Ceramics Manufacturing Processes

4th. Sintering Processes

Sintering is the process of transforming a powder into a solid body by using heat application. The idea of sintering is to join particles together without melting them. Hence, sintering is a heat treatment applied to the powder compact in order to impart the strength and integrity. The temperature used for sintering is below the melting point of the major constituent of the powder.

Sintering can occur in the presence or absence of a liquid phase. In former case, it is called liquid-phase sintering, where compositions and firing temperatures are chosen such that some liquid is formed during the processing, (a liquid may form if a component that has a low melting temperature is present) as shown schematically in the (fig.1a). In absence of a liquid phase, the process is referred to as the solid-state sintering (fig.1b).

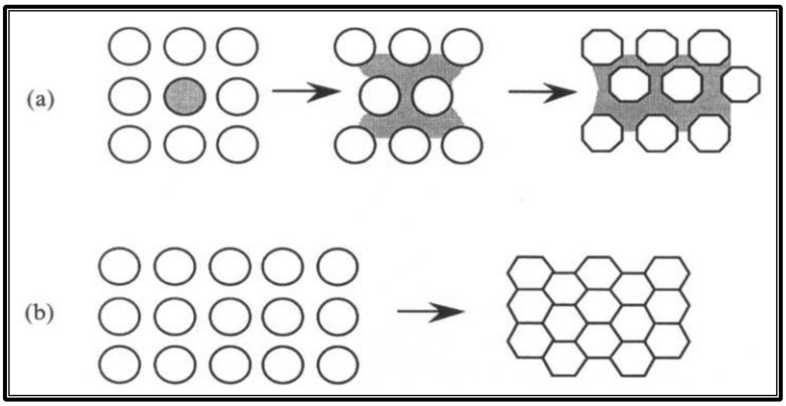

Fig (1): (a) Liquid-phase sintering; (b) Solid-state sintering.

Sintering is effective when the process reduces the porosity and enhances the properties. During the sintering procedure, the atoms in the materials diffuse across the boundaries of particles, fusing the particles together and creating one solid piece, starting from the formation of the necks between powders to final elimination of small pores at the end of the process as shown in fig.2.

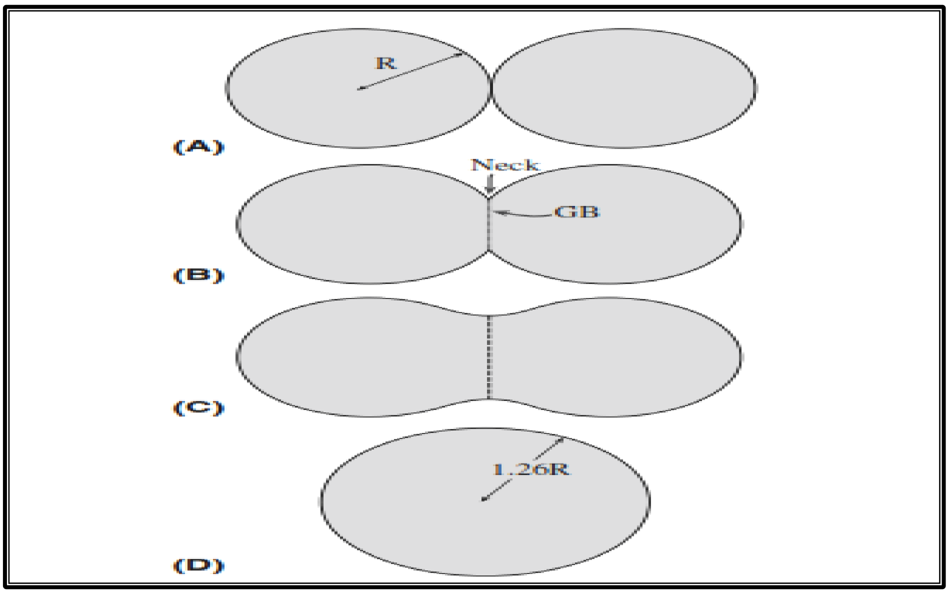

Fig (2): Coalescence of two spheres (A–D).

