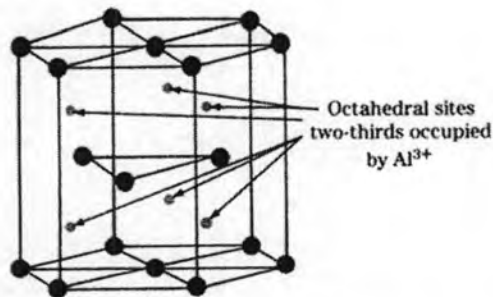


## CHAPTER II

### FUNDAMENTAL AND LITERATURE REVIEW

#### 2.1 Transparent polycrystalline alumina ceramic

Aluminium oxide is a chemical compound of aluminium and oxygen with a chemical formula of  $\text{Al}_2\text{O}_3$ . Aluminium oxide is an excellent thermal and electrical insulator. In its crystalline form, called corundum, its hardness makes it suitable for application as an abrasive and as a component in cutting tools. Alumina was originally developed for refractory tubing and high purity crucibles for high-purity crucibles for high temperature and widely used as substrate for electronic-device applications because of its low dielectric loss and smooth surface.

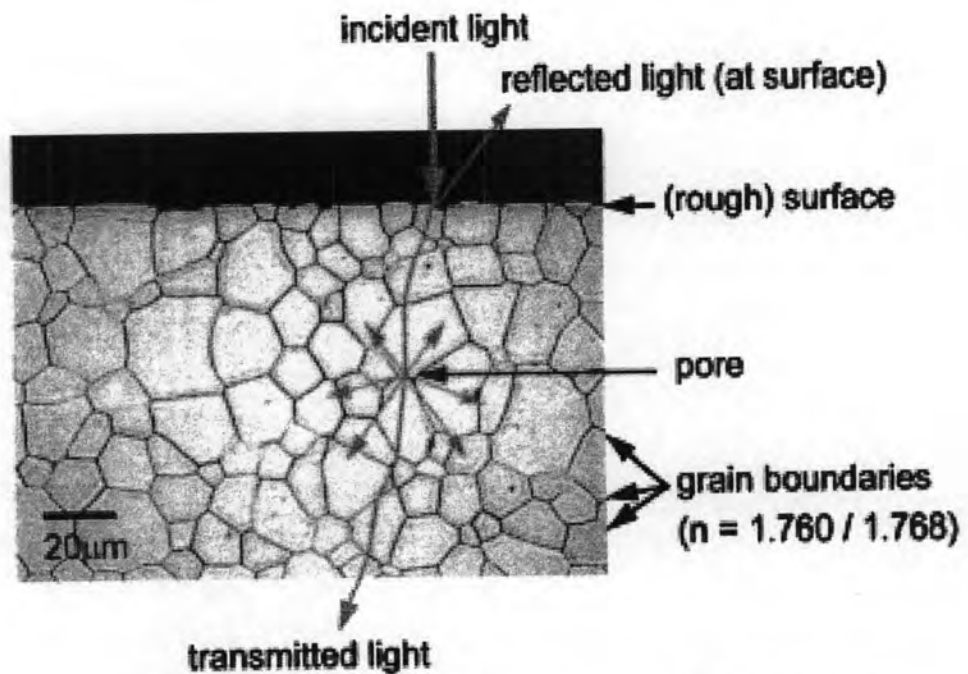


**Figure 2.1** Corundum ( $\text{Al}_2\text{O}_3$ ) crystal structure

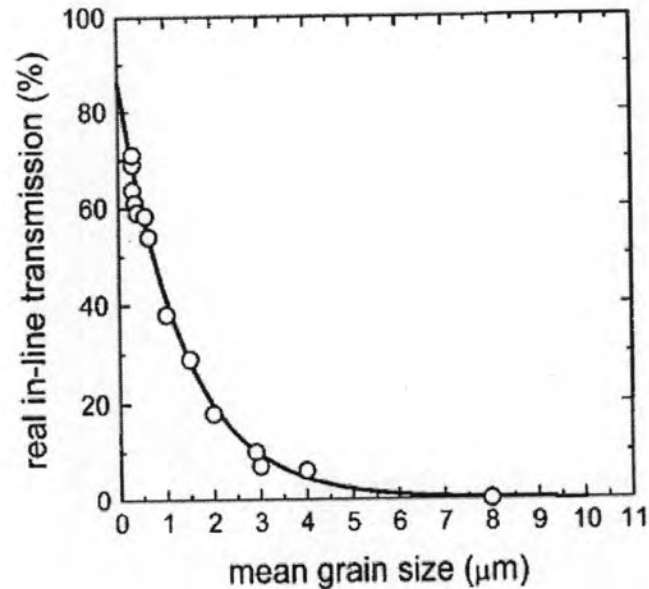
**Table 2.1** The physical properties of aluminium oxide

Properties	Value
Density and phase	3.97 g/cm <sup>3</sup> , solid
Solubility in water	Insoluble.
Melting point	2054°C
Boiling point	~3000°C
Thermal Conductivity	18 W/m·K

