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# Physical properties of slip casting of high pure $Al_2O_3$ slurry using porous $Al_2O_3$-glass mold

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Physical properties of advanced ceramics are influenced by impurities produced in the forming process. The forming compacts produced by slip casting using gypsum molds contain calcium and sulfur in green bodies. Therefore, a porous $Al_2O_3$-glass mold was produced and slip casting was performed in the present study. Porous $Al_2O_3$ ceramics as casting molds were examined in comparison with gypsum mold from viewpoints of free energy for wettability and rate of filter cake buildup. The sintered compact of $Al_2O_3$ produced by slip casting using the porous $Al_2O_3$-glass mold was compared with those using the gypsum mold. Transmittance of the sintered $Al_2O_3$ compacts using the porous $Al_2O_3$-glass molds was increased in comparison with that using the gypsum mold.


## 1. Introduction

Slip casting [1–10], which has been used in the forming process of traditional ceramics, enables one to make large and dense green compacts with complicated shapes. During slip casting into gypsum molds, dissolution of gypsum from the mold contaminates the green compacts with calcium and sulfur. Although sintered compacts of highly pure $Al_2O_3$ prepared by slip casting do exhibit transmittance properties [11, 12], the transmittance is very low in order to contain contamination from the gypsum mold. Mizuta *et al*. examined the slip casting under vacuum and pressure using resin mold to obtain the non-contaminating green compacts [13]. The slip casting needs under vacuum and pressure because the resin mold is hydrophobic. In general, ceramics are more hydrophilic than resin. Therefore it is considered that the filtering nature of water with the porous ceramics mold is strong than that with resin molds.

In this report, a porous ceramic mold of $Al_2O_3$ and glass compound body was produced and physical properties of the high pure $Al_2O_3$ cast using the porous ceramic molds that didn't penetrate contamination into green compacts were examined. Further, transmittance of the sintered compacts that were prepared by the porous ceramic molds was discussed.

## 2. Experimental

### 2.1. Produce of gypsum and porous $Al_2O_3$ molds

Gypsum was purchased from Wako Pure Chemical Industries, Osaka Japan. To prepare the gypsum mold, gypsum was added to water as 70 mass% of the water. The gypsum slurry was stirred for 1.5 min and was degassed for 3 min under vacuum. After degassed it, the slurry was put into resin mold of a diameter of 2 cm and a height of 3 cm.

A low soda spherical $Al_2O_3$ (AES-11C, Sumitomo Chemical Co., Ltd., Japan), a platy- $Al_2O_3$ (YFA10030, YKK Co., LTD., Japan) and a glass (GA-13/500, Nippondenkisyouseki, Japan) were used to produce porous $Al_2O_3$-glass molds. $Al_2O_3$ and glass (50 wt%) was mixed and was added to water and cardoran (Biopoly, Takeda-Seiyaku, Japan) (10 wt%). The paste was pressed at 25 kg/cm$^2$ pressure with an unaxial compression apparatus. After drying the forming bodies, spherical $Al_2O_3$-glass and platy $Al_2O_3$-glass green bodies were sintered at 1000 and 1200°C, respectively.

To investigate the physical properties of the gypsum and the porous $Al_2O_3$-glass molds, the absorbed water experiments were carried out (Fig. 1).

### 2.2. Preparation of $Al_2O_3$ slurry

Commercially available high pure $Al_2O_3$ (99.99% purity, Taimicron TM-DAR, Taimei Chemicals Co., Ltd., Japan) was used in the present work. The particle size distribution was determined by a light scattering and laser diffraction method (Particle size Analyzer, E-900, Horiba, Japan). The average particle size was 0.15 $\mu$m.

The rheological characteristics of the slurry were measured using a viscometer (Type E, Tokyoseiki Co., Ltd., Tokyo, Japan). A chemically available deflocculant (Aron A6114, Toagousei Chemical Industry, Japan) that was $NH_4^+$ salt of poly(methacrylic acid) was used to obtain a well-dispersed slurry. The composition of the slurry, which yielded a low viscosity at high solid content, is shown in Table I. The slurry was mixed for 16 h in a ball-mill with both mill and balls of high-grade

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TABLE I Composition of the slurry

| Generic | Specific | Composition (mass%) |
|---|---|---|
| Alumina | TM-DAR | 80 |
| Water | | 20 |
| Deflocculant | $NH_4^+$ salt of poly(methacrylic acid) | 2.61 (wt%/Alumina wt%) |

