CHAPTER III

FUNDAMENTAL

3.1 Optical properties in polycrystalline alumina ceramic

The optical properties such translucency and transparency can be determined by the light transmission pass through the sample. Especially, in-line transmission in sample is used to describe that material is transparent or not.

Conventional translucent polycrystalline alumina (PCA) which has the large grain size (about 15-30 μm) and low porosity (< 0.1%), has a highly diffuse forward transmission and low in-line transmission so it is translucent than transparent, as shown in Figure 3.1.

Figure 3.1 The light transmission of (a) large-grained PCA (translucent) with high diffuse transmission and a low in-line transmission and (b) fine-grained PCA (transparent) with a low diffuse transmission and a high in-line transmission.

In 2003, Rolf Apetz et al. proposed the light-scattering model for describing how the poly-crystal alumina (PCA) can transparent or translucent from the literature compared with their experiment. They concluded that the non-transparency of alumina due to the scattering of light at any position in sintered alumina which its mechanism could be schematically illustrated in Figure3.2 are as follows;

1. The scattering of light at (rough) surface
2. The scattering of light at second phase inclusion
3. The scattering of light at grain boundaries
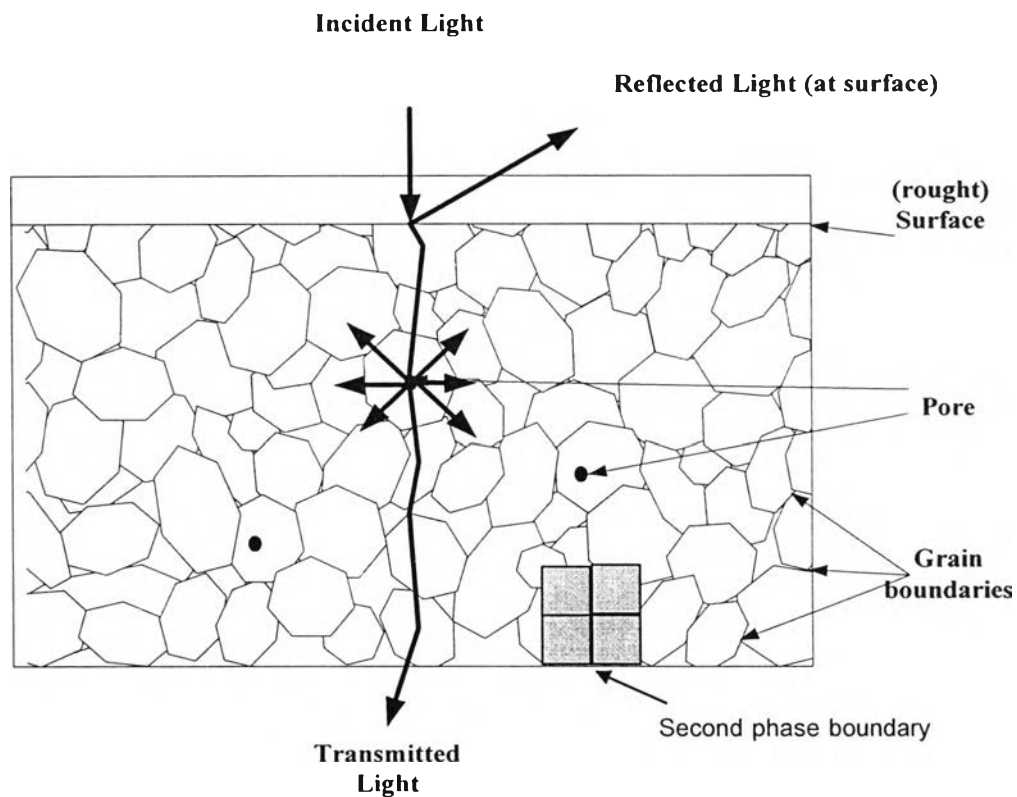4. The scattering of light at pores

Incident Light

Reflected Light (at surface)

(rought)
Surface

Pore

Grain
boundaries

Second phase boundary

**Transmitted
Light**

Figure 3.2 The light scattering mechanism in sintered body of polycrystalline alumina

It is noteworthy that the light scattering at rough surface can be eliminated by properly preparing or polishing. When the surface is smooth, the diffuse scattering at surface can be neglected. Light scattering at second-phase inclusion is not present in high-purity PCA (>99%).

Therefore, the most important factors governing light scattering inside the polycrystalline ceramic figure are grain boundaries and pore distribution of high-purity polycrystalline Alumina. Both of them cannot be avoided, but they can be minimized by controlling its sintered grain size and providing the high density body, respectively.

