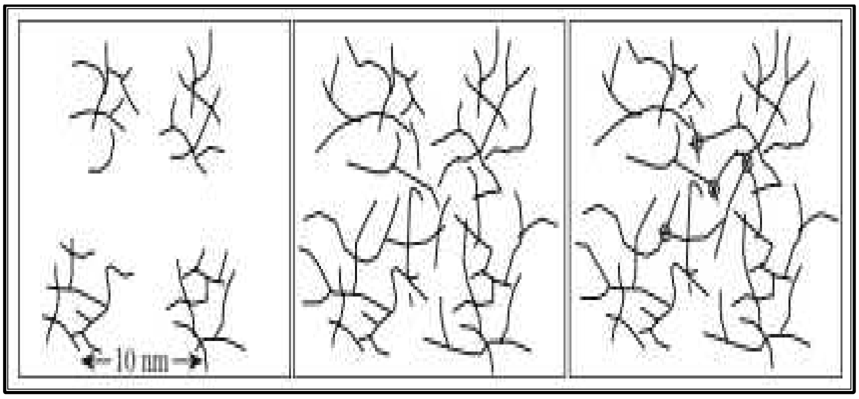

Fig (7): Structural changes that occur during gelation stage.

3. Drying and Firing

Removal of remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which solvent can be removed is ultimately determined by distribution of the porosity in the gel. Shrinkage during this step is usually large, and in some cases leading to cracking problems especially at high drying rates. There are several different methods used to dry gels and increase the drying rates without cracking. Each method produces a dried gel with a specific microstructure. In most cases, we obtain either an aerogel or a xerogel structure.

Afterwards, a thermal treatment, or firing process, is often necessary in order to precipitate fine and dense ceramic powders with enhanced mechanical properties and structural stability. The distinct advantage of using this approach as opposed to traditional techniques is that densification is often achieved at a much lower temperature. **Fig.8.** shows the stages of sol-gel process.