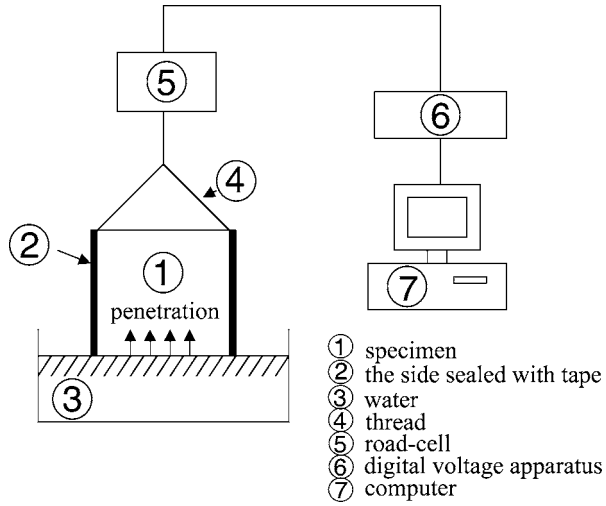


*Figure 1* Scheme of the absorbed water experiments.

$Al_2O_3$. The slurry was degassed for 10 min before slip casting. The slip casting were performed on a gypsum mold and porous $Al_2O_3$-glass molds.

### 2.3. Calcining and sintering

The green compacts were dried and calcined at 800°C for 2 h in air to remove deflocculant. Then, the green compacts were sintered at 1350°C for 2 h under vacuum.

Both the heating and cooling rates were 100°C/h, respectively.

### 2.4. Measurements of porosity, density, transmittance and SEM images

The porosity of the $Al_2O_3$-glass molds and the density of the sintered samples were determined by Archimedes method, respectively. The sintered samples were cut to a thickness of 1 mm and their surfaces polished for optical-transmittance measurement. The transmittance was determined using UV/visible-light spectrometer (Perkin Elmeter, Perkin-Elmer Corp., Lambola, France) in the range 300–900 nm. An average diameter of pore was measured with mercury porosimetry (Micromeritics, Pore Sizer 9320, USA). The porous $Al_2O_3$-glass molds were observed by scanning electron microscopy (SEM, S-3500N, Hitachi, Japan).

## 3. Results and discussions

### 3.1. Water absorption into gypsum mold and $Al_2O_3$-glass molds

Table II shows the porosity values of the porous molds. The values of spherical, platy $Al_2O_3$-glass molds and a gypsum mold were 49.8, 60.1 and 43.6%, respectively.

TABLE II Porosity of a spherical $Al_2O_3$-glass mold, a platy $Al_2O_3$-glass mold and a gypsum mold

| Porous material | Spherical $Al_2O_3$-glass | Platy $Al_2O_3$-glass | Gypsum |
|---|---|---|---|
| Firing temperature (°C) | 1000 | 1200 | |
| Porosity (%) | 49.8 | 60.1 | 43.6[a] |
| Average pore size ($\mu$m) | 4.17 | 4.49 | 4.12 |

[a]See ref (Y. Kondo, Y. Hasizuka, M. Nakahara, and K. Yokota, *J. Ceram. Soc. Japan* **101** (1993) 928.

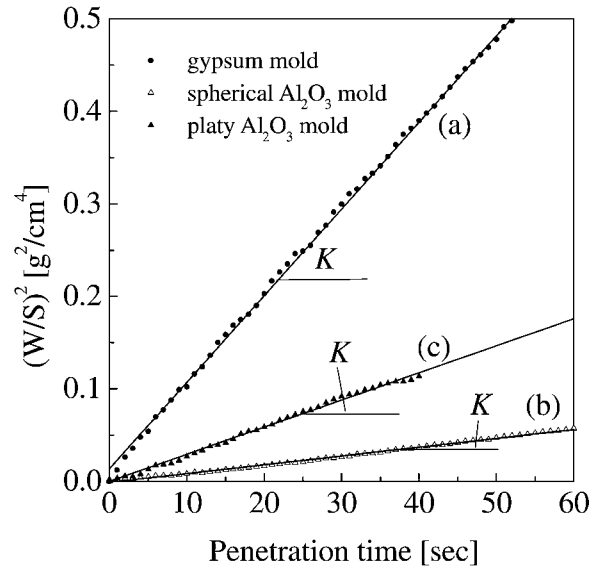


*Figure 2* Relationship between the square of water absorption weight immersed into (a) a gypsum mold, (b) a spherical $Al_2O_3$-glass mold, and (c) a platy $Al_2O_3$-glass mold, $(W/S)^2$, and penetration time.