Increasing of grain size is one way should improve the light transmission of PCA since a large grain size provides fewer grain boundaries. On contrary, it also has

been reported that the transparency can also improve by decreasing its grain size in range of sub-micron to a few micron results in increase of in-line transmission of PCA which is the main factor for transparency in body. So controlling the sintered grain size below a micron order is major factor for its transparency.

If the sintered grain size is controlled smaller than the wavelength of light, the possibility of hitting of light at grain boundaries will decrease, and transparency (real in-line transmission) will increase in case of no pores as illustrated in Figure 3.3. And if the density in the body is increased, the porosity will decrease, and transparency will also increase. To obtain these conditions, alumina ceramic must be employed with alumina powder below a micron order and sintering temperature for minimum grains-growth condition, and properly forming process.
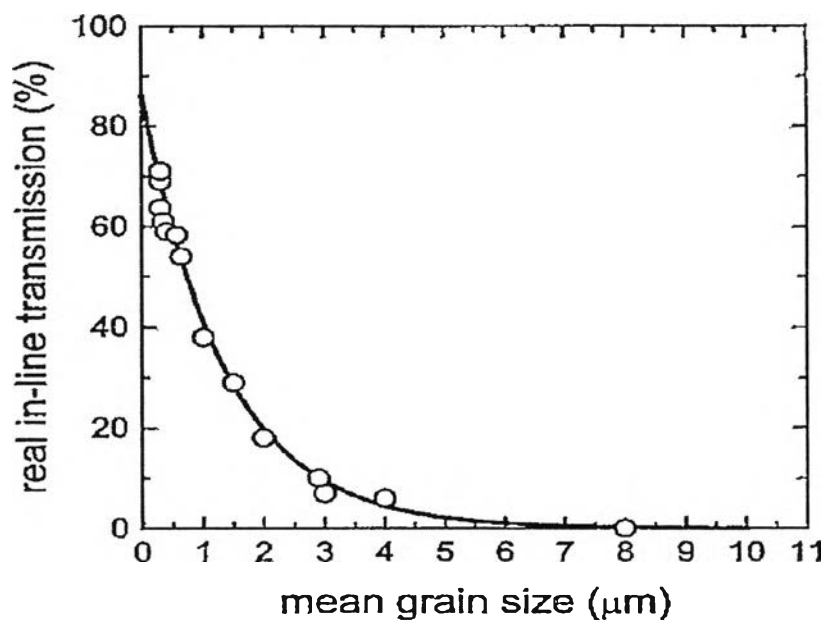

Figure 3.3 Real in-line transmission as a function of the mean grain size of sintered Alumina (0.8 mm thick sample), (O) experimental data points, (-) theorical curve.[1]

3.2 Fabrication of ceramic by slip casting

Slip casting is one of many popular techniques used in ceramics forming process. It can provide green body ceramic with high complicated figure. Slip casting process is schematically shown in Figure 3.4.
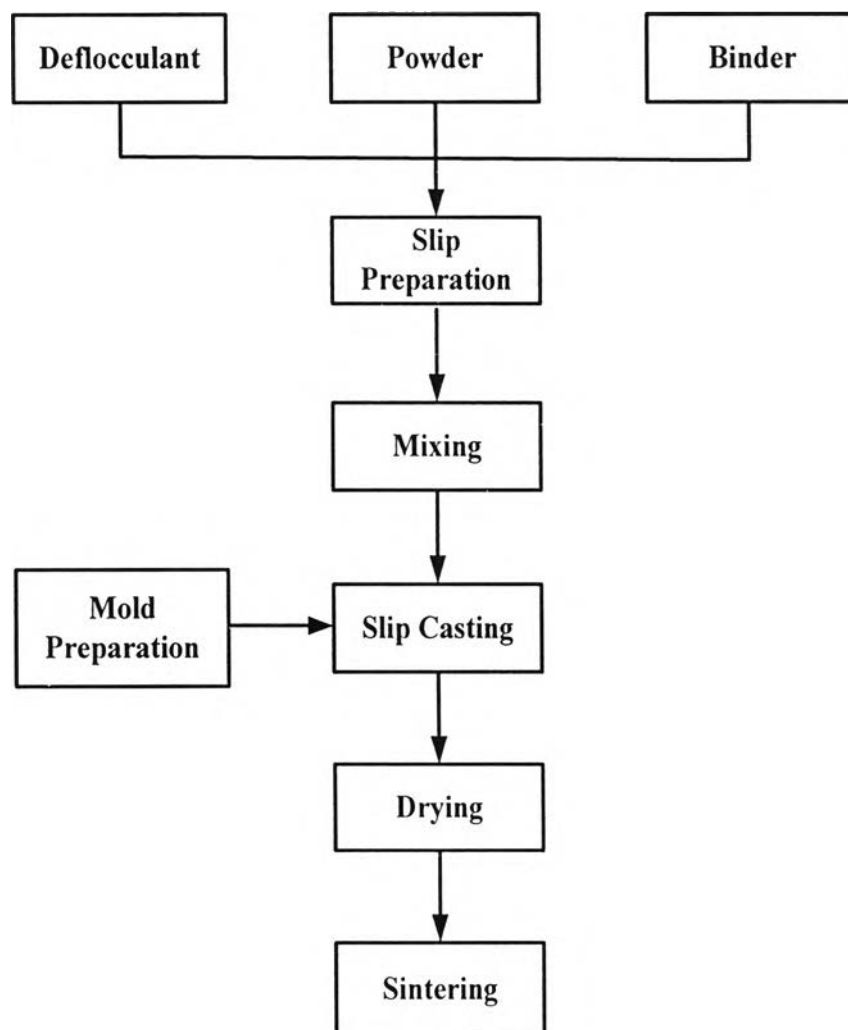