Densification and Grain Growth

Sintering in practice is the control of both the densification and the grain growth of particles. Densification is the act of reducing the porosity in a sample thereby making it denser. Grain growth is the process of grain boundary motion to increase the average grain size. Many of properties enhanced from both a high relative density and a small grain size for the final product.

Therefore, being able to control these properties during processing is of high technical importance. Since the densification of powders requires high temperatures, grain growth naturally occurs during sintering process. Reduction of this process is the main key for many engineering ceramics materials. In fact, the term of sintering process includes four phenomena, which take place simultaneously and often compete with each other:

- Consolidation: development of necks that "weld" the particles to one another.
- Densification: reduction of porosity.
- Grain coarsening: coarsening of particles and grains.
- Physicochemical reactions: in the powder, then in material under consolidation.

Sintering Mechanism

Sintering is possible only if the atoms can diffuse to form the necks that weld the particles with one another. The transport of matter can occur in vapor phase, in a liquid, by the diffusion in a crystal. Most mechanisms are activated thermally due to the action of the temperature is necessary to overcome the potential barrier between the initial state of compacted powder and final state of consolidated material. Atomic diffusion in the ceramics is sufficiently rapid only at temperatures in the range of (0.7-0.9 T_m). There are six common mechanisms for sintering process; all of them depend on the manner in which the matter is transported as shown in fig.3, and these mechanisms classified as:

- Surface diffusion – Diffusion of atoms along the surface of a particle.
- Vapor transport – Evaporation of the atoms, which condense on a different surface.
- Lattice diffusion from surface – atoms from surface diffuse through lattice.
- Lattice diffusion from grain boundary – atom from grain boundary diffuses through lattice.
- Grain boundary diffusion – atoms diffuse along grain boundary.
- Plastic deformation – dislocation motion causes flow of matter.

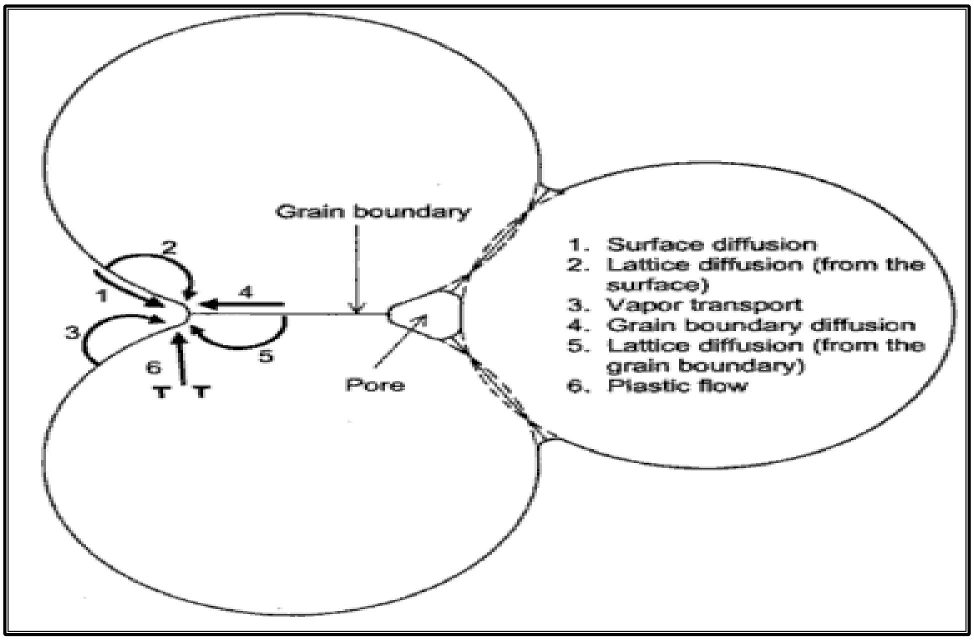

Fig (3): Sintering mechanisms.