Apetz and Bruggen (2003) proposed a light-scattering model of transparent alumina. The light-scattering mechanism is illustrated in Figure 2.2. The reasons for translucent of conventional PCA were the scattering of light at rough surface which can be avoided by polishing the surface, at second-phase inclusions of impurity in PCA. Moreover, the scattering at grain boundaries and at pores of PCA should be avoided by controlling the sintered grain size below a micron order and providing the high density body, respectively. They were proposed the submicron grain size conformed to the increasing real in-line transmission exhibited in Figure 2.3.



**Figure 2.2** The light scattering mechanism in polycrystalline alumina



**Figure 2.3** The real in-line transmission at 645 nm as a function of the mean grain size with sample thickness of 0.8 mm by (O) as experimental data points and (-) as theoretical curve (refractive index difference is 0.005)

## 2.2 Preparation of complicated specimens by slip casting

### 2.2.1 Slip casting process

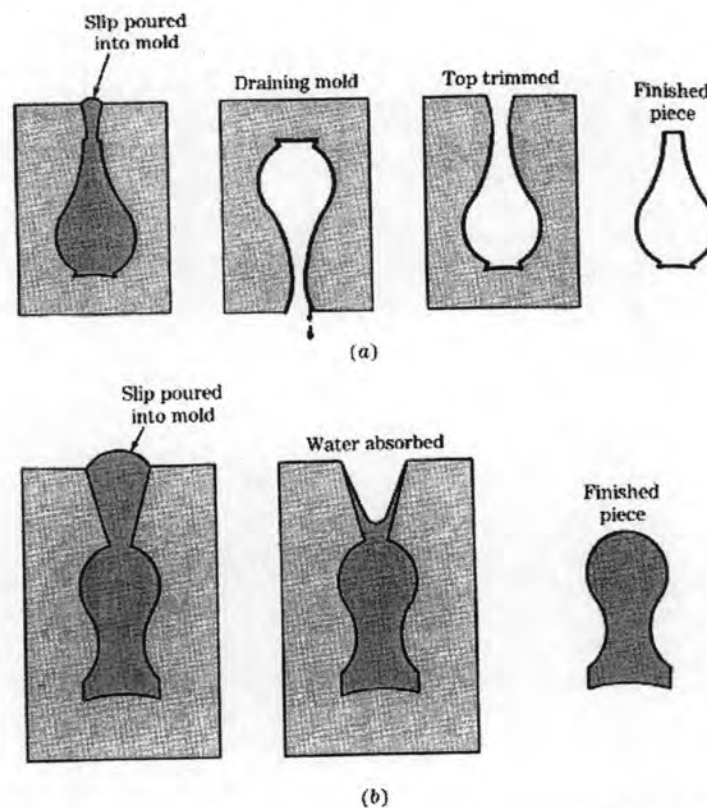
The basic steps in the processing of ceramics by the agglomeration of particle are (1) material preparation, (2) forming or casting, and (3) thermal treatment by drying and firing by heating the ceramic shape to a high-enough temperature to bond the particles together.

