Influence of Particle Size Distributions with Various Geometrical Standard Deviations on Slip-Cast Forming and Sintering Behavior in Submicron Alumina Powder Compacts

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種々の幾何学標準偏差の粒子径分布を有するアルミナ粉末の鋳込み成形及び焼結挙動に及ぼす影響

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The influence of particle size distributions of submicron high-purity α -alumina powders on forming and sintering behavior in an agglomerate-free condition were investigated. Nine kinds of alumina powders with the same median diameter ($d_{PM50} = 0.53 \mu\text{m}$) and different geometrical standard deviations ($\sigma = 1.2\text{--}2.0$) in lognormal particle size distributions were prepared by blending spherical-like commercial α -alumina powders, and were also adjusted to near ideal distributions so that σ of a mass distribution was comparable with one of the number distribution. In order to prevent the agglomerate and contamination of the impurities, forming was performed by means of the colloid process, i.e., the slip casting method using the porous alumina molds. Relative densities of green compacts and bodies sintered at up to 1300°C increased with increasing σ , but densities of bodies sintered at 1500°C or more increased with decreasing σ . The width of the grain size distributions of those bodies increased with increasing σ . The abnormal grains over $30 \mu\text{m}$ of the grain size generated at more than 1.7 of σ for alumina bodies sintered at 1700°C and those grains contained many pores. The powder with a narrow distribution in size is better to fabricate a translucent material. [Received July 4, 2006; Accepted October 19, 2006]

Key-words: Alumina, Particle size distribution, Geometrical standard deviation, Slip-casting, Densification, Grain growth

1. Introduction

Alumina is one of the most useful ceramic materials, and since it has the well-balanced physical properties, such as heat resistance, electric insulation, translucent, and wear resistance, it has been used for the broad industrial field. There are many factors that affect fabrication of alumina compacts and the sintering characteristics; especially particle size, impurity and additives have been investigated enthusiastically. Particle size distribution of powder is also known the important factor that influence on compact density, pore size, pore size distribution and grain size of microstructure of sintered body etc.^{1)–8)}

It has been suggested that mono-sized powders are desirable in fabricating dense, uniform, fine-grained microstructure of sintered body.^{1)–4)} Tin et al. modeled the influence of the particle size distribution on densification and grain growth in sintering. They noted prior to the occurrence of grain growth, the densification rate increased as the particle size distribution width of the powder increased, but after grain growth occurs, vice-versa.¹⁾ So, they concluded powder with a narrow size distribution was preferable and also exhibited the some experimental data in dry-pressed alumina compacts.²⁾ Roosen et al.⁴⁾ and Hay et al.⁵⁾ reported similar results using narrow-sized, well-dispersed powders with colloidal-forming techniques.

On the other hand, Yeh et al.⁶⁾ suggested broad particle size distribution was preferred than narrow one, because the compact made by powder of broad particle size distribution had advantages of high green density and less total shrinkage during sintering although final density and grain size distribution of both alumina sintered bodies were almost the same. Ting et al.⁷⁾ also indicated commercial alumina powder, which had a narrow particle size distribution and a high impurity level, was sintered to relatively low density in spite of addition of MgO.

Recently, Ma and Lim⁸⁾ reported detail experiments using agglomerate-free submicron alumina powder compacts with almost the same average particle size and different geometrical standard deviation in log-normal particle size distribution by centrifugal forming. They suggested the optimum particle size distribution for best sinter-ability had a geometrical standard deviation value lying in between 1.6 and 1.9. They also indicated resultant grain size at final stage of sintering was governed by the sintering condition used but not particle size distribution of starting powder.

Although there are several reports that studied the effects of particle size distributions on sintering behavior of alumina powders, the results are not consisting at all. These confusions are due mainly to the difference in the forming method and condition, and powder characteristics: particle size, shape, the impure amount and the quantity of an additive agent. Another reason is that the mode of expression of the particle size distribution is vague and the systematic and statistical research of the particle size distribution has not been carried out.

The purpose of this study is to clarify it statistically and

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systematically what particle size distribution is most appropriate for sintering alumina. To achieve this purpose, the experiment was carefully executed under following experimental conditions. Firstly, high purity submicron alumina powder with spherical-like particle shape was used as starting powder because irregular necks between particles might locally form during sintering when the particle shape is unevenness. Secondly, slip casting method using porous alumina mold was conducted for forming to avoid the agglomerated particle and the impurity contamination as much as possible. Slip casting is one of the most useful and practicable methods due to obtaining high-density compacts with very little agglomerated particle. In general, the gypsum mold has been used for the casting mold; however, the casting speed is slow and there is a problem of contamination with calcium. The porous alumina mold is the most suitable for forming high purity alumina powder because the mold has an excellent wet characteristic and there is not worry of the contamination by the wear-out of the mold either.⁹⁾ Thirdly, the particle size distribution of the powder has been adjusted to apply lognormal distribution with various geometrical standard deviations. And then, it has been adjusted that the geometrical standard deviation of the number-size distribution and the mass-size distribution becomes as equal as possible.

Nine kinds of alumina powder that has different geometric standard deviation with the same median diameter in lognormal particle size distribution were prepared. Influence of geometric standard deviations on forming and sintering behavior of alumina compacts in agglomerate-free condition were investigated in detail.