Fig. 2 shows the relation between the square of water absorption weight per area immersed into (a) a gypsum mold, (b) a spherical $Al_2O_3$-glass mold, and (c) a platy $Al_2O_3$-glass mold, $(W/S)^2$, and penetration time. $(W/S)^2$ was increased linearly for penetration time. The average pore size of a spherical $Al_2O_3$-glass mold and a platy $Al_2O_3$-glass mold was almost the same as that of a gypsum mold (Table II). Porosity of a spherical $Al_2O_3$-glass mold and a platy $Al_2O_3$-glass mold was larger than that of a gypsum mold. However, the inclination of the straight line of gypsum mold was larger than that of a spherical $Al_2O_3$-glass mold and a platy $Al_2O_3$-glass mold. Thus it is considered that the water absorption speed of gypsum mold was faster than that of the porous $Al_2O_3$-glass molds.

The majority of porous ceramics solids can be thought of as a complicated mesh of capillaries with winding trajectories and various radii. A simplified model has been resorted by Beletran *et al.* [14]. This assumes that the liquid flow throughout the bed is equivalent to a hypothetical flow of the fluid through a mass or bundle of capillaries with more or less winding trajectory and which are cylindrical, parallel and equal, aligned perpendicularly to flat and parallel interface. Rate ($v$) of liquid penetrated into a porous mold is represented as the following equation [14, 15];

$$v = \frac{dl}{dt} = \frac{r^2 \Delta P}{8\eta l} \quad (1)$$

where $r$ is Average porous radius, $l$ is Distance when liquid is immersed into porous mold after $t$ hours, $\eta$ is Liquid viscous coefficient, $\Delta P$ is Osmotic pressure.

When immersing phenomena is caused by external pressure ($\Delta p$) and wet effect, $\Delta P$ is represented as follows [16]

$$\Delta P = \frac{2\gamma \cos\theta}{r} + \Delta p \tag{2}$$

where $\theta$ is Contact angle, $\gamma$ is Surface tension of the liquid, $\gamma \cos\theta$ is Free energy of wettability, $\Delta p$ is External pressure.

From (1) and (2),

$$v = \frac{dl}{dt} = \frac{r^2}{8\eta l}\left(\frac{2\gamma \cos\theta}{r} + \Delta p\right) \tag{3}$$

Equation 3 is integrated ($\Delta p = 0$ because the present study was carried out at atmospheric pressure, $t = 0$, $l = 0$).

$$l^2 = \frac{r\gamma \cos\theta}{2\eta} t \tag{4}$$

Weight of liquid that immersed into a porous mold after $t$ hours is represented as follows:

$$W = Sl\varepsilon\rho \tag{5}$$

where $\varepsilon$ is Porosity in percent, $\rho$ is Liquid density, $S$ is crossection area of the porous solid (contact area of liquid and solid interface)

$$\left(\frac{W}{S}\right)^2 = \varepsilon^2\rho^2 l^2 = \frac{r\gamma \cos\theta}{2\eta}\varepsilon^2\rho^2 t \tag{6}$$

Equation 6 satisfies the relation between the square of water absorption weight per area, $(W/S)^2$, and the penetration time in Fig. 2. Thus Equation 6 is represent as follows:

$$K = \varepsilon^2\rho^2 \frac{r\gamma \cos\theta}{2\eta} \tag{7}$$

From the Equation 7, the gradient $K$ of a porous body in high-porosity, big-porous size and the bigger free energy of wettability ($\gamma \cos\theta$) become larger. The porosity and the pore size became large in the order of a gypsum mold, a spherical $Al_2O_3$-glass mold, and a platy $Al_2O_3$-glass mold (Table II). However the gradient $K$ became large in the order of a spherical $Al_2O_3$-glass mold, a platy $Al_2O_3$-glass mold, and a gypsum mold (Fig. 2). The gradient $K$ that represents water absorption speed is dependent on the free energy of wettability rather than the porosity and the pore size of the porous body. It is considered that the free energy of wettability between gypsum and water is larger than that of the porous $Al_2O_3$-glass because the gradient of the straight line of gypsum mold is larger.

The results of the free energy of the wettability and the contact angle at 20°C calculated from Equation 7 are shown in Table III. The contact angle for the gypsum mold, the spherical $Al_2O_3$-glass mold, and the platy $Al_2O_3$-glass mold was 88.1, 89.8, and 89.7 degree, respectively. The free energy of wettability

TABLE III Free energy of wettablility, $\gamma \cos\theta$, and contact angle, $\theta$, between water and porous materials

| Porous material | Spherical $Al_2O_3$-glass | Platy $Al_2O_3$-glass | Gypsum |
|---|---|---|---|
| $\gamma \cos\theta$ mN/m | 0.194 | 0.359 | 2.36 |
| $\theta$ degree | 89.8 | 89.7 | 88.1 |