Types of Sintering Processes

1. Solid State Sintering

Normal solid state sintering is cost-effective and simple, which is of the great attraction for the mass production. In this method, only solid phases are present at sintering temperature and it include three stages. During initial stage, the interparticle contact area increases by neck growth (fig.4b) and the relative density increases from about (60 to 65%). The intermediate stage is characterized by continuous pore channels that are coincident with the three-grain edges as seen in (fig.4c). During this stage, relative density increases from 65 to about 90 percent by having matter diffusion. The final stage begins when pore phase is finally pinched off and is characterized by the absence of a continuous pore channel (fig.4d).

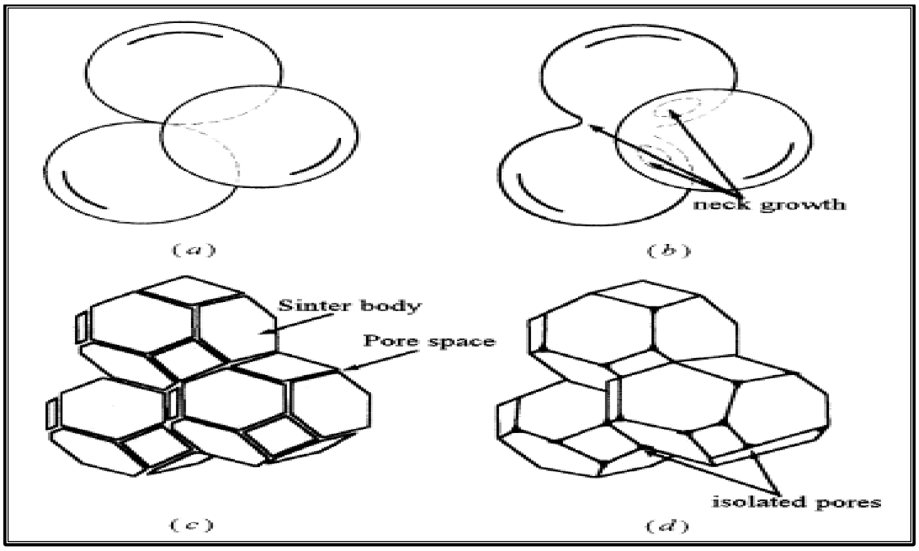

Fig (4): Stages of solid state sintering.

2. Liquid Phase Sintering

For materials that are difficult to sinter, a process called liquid phase sintering is commonly used where small amounts of liquid phase are present during sintering process. Materials for liquid phase sintering is common are Si_3N_4, WC, SiC, and more. Liquid phase sintering is the process of adding an additive to powder which will melt before the matrix phase. The process of liquid phase sintering has three stages:

- Rearrangement: As the liquid melts, capillary action will pull the liquid into pores and cause the grains to rearrange into a more favorable packing arrangement.
- Solution-Precipitation: The solubility of solid in the liquid increases at the inter-particle points of the contact. The transfer of the matter followed by the precipitation in the low energy areas results in the densification.
- Final Densification: Densification of solid skeletal network, liquid movement from efficiently packed regions into pores.

3. Reactive Sintering

In this method, particles react with each other to form new product phases. The reaction is normally exothermic and can contribute to an enhancement of sintering process. In some cases, the reaction is so exothermic that it can generate the sufficient heat to cause self-sintering without external heating except that required for initiating the reaction. In reactive sintering, atmospheric conditions of process play a critical role in enhancing the structure and produce a relatively dense compact. For example, the silicon nitride is produced by heating silicon powder in a nitrogen atmosphere; the gas has to penetrate to center of compressed silicon: ($3Si + 2N_2 \longrightarrow Si_3N_4$).

4. Microwave Sintering

Microwave sintering of materials is a technology that useful in a number of applications, presenting some important advantages over conventional heating methods. In microwave sintering, the heat is generated internally within the material, rather than via heat transfer from an external heat source. Other benefits of microwave sintering are a better heat diffusion, less time needed to reach the sintering temperature, less heating energy required and improvements in the product properties.

In microwave sintering, heat is generated internally through the interaction of the microwaves with atoms, ions, and molecules of the material when absorbed the microwave energy. In contrast to all the other techniques commonly used, the microwaves sintering allow for volumetric heating of the materials in which the microwave energy transforms into heat inside the material, which generally result in significant energy savings and shorter processing times.