#### 1. Material preparation:

Ceramic particles and other ingredients such as binder and lubricants may be blended wet or dry. The blending of the ingredients with water is common used in practice.

## 2. Forming:

Ceramic shapes can be cast by using a unique process called slip casting, as shown in Figure 2.4. The main steps in slip casting are preparation of a powdered ceramic material and a liquid into a stable suspension called a slip. Second, pouring the slip into a porous mold which is usually made of plaster of paris. As the liquid is removed from the slip, a layer of semihard material is formed against the mold surface. When a sufficient wall thickness has been formed, the casting process is interrupted and the excess slip is poured out of the cavity. This is known as drain casting (in Figure 2.4 (a)). Alternatively, a solid shape may be made by allowing the casting to continue until the whole mold cavity is filled, as Figure 2.4 (b). This type of slip casting is called solid casting. Finally, the material in the mold is allowed to dry to provide adequate strength for handling and the subsequent removal of the part from the mold.



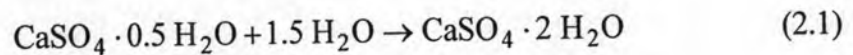
**Figure 2.4** Slip casting of ceramic shapes: (a) drain casting (b) solid casting

### 3. Thermal treatments:

Thermal treatment is essential step in the manufacturing of most ceramic products. In this subsection we shall consider the following thermal treatments as drying and sintering. The purpose of drying ceramics is to remove water and additives from the plastic ceramic body before it is fired at higher temperatures in the next step. The mechanical property of ceramic is enhanced in the sintering step.

Generally, slip casting is advantageous for forming thin-walled and complex shapes of uniform thickness. Slip casting is especially economical for development parts and short production runs. Several new variations of the slip-casting process are pressure and vacuum casting in which the slip is shaped under pressure or vacuum.

By the way, the most commonly used porous mold material for slip casting is gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) formed from the reaction between plaster of Paris ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) and water:



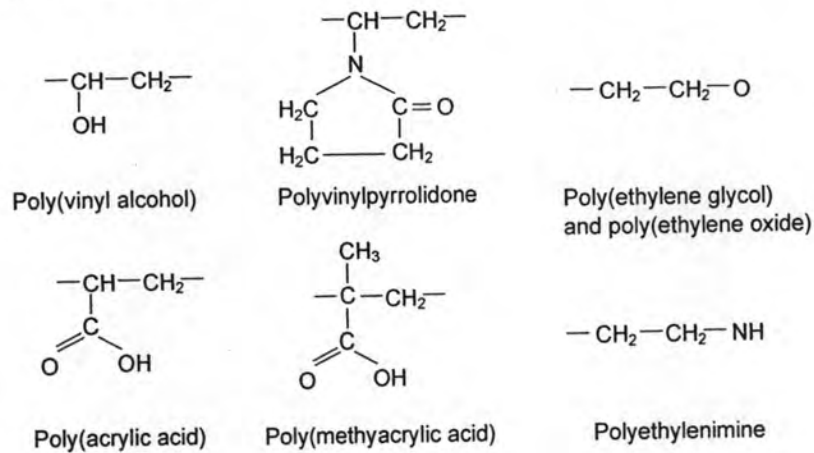
This technology is used because of the ability to fabricate molds with good surface smoothness and detail, high ultimate porosity and micron-size pores, the short setting time, the small dimensional expansion (about 0.17%) on setting with aid release from models and its relative low cost.

#### 2.2.2 Additives for slip casting

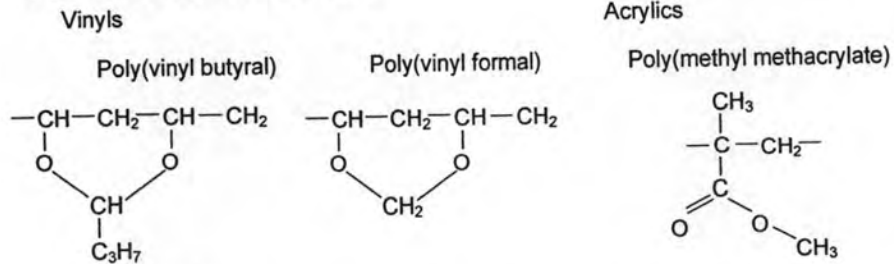
There are two kinds of additives for slip casting that is dispersant and binder. Dispersant, also referred to as deflocculant, is normally used to stabilize slurry against flocculation by increasing the repulsion between particles. While normally used in very small concentrations, the dispersant play a key role in maximizing the particle concentration for some usable viscosity of the slurry.