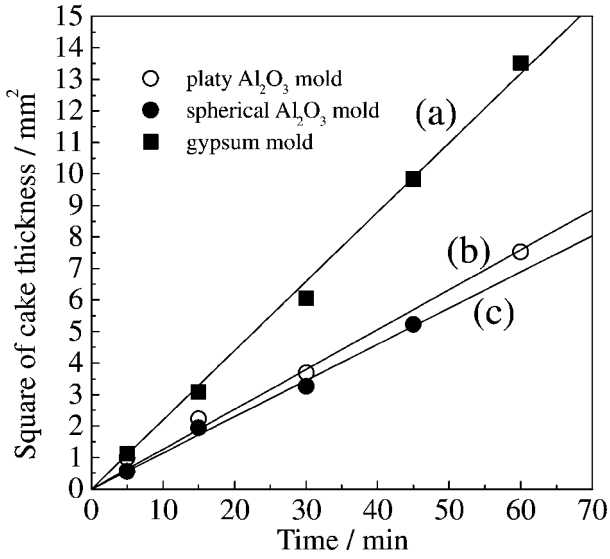


*Figure 3* Relationship between the square of the thickness of green compact and casting time. (a) a gypsum mold, (b) a porous spherical mold, and (c) a porous platy mold.

in the porous $Al_2O_3$-glass mold was smaller than that in the gypsum mold. Thus, it was suggested that the gypsum mold was the wetting material rather than the porous $Al_2O_3$-glass molds.

## 3.2. Slip casting on porous $Al_2O_3$-glass mold

Fig. 3 shows the relationship between the square of the thickness of green compacts and casting time. The square of the thickness of green compacts was proportional to time.

Many kinetics and mechanism researches of slip casing have been reported [17–23]. In general, the casting can be quantified as a filtration process on the base of Darcy's law [24], which obtain the flux of a filtrate volume through a porous bed by:

$$J = dV/A\,dt = K_1\Delta P/\eta H \tag{8}$$

where $J$ is the fluid flux, $V$ the filtrate volume, $A$ the filter area, $K_1$ the permeability of the porous bed, $\Delta P$ the pressure difference across the porous bed, $\eta$ the fluids viscosity and $H$ the thickness of the porous bed. The Equation 8 is converted as follows

$$\begin{aligned} V &= AK_1\Delta P t/\eta H \\ H &= AK_1\Delta P t/\eta V \\ H &= K_1\Delta P t/\eta H \\ H^2 &= (K_1\Delta P/\eta)t = kt \end{aligned} \tag{9}$$

where $t$ is casting time.

According to the Equation 9, it is suggested that the square of the thickness of green compacts produced by the slip casting method is proportional to slip casting time. As shown in Fig. 3, the square of the thickness of green compacts was proportional to time. It was suggested that the slip casting was performed well on the gypsum mold, the spherical $Al_2O_3$-glass mold, and the platy $Al_2O_3$-glass mold.

Growth rate of cake thickness became large in the order of gypsum mold, platy $Al_2O_3$-glass mold, and spherical $Al_2O_3$-glass mold. This order is agreed with the data of the free energy of the wettability (Table III) and the relation between the square of water adsorption weight $(W/S)^2$ and penetration time (Fig. 2). It is suggested that the free energy of the wettability participated in the cake buildup of slip casting. From Equation 9,

TABLE IV Relative density of the each $Al_2O_3$ ceramics sintered at 1350°C under vacuum

| Mold[a] | Gypsum | Spherical $Al_2O_3$-glass | Platy $Al_2O_3$-glass |
|---|---|---|---|
| Relative density (%) | $99.3 \pm 0.16$ | $99.6 \pm 0.2$ | $99.6 \pm 0.2$ |

The "a" mark shows the using porous mold to product the $Al_2O_3$ ceramics. The slurry of 80 mass% $Al_2O_3$ was used.

$$k = H^2/t = K_1 \Delta P/\eta \tag{10}$$

In this work, slip casting was carried out at atmospheric pressure. Therefore, $\Delta p$ in the Equation 2 is zero.