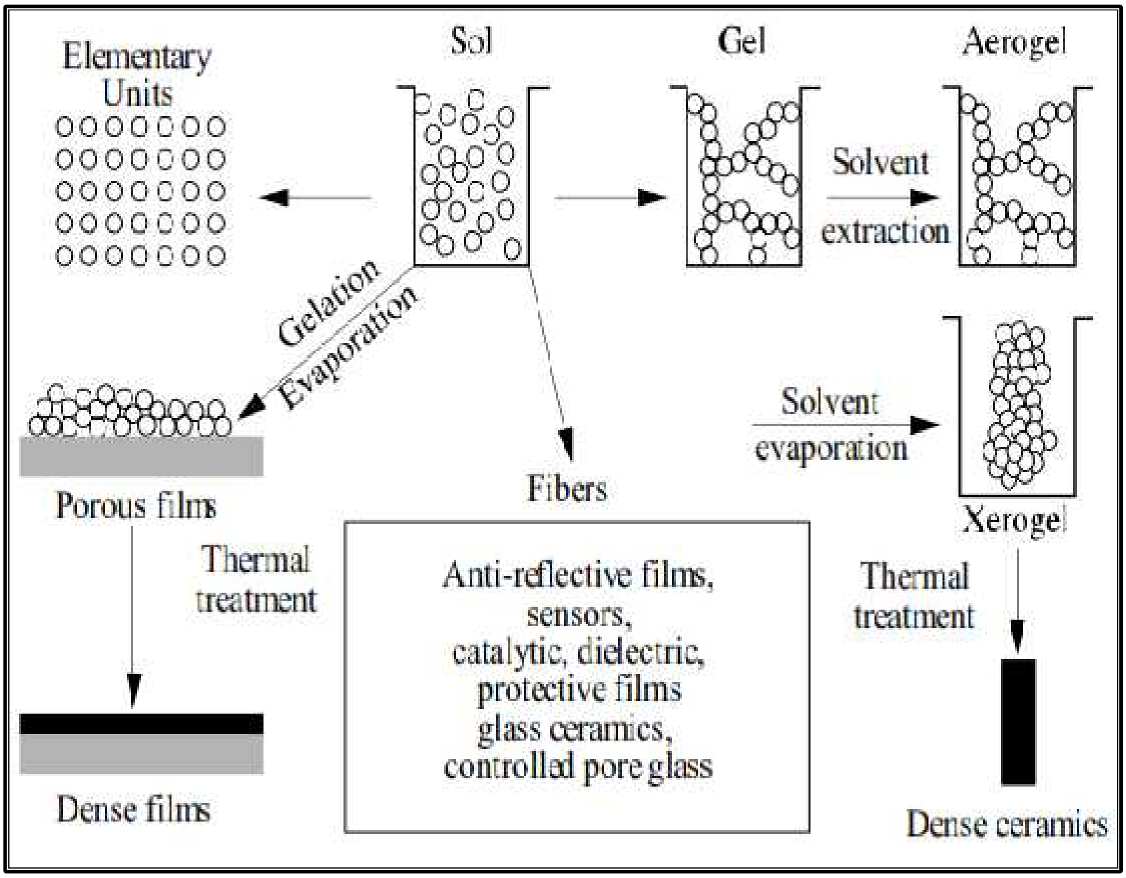

Fig (8): Stages of sol-gel process.

D. Vapor-Phase Reactions

Vapor phase processes are relatively expensive, but there are several good reasons for using them to prepare powders, particularly when we want:

- High purity.
- Discrete and non-aggregated particles.
- Nanoparticles with narrow size distributions.
- Versatility in producing powders of oxides and non-oxides.

Fig.9 illustrates a gas-condensation chamber developed specifically for this purpose. Material is evaporated from two sources and condenses in the gas phase. The condensate is transported by the convection to liquid nitrogen cold finger. The clusters are scraped from cold finger and collected via a funnel. With this technique, TiO_2 powders with an average particle size of (10–15) nm have been produced.

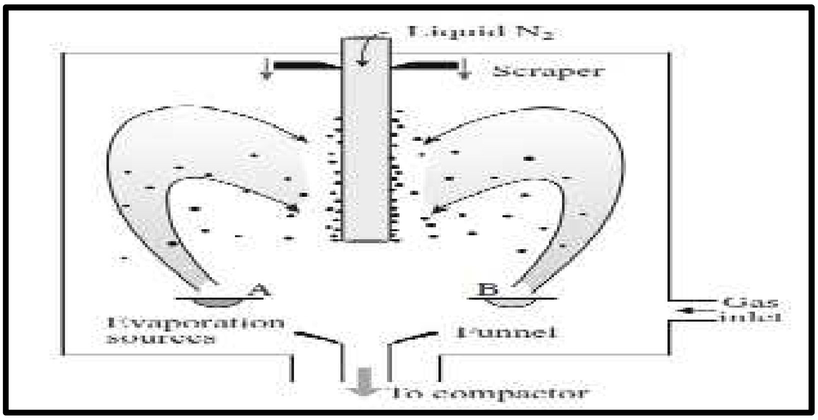

Fig (9): Gas-condensation chamber.

Determining Particle Composition and Purity

In addition to knowing particle size and particle size distribution of powder we often need to know its composition and purity. Many industries use wet chemical techniques such as precipitation and titration for such analysis. These techniques are used because they are often simple to perform and give a quick result. In addition to using wet chemistry there are numerous analytical methods that can give us chemical composition and impurity levels and these are summarized below.

- X-ray fluorescence (XRF) would not be a good choice to determine the amount of low-Z elements present.
- Flame emission spectroscopy (FES) is a good choice if we have very small amounts of the alkali metals.
- Nuclear magnetic resonance (NMR) can be used to determine H concentrations, but it is often expensive to use and not as widespread as atomic absorption spectroscopy (AAS).
- X-ray diffraction (XRD) for phase determination and phase proportions in a powder mixture.
- TEM for chemical analysis with atomic resolution.