Figure 3.4 Diagram of ceramics forming by slip casting

Slip casting process is begun by preparation of slurry and suspension of green body ingredient called slip. Slip consisting of liquid, solid and processing additives can be prepared in a variety of mixers, for instance, ball mill, planetary ball mills, and vibratory mills. Intensive mixing and milling will help disperse agglomerates more

completely and shorten the mixing time. Additives such as binders of medium to high molecular weight which can degrade during mixing are added in the end of mixing cycle.

A mixed slip filled in the mold to making a cast. Two types of casting process normally used (Figure 3.5), are drain casting and solid casting. In drain casting, the cast forms near the mold surface, and after we get the desired thickness of grown wall, excess slurry is drained from mold. On the other hand, solid casting produces a solid cast having the shape of the cavity of mold. The removed cast from mold is sent into drying process to remove the residue liquid such binders, deflocculants and water content in cast body and to shape products ready for firing called green body ceramic.

Finally, the green body will be sent to sintering process, which makes use of an oven at high temperature. Green body particles will be molten and joint together into aggregates to form the sintered ceramic.
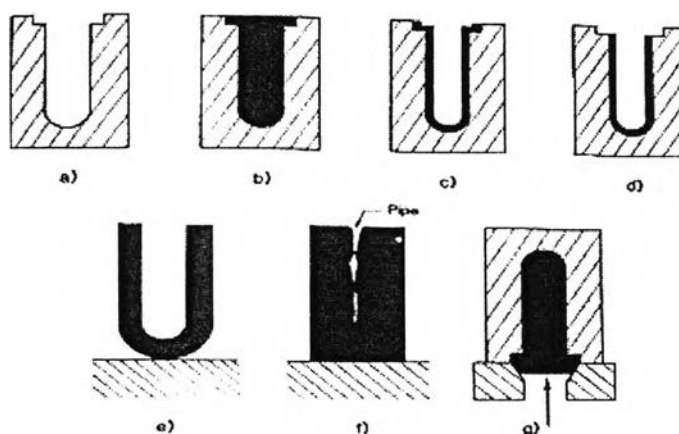

Figure 3.5 Drain casting process (a) a porous mold is (b) filled with slurry; after a period of casting (c) excess slurry is drained from the mold leaving a hollow cast which (d) may be trimmed in place if of sufficient strength and toughness. A longer casting time will produce a casting having (e) a thicker wall and when continued (f) a nearly solid cast is formed. In (g) pressure casting, the slurry is pressurized and pumped into the mold [2]

3.3 Porous mold

The most common porous material employed for slip casting is gypsum ($CaSO_4 \cdot 2H_2O$) formed from the reaction between plaster of Paris ($CaSO_4 \cdot 0.5H_2O$) and water, as follows reaction:

$$CaSO_4 \cdot 0.5H_2O + 1.5\ H_2O \quad \rightarrow \quad CaSO_4 \cdot 2H_2O \quad \text{-----------(1)}$$
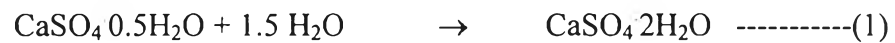
This technique is used because of the ability to fabricate mold with good surface smoothness and detail, high ultimate porosity and micron-size pores, the short setting time, the small dimension expansion (about 0.17%) on setting which aids release from models, and relatively low cost.