Meanwhile, binder is to improve strength of as-formed product (green strength) before being densified by firing that is an important function of binder. A large number of organic substances can be utilized as binders, some of which are soluble in water, while others are soluble in organic liquids. The monomer formulas of some common synthetic binders are shown in Figure 2.5.

### Soluble in water



### Soluble in organic solvents



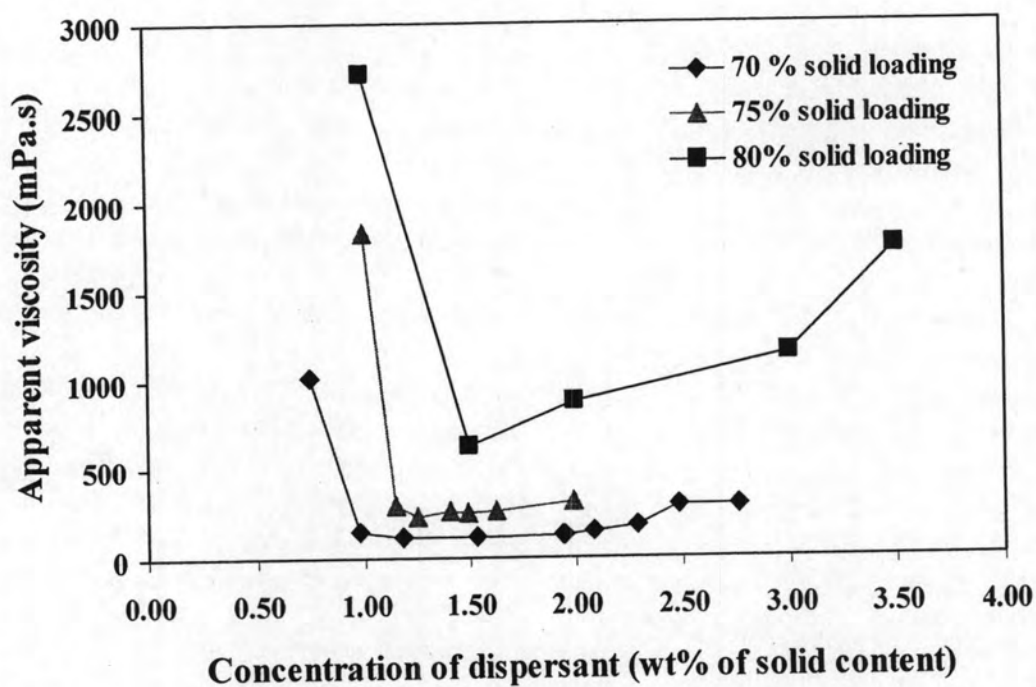
**Figure 2.5** Monomer formulas of some synthetic binder

The selection a binder for a given forming process involves the consideration of several factors, for example molecular weight, compatibility with dispersant, effect on the viscosity of the solvent and solubility in the solvent.

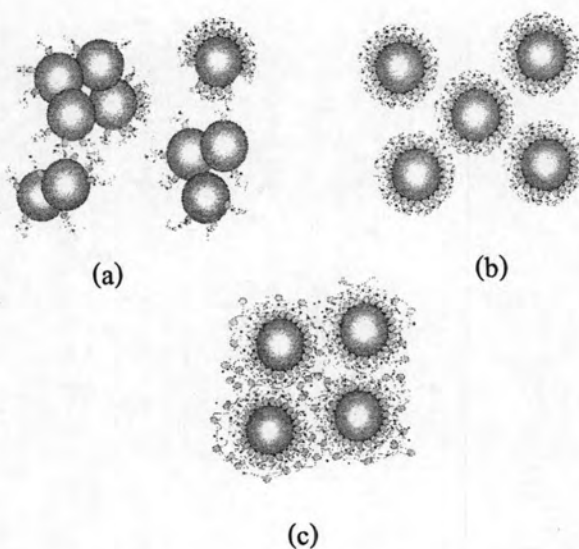
Many researchers have been interested in study the rheology of dispersant and binder on suspension that is usefulness in the preparation alumina suspension for slip casting. These researches are shown below:

Tsetsekou, Agrafiotis and Miliias (2001) investigated preparing conditions for stable alumina slurries with high solid content for the production of slip-casted objects. Three commercial dispersant, Darvan C, Dolapix CE64 and Duramax D3005 were compared. It was found that all three dispersants were capable of achieving stabilization of high solid content slurries, but they showed differences with respect to the optimum concentration and the concentration range required for the achievement of minimum slurry viscosity. The slurries with optimized rheological properties were utilized for the preparation of slip-cast specimens. An increase in the slurry solids content could provide green body and sintered body with high density, but the shrinkage after sintering became more suppressed result in specimens with better mechanical properties.

Sakkapas Areeraksakul (2005) successfully researched the effect of ammonium salt of poly(methacrylic) acid ( $\text{NH}_4^+$ -PMAA) dispersant concentration to apparent viscosity of 70, 75 and 80 wt% alumina loading slurry. It was found that the optimum content to provide well-dispersed slurries for slip casting were 1.18%, 1.25% and 1.5% of dispersant content, respectively as illustrated in Figure 2.6. It was concluded that this phenomenon was reasonably attributed to the fact that when the amount of dispersant added to the alumina suspension was low, insignificant repulsive force acting among each suspended particle could not hinder the agglomeration of fine alumina particles as illustrated in Figure 2.7 (a). At the optimal addition of dispersant content, sufficient amount of dispersant molecules would attach to the surface of suspended alumina particles, resulting in a balance of repulsive and attractive forces acting on suspended particles (Figure 2.7 (b)). However, with a further increase in dispersant concentration, the excessive amount of dispersant molecules would oppositely hinder movement of particles, leading to agglomeration of dispersed particles due to surface tension effect of dispersant as depicted schematically in Figure 2.7 (c).



**Figure 2.6** Effect of  $\text{NH}_4^+$  salt of PMAA dispersant concentration on viscosity of 70, 75 and 80 wt% solid loading



**Figure 2.7** A proposed model of alumina particle dispersion with different content of dispersant (a) insufficient dispersant (b) optimal dispersant (c) excessive dispersant



Tsetsekou, Agrafiotis, Leon and Miliadis (2001) exhibited the binder such as carboxy-methyl-cellulose significantly increases the viscosity of alumina slurry whereas acrylic-based binders have a high tendency for foaming. Besides, the pair Darvan C-polyethylene glycol (PEG) produced the best result in terms of stability, anti-foaming and viscosity.

Khan, Briscoe and Luckham (2000) conducted the addition of polyvinyl alcohol (PVA), without any included dispersant did not significantly influence the rheology of the system. However, in the presence of a dispersant the rheology was greatly affected. At a given concentration of the dispersant, the viscosity, storage and loss moduli all increase, as the PVA concentration is increased. Also, for a given concentration of the PVA, it was observed that the viscosity, storage and loss moduli values increased as the concentration of the dispersant is increased. It was argued that at low PVA concentrations, an excess concentration of the unadsorbed dispersant caused flocculation of the particles in the suspension by a reduction of the repulsive electrostatic (double layer) effect. In contrast, at higher concentrations of the PVA the flocculation of the suspension was promoted via a depletion mechanism.