The choice of technique depends on several factors:

- Type of material.
- Amount of material (milligrams or kilograms).
- Possible impurities (alkali metals, H, rare earths).
- Amount of impurities (ppm or percent).
- Availability and cost of instrument.

Determining Particle Size Distribution

Sieving is the oldest method to determine particle size distribution of powder. Actually, sieving is used for sorting particles according to size rather than measuring their size. Typically, sieves with decreasing mesh size are stacked with the largest mesh at the top. The term "mesh size" denotes the number of openings per linear inch in the sieve screen.

Sieving is not applicable to the smallest particle sizes (<5 μm), which are often used in the fabrication of the components from advanced ceramics. However, sieving is used in traditional ceramics industry for powders with particle size >56 μm. The particle size distribution obtained by sieving is normally only approximate because it is often too time consuming to sieve for long enough periods to achieve the final distribution of particles in the various sieves.

Characterizing Powders by Light Scattering

When a beam of light strikes a particle, some of it is transmitted, some is absorbed, and some is scattered. When the particles are larger than the wavelength of the incident light they cause the diffraction. The intensity of the scattered light is proportional to d^2, and **fig 10.** shows examples of the light scattered from two particles of different sizes.

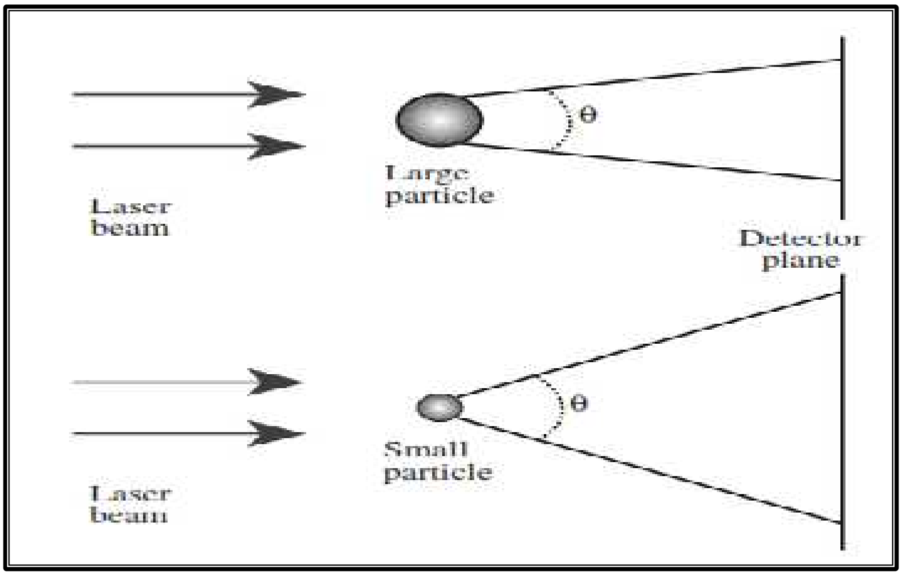

Fig (10): Scattering of light by large and small particles.

- Smaller particles scatter a small amount of light through a large angle.
- Large particles scatter a greater amount of light but through a smaller angle.

The relationship between the scattering angle (θ) and the particle size is $\sin\theta = 1.22\lambda/d$. The light source is usually an (He–Ne) laser with $\lambda = 0.63\ \mu m$. For this wavelength, the reliable particle size range is (2–100) µm. The light-scattering methods have the following advantages:

- Accuracy.
- Speed.
- Small sample size.
- Can be automated.

Specific Surface Area of Powders

Specific surface area (SSA) is a property of solids that defined as the total surface area of a material per unit of weight (m^2/kg), it depend on size, shape, density and surface condition of particles. Surface area are measured by adsorption of gases onto a particle surface at low temperature. The mass of the gas adsorbed is measured as a function of gas pressure at a fixed temperature.