5. Spark Plasma Sintering

In spark plasma sintering (SPS), external pressure and an electric field are applied simultaneously to enhance the densification of ceramic powder. This densification uses lower temperatures and shorter amount of the time (takes only a few minutes to complete the sintering process) compared to conventional sintering. Also high sintering rate is possible in SPS due to high heating rates can be easily attained due to internal heating of the sample as opposed to external heating in case of conventional sintering. Show fig.5.

High (DC) Pulse is passed between graphite electrodes and axial pressure is simultaneously applied. The sparking among the particles of the sintered material leads to faster heat and mass transfer instantaneously. After sintering, the power is turned off and sample is allowed to cool.

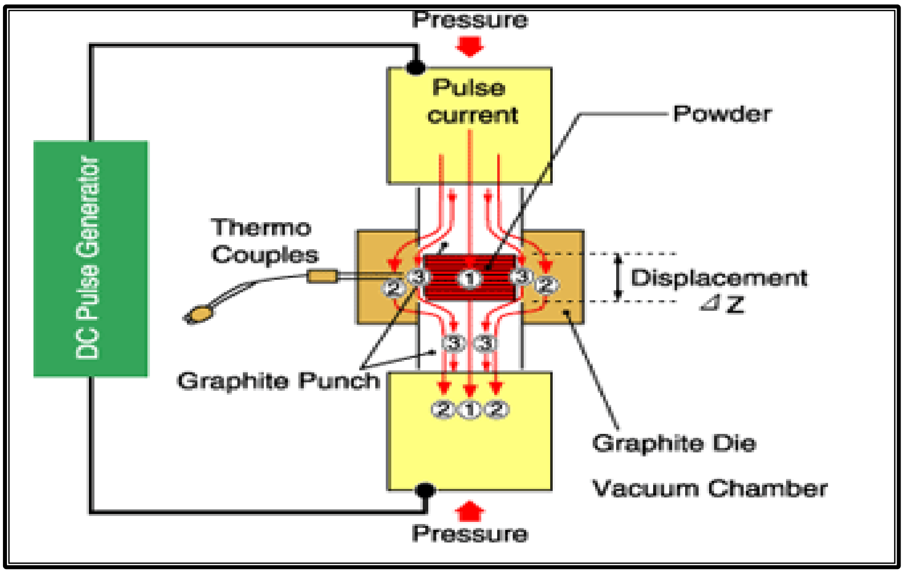

Fig (5): Schematic of spark plasma sintering.

6. Pressure Sintering

Like hot pressing and hot isostatic pressing, in which pressure and temperature are applied simultaneously to enhance the densification of the final product as mentioned earlier.

Driving Force for Sintering

As with all processes, sintering is accompanied by an increase in the free energy of the system. The sources that give rise to the amount of the free energy are commonly referred to as the driving forces for the sintering. The main possible driving forces are:

- The curvature of the particle surfaces.
- An externally applied pressure.
- A chemical reaction.

Sintering Additives

The spectacular effect of the addition of a few hundred ppm of the magnesia on the sintering behavior of alumina is the best example of the role of sintering additives. These additives help to control the microstructure and enhanced the properties of the sintered materials; they can be classified into two categories:

A. Additives that react with the basic compound to give a liquid phase, for example, magnesia (MgO) reacts with (SiO_2) to form the enstatite $MgSiO_3$ that have a liquid phase at about 1550°C. The liquid film wets the grain and enhanced the densification of the sintered powders.

B. Additives that do not lead to the formation of a liquid phase and which consequently enable the sintering to take place in solid phase by increasing the values of the diffusion coefficient and the mobility of grain boundaries. This is the case of doping of Al_2O_3 with a few hundred ppm of MgO.

Important parameters in sintering

There are several parameters influence on the final properties of ceramics; these parameters can be mainly divided into four broad categories:

A. Powder Preparation

- Particle size.
- Shape.
- Particle size distribution.

B. Distribution

- Second phases.

C. Powder Consolidation

- Green density.
- Pore size distribution.
- Processing.

D. Firing/Sintering

- Heating rate.
- Temperature.
- Time.
- Applied pressure.
- Atmosphere.