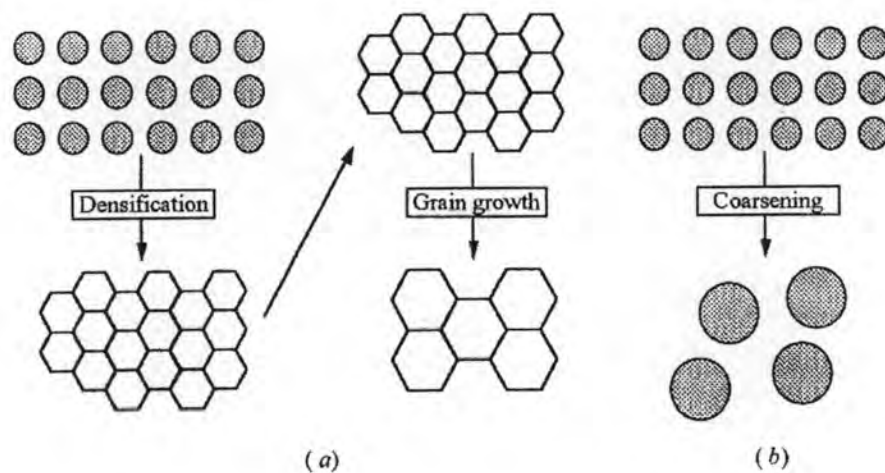
Satapathy (2000) evaluated the green properties of the alumina ceramics using five different commonly used water soluble binders, such as PEG, PVA, Methyl Cellulose (MC), dextrin and corn flour. It was found that the green density of alumina decreased with the increase in binder content after correcting the organic content. The green strength of alumina followed the increasing trend with the increase in amount of binder.

### **2.3 Fundamental of sintering process**

Sintering process is the small particles of a material bonded together by solid-state diffusion. In ceramic manufacturing this thermal treatment results in the transformation of a porous compact into a dense, coherent product. Sintering is commonly used to produce ceramic shapes made of, for example, alumina.

The macroscopic driving force operative during sintering is the reduction of the excess energy associated with surfaces. This can happen by (1) reduction of the total

surface area by an increase in the average size of the particles, which leads to coarsening (Figure 2.8 (b)), and/or (2) the elimination of solid/vapor interfaces and the creation of grain boundary area, followed by grain growth, which leads to densification (Figure 2.8 (a)). These two mechanisms are usually in competition. If the atomic processes that lead to densification dominate, the pores get smaller and disappear with time and the compact shrinks. But if the atomic processes that lead to coarsening are faster, both the pores and grains coarsen and get larger with time.



**Figure 2.8** Schematic of two possible paths by which a collection of particles can lower its energy.

(a) densification followed by grain growth where the shrinkage of the compact occur

(b) coarsening where the large grains grow at the expense of the smaller ones

Many researchers have been interested in roles of sintering mechanism on the full density and the suppression of grain growth behavior as the followings.

Bernard-Granger, Guizard and Addad (2007) clarified the ultra pure  $\alpha$ -alumina sample prepared by slip casting was sintered in air at a heating rate of  $100^{\circ}\text{C}/\text{h}$ . They described two distinct regimes of grain growth and densification kinetics. The first regime was controlled by a Frenkel disorders formation step. Grain growth in the second regime would be controlled by the diffusion of atmos associated to the Frenkel

disorder through grain boundaries and more especially by the diffusion of the  $\text{Al}^{3+}$  cations. Meanwhile, the densification is controlled by the formation of Schottky disorders and by the diffusion of the atoms associated to the Schottky disorders, the grain boundary diffusion of the  $\text{Al}^{3+}$  cations being the limiting step.

Li and Ye (2005) synthesized the  $\alpha$ -alumina powder with a mean particle size of about 10 nm and a weak agglomeration by the doped  $\alpha\text{-Al}_2\text{O}_3$  seed polyacrylamide gel method. And they successfully fabricated the alumina nanoceramics with an average grain size of 70 nm and a relative density of 95% were prepared by a two-step sintering.

Wei Chen and Wang (2000) exhibited a simple two-step sintering method at temperature of about  $1000^\circ\text{C}$  without applied pressure. The suppression of the final-stage grain growth was achieved by exploiting the difference in kinetics between grain-boundary diffusion and grain-boundary migration.