Ceramic Fibers and Whisker

Ceramic fibers and whiskers are used in fabrication of composites where they are dispersed within a matrix, which may be a ceramic, a polymer, or a metal. The choice of matrix depends on proposed applications for composite. A primary consideration is the desired operating temperature. Polymers are stable up to a temperature of 300°C, metals up to 900°C, and ceramics are usable at temperature >1800°C. Ceramics can be used as the reinforcement phase in all types of matrix. The major requirements are that they are strong and stiff.

Whiskers are small single crystals a few tens of micrometers in length with a diameter typically <1 μm. Whiskers have extremely high strengths, approaching the theoretical strength, because of the absence of crystalline imperfections such as the dislocations. SiC whiskers are the strongest materials known that are produced in commercial volumes.

The common process for obtaining SiC whiskers by pyrolyzing rice hulls which is a waste byproduct of rice milling. The rice hulls are heated in an oxygen free atmosphere at 700°C and the volatile constituents are driven off. The coked rice hulls, containing about equal amounts of SiO_2 and free carbon, are further heated in an inert or reducing atmosphere (flowing N_2 gas) between 1500 and 1600°C for about 1 hour to form SiC:

$$\boxed{3C + SiO_2 \rightarrow SiC + 2CO}$$

About 10% of the product is in the form of whiskers and the remaining product is in form of particles, generally platelets. The whiskers may be separated to give a (90–95%) “pure” product. SiC whiskers are used in a number of different applications. Alumina reinforced with (25–30 wt%) SiC whiskers is the material of choice for inserts used in high-speed cutting of nickel-based super alloys (for aerospace applications).

Oxide fibers have been commercially available since 1970s. Control of microstructure through careful processing is essential to obtain the desired properties, which for ceramic fibers for structural applications are:

- Low porosity.
- Small grain size (for low-temperature applications).
- Large grain size (for high-temperature applications where creep is a concern).
- High purity.

Ceramic fibers cannot usually be produced by techniques used to produce glass fibers because of the very high melting temperatures (often >2000°C) and the low viscosities when molten. There are four general methods to produce ceramic fibers:

- From slurry. (e.g., Alumina fibers from slurry)
- By sol-gel processing. (e.g., Zirconia fibers by Sol-Gel process)

- By chemical vapor deposition. (e.g., Silicon carbide fibers)
- From polymer precursors.

Alumina Fibers from Slurry

In this technique, alumina fibers are produced by three steps:

- **Slurry formation,** the slurry is an aqueous solution containing aluminum oxychloride [$Al_2(OH)_5Cl$] together with additions to stabilize the suspension (deflocculents) and polymers to modify the viscosity. The viscosity must be adjusted such that the slurry is spinnable.

- **Spinning,** The slurry is extruded through aspinnerette into "green" fibers and dried.

- **Firing,** the "green" fibers are fired initially at low temperatures to drive off the organic additive and convert the aluminum oxychloride to oxide. It is during this stage that shrinkage of the fiber is controlled. Firing at higher temperature causes sintering that result in solid fibers with a controlled amount of porosity and grain size. The resulting fiber is 99% α-Al_2O_3, 98% theoretical density, with a diameter of 10–20 μm and a grain size of ~0.5 μm.

Silicon Carbide Fibers by Chemical Vapor Deposition

Chemical vapor deposition often involves decomposition of a volatile gas to produce a nonvolatile solid. The reaction usually proceeds at high temperature and the solid is deposited onto some form of substrate. In the case of fiber formation, the substrate is a wire and (SiC) can formed by decomposing methyltrichlorosilane (CH_3SiCl_3):

$$\boxed{CH_3SiCl_3\ (\text{gas}) \rightarrow SiC\ (\text{solid}) + 3HCl\ (\text{gas})}$$

The substrate or core in this case is a 10-μm-diameter tungsten wire. The deposit consists of fine crystals of β-SiC have diameters in the range of 100–150 μm.