From reaction (1), the weight ratio of water to plaster required for hydration forming gypsum is 18.6/100. A range of 60/100 to 80/100 water /plaster weight ratio is used in slurry for production molds. During setting, an interconnected network of needle and plate-like arrangements of gypsum crystal is formed, giving the mold strength. The high water/plaster ratio used for industrial casting molds produces the highest porosity and a slightly larger pore size, which increases the water absorption but lowers the strength. Stronger molds for mechanical pressing are prepared at a water/plaster ratio of about 40/100. The setting time and pore structure of the gypsum mold depends on the temperature and electrolytes in the water and the mixing intensity and time. These variables must be controlled to obtain molds with reproducible behavior.

New molds are brought to low water content on drying in a mold drying room or a dryer. Water evaporation from the molds occurred rapidly. Overheating above about 40 $^\circ$C may cause dehydration and should be avoided. The mold is conditioned by wetting the mold with less than 15% water; this will prevent very strong water adsorption when slip contacts the surface on the first cast. With each casting cycle, the water content of the mold increases and the casting rate will be reduced for the next cast. After a certain number of casts, the casting rate becomes too slow and the waterlogged mold must be partially dried.

Limitations of gypsum molds are their low compressive strength when partially saturated with water, erosion in use due to their low abrasion resistance and the significant solubility of gypsum in water, their relatively low thermal shock resistance, and the potential desiccation of gypsum when heated above 40 ^{O}C during drying, as indicated in Table 3.1 The life of gypsum molds is lower when using acidic aqueous slurry or an alcohol medium.

Improved porous polymer molds, which combine higher porosity, relatively high mechanical strength, and good elasticity have been developed for pressure casting applications. The formulation may be cast into a complex shape having sections of different thickness. Elimination of solvent produces the porous structure.

Table 3.1 Properties of conventional Gypsum Mold

Properties	Value
Aqueous solubility at 25 ^{o}C (g/L)[a]	2.6
Tensile strength (dry,MPa)	3
Compressive strength (MPa)	
Dry	14
Wet	7
Thermal expansion (mm/K)	155
Deseiccation	Dehydrates in dry air

3.4 Drying process

Drying is an important process in producing ceramic raw materials and shaped products ready for firing. During drying, heat is transported to the liquid in the body, and evaporated liquid is transported into the surrounding atmosphere. The drying rate depends on the temperature of the liquid in the body and the temperature, humidity, and flow rate of the drying air. Radiation may be used to augment conduction and convective heating or as the primary heating source. After initial heating, and product

dries at a constant rate during which shrinkage commonly occurs. Transition to a decreasing drying rate occurs when the external surface of the product is incompletely covered with liquid. When the drying rate is very fast, or nonuniform, the constant rate period is relatively short, and the differential shrinkage can cause cracks. Warping is produced by non-uniform drying when the body is shrinking and can deform plastically. Dried products are commonly hygroscopic and may re-adsorb moisture in proportion to the relative humidity of the atmosphere.

3.4.1 Drying shrinkage

Shrinkage occurs during drying as the liquid between the particles is removed and the interparticle separation decreases. When the shrinkage is isotropic; the volume shrinkage ($\Delta V/V_o$) is related to the linear shrinkage ($\Delta L/L_o$) by the equation

$$\frac{\Delta V}{V_o} = 1 - \left(\frac{\Delta L}{L_o}\right)^3$$

The linear shrinkage is proportional to the mean reduction in interparticle spacing $\Delta \bar{l}$ and the mean number of interparticle liquid films per unit length $\bar{N}_1$ when particle sliding and rearrangement do not contribute significantly to the shrinkage:

$$\frac{\Delta L}{L_o} = \bar{N}_1 \Delta \bar{l}$$

A variation of $\bar{N}_1$ or $\Delta \bar{l}$ with direction due to particle orientation or liquid gradients may cause the linear shrinkage to be anisotropic; variations with position produce differential shrinkage.

Shrinkage during drying can be reduced by forming the product at a lower liquid content to reduce $\Delta \bar{l}$ and increasing the mean particle size to decrease $\bar{N}_1$.

Bonds that develop a chemical set may reduce or eliminate $\Delta \bar{l}$ and the shrinkage on drying.

3.5 Sintering process

After forming product and drying, the green compact product must be fired in furnace in order to develop the desired microstructure and properties. This process, called firing, which was proceeded in three stage: 1. reaction preliminary to sintering, which include organic burn out and the elimination of gaseous products of decomposition and oxidation; 2 sintering; and 3 cooling, which may include thermal and chemical annealing.