$$\Delta P = 2\gamma \cos\theta/r \tag{11}$$

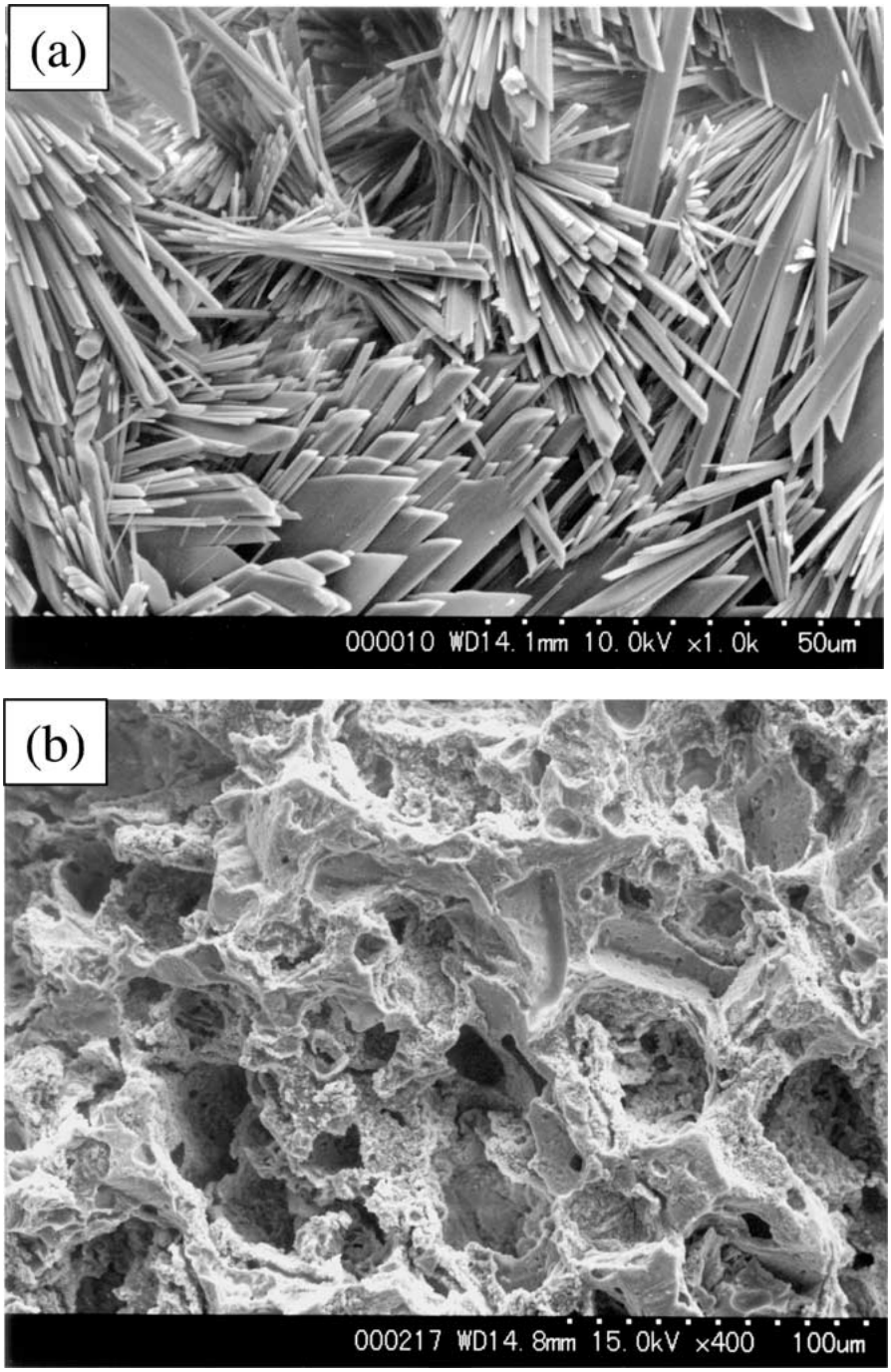


*Figure 4* SEM images of fragments of (a) a gypsum mold, (b) a porous spherical $Al_2O_3$-glass mold and (c) a porous platy $Al_2O_3$-glass mold. (*Continued*.)