Scott and Kaliszewski (2002) used the solid-state crystal conversion technique for producing the transparent alumina by converting the polycrystalline ceramics into the single crystal via abnormal grain growth behavior. They found that more than 30-40% of polycrystalline Mg-O doped alumina tube can be converted to sapphire crystal at  $1880^\circ\text{C}$  in  $\text{H}_2$  gas via this method.

Echeberria et al. (2002) employed the effect of sinter-HIP on pure nano alumina powder. Specimens with sub-micron grain size and determined the low temperature to obtain close porosity by dilatometry using pressureless sintering in air. They found that Taimicron TM-DAR powder could be sintered to the highest density (97.2% TD) at the lowest temperature ( $1300^\circ\text{C}$ ) to gain close porosity at  $1350^\circ\text{C}$  pressureless sintered, 1h dwelling time and  $10^\circ\text{C}/\text{min}$  heating rate corresponding to the different powders; AKP50 and Ceralox. Moreover, the microstructure characteristic of Taimicron TM-DAR of sinter-HIP can be fully densified at below  $1,300^\circ\text{C}$  and show the smallest grain size to uniform sub-micron scale ( $<0.5 \mu\text{m}$ ). In mechanical

properties, hardness and fracture toughness of Taimicron at sinter-HIP below 1,300°C is very high (23-24 GPa) due to the submicron grain size.

Krell, Blank, Ma, Hutzler and Nebelung (2003) developed wet processing to associate minimum grain size at highest densities with lowest population of macro defects. A closet ratio of powder particle size and sintered grain size was important for obtaining most fine-grained microstructures. The aim was approached best by using powders with particle sizes in the range of 100-200 nm rather than with smaller nanoparticles.

#### **2.4 Hot isostatic press sintering**

Hot isostatic pressing (called HIP), in which a product previously sintered to final stage of sintering is subjected to a hot pressurized gas, is used industrially to reduce the size of closed pores in high-performance structural materials. Applied pressures used are in the range of 10-200 MPa. Porous materials or products may be hipped if first enclosed in a refractory, compressible enclosure or when the surface is sealed.

The major advantage of hot pressing and HIP is the fact that the densification occurs quite readily and rapidly, minimizing the time for grain growth, which results in a finer and more uniform microstructure. The major disadvantages, however, are the costs associated with tooling and dies and the fact that the process does not lend itself to continuous production, since the pressing is usually carried out in a vacuum or an inert atmosphere.

#### **2.5 Literature reviews of transparent polycrystalline alumina ceramic**

Krell, Blank, Ma, and Hutzler (2003) reported on the technological and microstructure conditions by used commercial corundum powder (particle size about 0.2 $\mu$ m) and a wet-shaping process to fabricated transparent submicrometer corundum ceramics for large flat windows and for complex hollow components used in lighting equipment. They investigated on the effect of the amount of solid content, the MgO

and ZrO<sub>2</sub> doping and the pre sintering and HIP condition. They found that the required properties of transparent alumina are 0.4-0.6 μm grain size at >99.9% relative density, the high hardness as 20-21 GPa (used in scratch-resistant windows and transparent alumina armor), the four-point bending strength as 600-700 MPa and the 60% real in-line transmission (at 0.8 mm thickness, with lapped surfaces and at  $\lambda = 650$  nm).

Hotta et al. (2002) produced translucent alumina by slip casting using gypsum mold, which has CaSO<sub>4</sub> impurities. The absorbed soluble CaSO<sub>4</sub> in the green bodies was removed by the washing of HCl aqueous solution before sintering. They found that the relative densities of the sintered Al<sub>2</sub>O<sub>3</sub> ceramics after the washing were higher than that of HCl-unwashed bodies. In addition, the average grain size of HCl-washed and sintered bodies at 1350°C were homogeneously at 1 μm. For untreated with acid, the grain grew heterogeneously at the same sintering condition. The sintered Al<sub>2</sub>O<sub>3</sub> ceramics with acid treatment were translucent. The transmittance value increased from 0 to 12 % with increasing wavelength from 300 to 900 nm. The transmittance was influenced by the solid contents of slurry.