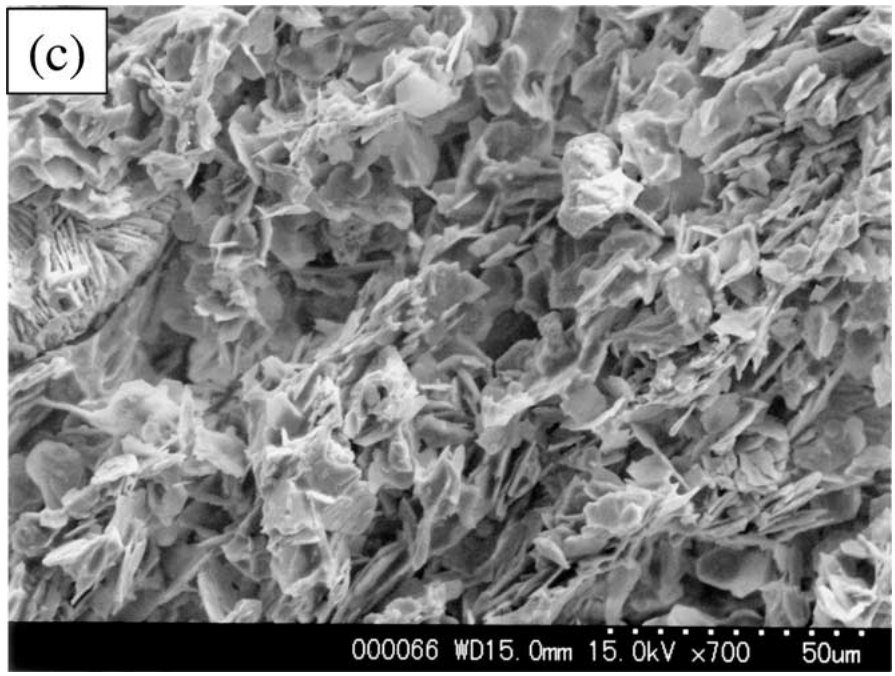


*Figure 4* (*Continued.*)

From Equations 10 and 11,

$$k = (K_1/\eta)(2\gamma \cos\theta/r) = (2K_1/\eta r)\gamma \cos\theta = A\gamma \cos\theta \quad (12)$$

After all, $k$ in the Equation 9 is a function of free energy of wettability ($\gamma \cos\theta$) between water and the mold. As increasing a free energy of wettability, the growth rate of cake becomes larger.

### 3.3. Observation of fragment

Fig. 4 show SEM images of fragments of (a) a gypsum mold, (b) a porous spherical $Al_2O_3$-glass mold and (c) a porous platy $Al_2O_3$-glass mold. The gypsum mold was formed at needle-like crystal. It is considered that water was absorbed between the needle-like crystals. On the other hand, the porous spherical $Al_2O_3$-glass mold was formed at pore structures. It is considered that water was absorbed through these pores. The porous platy $Al_2O_3$-glass mold was composed of the array of the platy $Al_2O_3$ crystal. The microstructure of the platy $Al_2O_3$-glass mold was different from the microstructure of the spherical $Al_2O_3$-glass mold. The microstructure of the platy $Al_2O_3$-glass mold, which was composed of the array of the platy crystal, was similar to the microstructure of the gypsum mold, which was composed of array of the needle-like crystal. It is considered that the water absorption of the platy-$Al_2O_3$ mold is occurred between crystals as well as the case of the gypsum mold.

As shown in Table II, the average pore size of the spherical $Al_2O_3$-glass mold, the platy $Al_2O_3$-glass mold, and the gypsum mold was about 4 $\mu$m. The pore size of the molds which were used in this work was similar size. The porosity of the spherical $Al_2O_3$-glass mold, the platy $Al_2O_3$-glass mold, and the gypsum mold were 49.8, 60.1 and 43.6%, respectively. As shown in Table III, the free energy of wettability ($\gamma \cos\theta$) of the spherical $Al_2O_3$-glass mold, the platy $Al_2O_3$-glass mold, and the gypsum mold were 0.194, 0.359, and 2.36 mN/m, respectively. The free energy of wettability of gypsum mold was larger than that of two kinds of $Al_2O_3$-glass molds. Though the porosity of the spherical $Al_2O_3$-glass and the platy $Al_2O_3$-glass mold was larger than that of the gypsum mold, the growth rate of the cake produced by slip casting was small. $k$ in the Equation 9 is a function of free energy of wettability between water and the molds. From Equations 9 and 12, the growth of the cake is represented as follows.

$$H^2 = kt = (2K_1/\eta r)t\gamma \cos\theta = At\gamma \cos\theta \quad (13)$$

In this work, average pore size of the three molds was similar. Thus the growth of the cake greatly depended on the free energy of wettability ($\gamma \cos\theta$).

### 3.4. Translucent $Al_2O_3$

Fig. 5 shows the microstructures of the $Al_2O_3$ bodies sintered at 1350°C for 2 h under vacuum after slip casting using a gypsum mold and a porous $Al_2O_3$-glass mold. The grain growth of the samples using the porous $Al_2O_3$-glass mold was normal. On the other hand, the grains of the samples using the gypsum mold grew abnormal.

Table IV shows the relative density of the each $Al_2O_3$ ceramics sintered at 1350°C under vacuum. The relative density of the sintered $Al_2O_3$ compacts prepared by slip casting using the gypsum mold, the porous spherical $Al_2O_3$-glass mold, and the porous platy $Al_2O_3$-glass mold was $99.3 \pm 0.16\%$, $99.6 \pm 0.2\%$, and $99.6 \pm 0.2\%$, respectively. The relative density of the

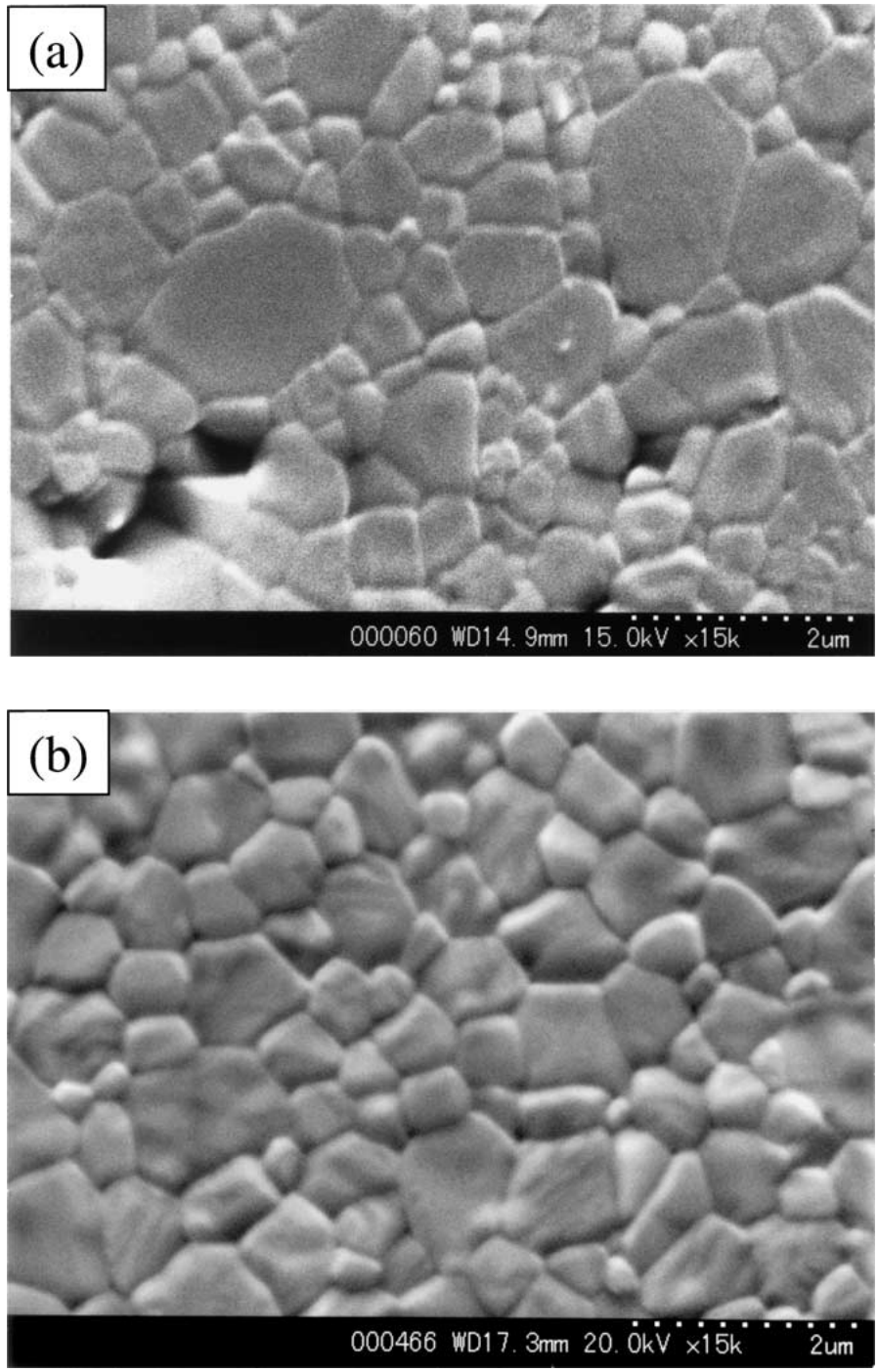


*Figure 5* Microstructures of the $Al_2O_3$ bodies sintered at 1350°C for 2 h under vacuum after slip casting using (a) a gypsum mold and (b) a porous $Al_2O_3$-glass mold.

sintered $Al_2O_3$ compacts prepared by using the porous $Al_2O_3$-glass mold was higher than that prepared by using the gypsum mold. The difference in the relative densities between the samples prepared by using the gypsum mold and those prepared by using the porous $Al_2O_3$ molds was attributed to anomalous grain growth (Fig. 5) caused by impurities form gypsum mold to $Al_2O_3$ green compact [25].