Takao et al. (2000) studied the microstructure of alumina ceramics made by slip casting with focus on the large detrimental defects. From the experiment, both of specimens from dispersed slurries (dispersant 0.2 mass%) and the flocculated slurries (dispersant 2 mass%) had the pore defects. The two types of pore defects in the ceramics are elongated shape and spherical shape. The pores of elongated shape were formed through liquid flow during the casting process in all slip casting specimens and not appeared in the spontaneously dried specimen. For the spherical pores were formed to entrapped air bubbles during de-airing process. So, It was easy for dispersed slurry having low viscosity. Specimens made from the flocculated slurry were higher concentration of the spherical pore and had the lower strength.

O et al. (2004) reported the transmittance abruptly increased due to Rayleigh scattering. The sintered alumina with a grain size of between 2 and 7 μm showed no transmittance. The transmittance slightly increased when the grain size was increased

to more than 7  $\mu\text{m}$ . Polycrystalline alumina with an average grain size of 0.8  $\mu\text{m}$  exhibited high transmittance and high mechanical strength.

Kim et al. (2007) evaluated the MgO doping and pre-sintering heat treatment was combined to accomplish a high translucency in polycrystalline  $\text{Al}_2\text{O}_3$  ceramics. The pure  $\text{Al}_2\text{O}_3$  ceramics did not show any improvement in transmittance by pre-sintering heat treatment, while the transmittance in the visible wavelength regime was greatly increased by pre-sintering heat treatment in 140, 500, and 2500 ppm MgO-doped  $\text{Al}_2\text{O}_3$  specimens.

Mizuta et al. (1992) offered a low-viscosity and high-solid-content slurry (46 vol% solids) was prepared a vacuum-pressure slip casting technique, and a dense green compact was formed. The samples were sintered and subjected to HIPing. Extremely high-density (99.9%) and fine-grained (0.7 to 15  $\mu\text{m}$  in diameter) alumina ceramics were obtained. The HIPed samples showed high bend strength and translucency with in-line transmittance of 30% to 46% (1 mm thick).

Soontorn Tansungnoen (2005) described commercial  $\alpha$ -alumina powder with high-purity, sub-micrometer particle size and narrow particle size distribution is used as starting material to prepare dense ceramics with translucency. The powders were mixed with small amount of MgO. Alumina compacts were preformed by both cold isostatic pressing (CIP) and gel casting using agar as a gelling additive. The green compacts were sintered at 1200-1550°C for 2 h under vacuum. The green body formed by CIP could be sintered to nearly theoretical density at lower temperature than gel casted body. Relative densities of sintered specimens formed by both methods were in the range of 74 to 99.8 % T.D. The maximum relative densities were 99.8 and 99.6 % T.D. for CIP and gel cast bodies, respectively. The sintered bodies formed by CIP showed translucency. On the other hand, sintered body formed by gel casting was opaque.

Jutinun Kraikrer (2006) purposed the microwave sintering resulted in the fast processing time and accelerated densification to sinter  $\text{Al}_2\text{O}_3$  ceramic. But it did not

show the higher density than that of conventional sintering. The transmittance of microwave sintered specimens was lower than that of conventional one because of the larger grain size distribution. The optimum HIP condition selected from the results was 1300°C for 0.5 hr with a heating rate of 10°C/min. Moreover, the effect of zirconia addition on microstructure was observed ZrO<sub>2</sub> addition inhibited grain growth of Al<sub>2</sub>O<sub>3</sub> grain. However, it also disturbed densification. The sintering temperature of Al<sub>2</sub>O<sub>3</sub> with ZrO<sub>2</sub> to attain the same high density shifted to higher temperature than Al<sub>2</sub>O<sub>3</sub> with no ZrO<sub>2</sub> composition. Then the grain size of the full density specimen with ZrO<sub>2</sub> was a little larger than that without ZrO<sub>2</sub>. As a result, better optical transmittance was not attained from the composition with ZrO<sub>2</sub>.