Fig. 6 shows photographs of the sintered compacts prepared by using (a) the gypsum mold, (b) the porous spherical $Al_2O_3$-glass mold and (c) the porous platy $Al_2O_3$-glass mold. The sintered $Al_2O_3$compact prepared by using a gypsum mold was white and opaque. On the other hand, the sintered $Al_2O_3$ compact prepared by using the porous $Al_2O_3$-glass mold allows the back ground to pass through.

Fig. 7 shows the relationship between wavelength and transmittance for wavelength from 300 to 900 nm. The transmittance was measured in the range of visible light. No transmittance occurred in the sample prepared by slip casting using a gypsum mold, whereas transmittance was present in the sample prepared by slip casting using porous $Al_2O_3$-glass molds in the visible region. Thus, the sintered $Al_2O_3$ was offered by using the present porous $Al_2O_3$-glasss molds.

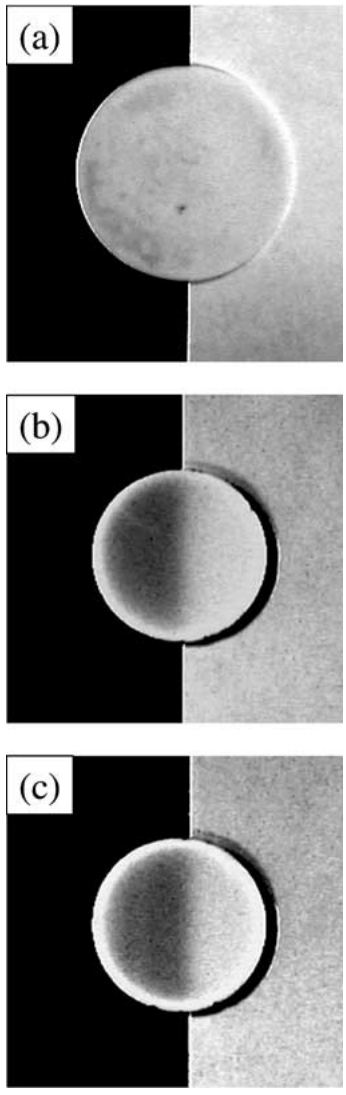


*Figure 6* Photographs of the sintered compacts prepared by using (a) a gypsum mold and (b) a porous spherical $Al_2O_3$-glass mold, and (c) a porous platy $Al_2O_3$-glass mold.

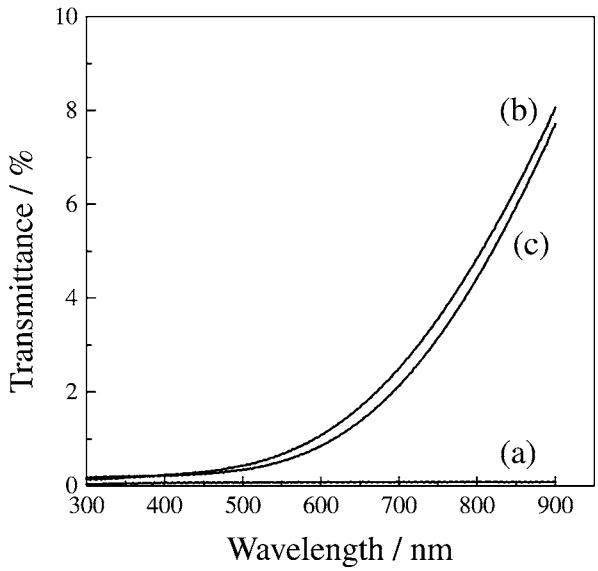


*Figure 7* Transmittance of the sintered $Al_2O_3$ compacts produced by slip casting using (a) a gypsum mold, (b) a spherical $Al_2O_3$-glass mold, and (c) a platy $Al_2O_3$-glass mold. The sample thickness was 1 mm.

## 4. Conclusion

To prepare translucent $Al_2O_3$ ceramics by slip casting, porous ceramic molds was produced. The $Al_2O_3$ ceramics were prepared by sintering at 1350°C for 2 h under vacuum. The present results demonstrated that the sintered $Al_2O_3$ compact after slip casting using porous $Al_2O_3$ molds might successfully produce transmittance in $Al_2O_3$ ceramics. Transmittance of the sintered compacts using the porous $Al_2O_3$-glass molds was increased in comparison with that using the gypsum mold.

Water absorption speed of the porous molds was dependent on the free energy of wettability rather than the porosity and the pore size of the porous body. The square of the thickness of green compact prepared by using the porous $Al_2O_3$-glass molds was in proportion to slip casting time. It was suggested that the slip casting were performed well on the porous $Al_2O_3$ molds.

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