2. Particle size distributions

There are Rosin–Rammler distribution, normal distribution and log normal distribution, etc. as expression method of the particle size distribution. It is known that the distribution of powder generally prepared by the vapor-deposition method or the sol gel process follows log normal distribution. Then, in this study, the particle size distribution is evaluated by using log normal distribution. In the distribution, the probability function $P(d)$ of the particle of a diameter d is given by the following formula:

$$P(d) = \frac{1}{\ln(\sigma)\sqrt{2\pi}} \left\{ -\frac{[\ln(d) - \ln(d_{PM50})]^2}{2 \ln^2(\sigma)} \right\} \quad (1)$$

where σ is geometrical standard deviation and d_{PM50} is mass median diameter. The geometric standard deviation σ is given by the following formula.

$$\ln(\sigma) = \left\{ \frac{\sum \{v [\ln(d) - \ln(d_{PM50})]^2\}}{\sum v} \right\}^{\frac{1}{2}} \quad (2)$$

where v is the weight between the diameter d of a particle, and $d + \Delta d$.

Figure 1(a) shows nine kinds of lognormal particle mass-size distributions, which have same mass median diameter ($d_{PM50} = 0.53 \mu\text{m}$) and different geometrical standard deviations ($\sigma = 1.20, 1.35, 1.44, 1.53, 1.62, 1.70, 1.80, 1.90, 2.00$), calculated by Eqs. (1) and (2). Widths of those distributions increase with increasing σ . **Figure 1(b)** is nine kinds of lognormal particle number-size distributions when **Fig. 1(a)** is converted into the number base. Although number median diameter decrease with increasing σ , each width of distribution is the same corresponding to the width of distribution of **Fig. 1(a)**. This means σ is constant even if the base changes from the mass into the number in ideal lognormal distribution.

Fig. 1. Nine kinds of lognormal particle size distributions, which have same mass median diameter ($d_{PM50} = 0.53 \mu\text{m}$) and different geometrical standard deviations ($\sigma = 1.20\text{--}2.00$), calculated by Eqs. (1) and (2). (a) mass-size distributions (b) number-size distributions.

3. Experimental procedures

Eight kinds of high-purity $\alpha\text{-Al}_2\text{O}_3$ powders (purity > 99.995%, SUMICORANDAM, Sumitomo Chemical Co., Ltd., Japan) were used as starting materials. Particle size distributions of each powder were measured by Laser Doppler method (UPA150, Microtrac. Co., Ltd.) at the temperature of 25°C constant. The mass median diameter and amount of impurities of each powder are shown in **Table 1**. Here, AA02 (a) is the fine powder that prepared by sedimentation of AA02 (b) 1-vol% slurries by means of a centrifugal separator. Nine kinds of alumina powders with same mass median diameter ($D_{50} = 0.53 \mu\text{m}$) and different geometrical standard deviations ($\sigma = 1.20, 1.35, 1.44, 1.53, 1.62, 1.70, 1.80, 1.90, 2.00$) in lognormal particle mass-size distributions were prepared by blending these powders. There were also adjusted so that σ of a mass-size distribution was comparable with one of a number-size distribution. The particle mass-size distribution of nine kinds of alumina powders is shown in **Fig. 2(a)**. The distribution curves of **Fig. 2(a)** are corresponding very well

Table 1. Characteristics of Starting Alumina Powders

	Mass median diameter d_{PM50} (μm)	Impurity content (ppm)		
		Si	Fe	Na
AA02(a)	0.18	7	5	16
AA02(b)	0.27	7	9	16
AA03	0.37	7	9	5
AA04(a)	0.56	15	15	10
AA04(b)	0.57	5	12	5
AA05	0.65	2	4	6
AA07	1.05	15	15	10
AA1.5	1.75	20	15	15

Fig. 2. Nine kinds of lognormal particle size distributions, which have same mass median diameter ($d_{PM50}=0.53\mu\text{m}$) and different geometrical standard deviations ($\sigma=1.20\text{--}2.00$), prepared by eight kinds of high-purity $\alpha\text{-Al}_2\text{O}_3$ powders. (a) mass-size distributions (b) number-size distributions.

for those of Fig. 1(a). Figure 2(b) is conversion of Fig. 2(a) into the particle number-size distribution. The number median

diameter has become small as σ increasing as well as Fig. 1(b). The curve shape and width of the number distribution and the mass distribution resemble well although those are deviating a little bit from calculated distribution in Fig. 1(b) as σ increasing.

In order to prevent agglomerate and contaminating of impurities, forming was carried out by the slip casting method using the porous alumina molds (purity: 99.9%, porosity: 28%, average pore size: $0.18\mu\text{m}$, mold size: $30\times 30\times 10\text{mm}$). All the powders that were blended were mixed with about 0.4 mass% polyacrylic ammonium salt as a dispersant (Chukyo Yushi Co., D-305) in distilled water such that each solid concentration was 30 vol%. Alumina slurries were prepared by wet rotation ball milling for 20 h using 10 mm nylon balls and a nylon pot. After de-airing of bubble in the slurry in the vacuum, the slurry was poured into porous alumina molds. Casting was conducted for 1 min and then the slurry was drained. To investigate relationship between the cast layer thickness and the casting time, the thickness was also measured at various casting time for 15, 30, 120 and 180 s. The green compacts were separated from the mold about 60 min later. These compacts were fired at $1200\text{--}1700^\circ\text{C}$ for 1 h with a heating rate of $10^\circ\text{C}/\text{min}$ in air using a MoSi_2 -element resistance furnace. To prevent the contamination under firing, compacts were placed in a high purity alumina crucible. Densities of green and sintered bodies were measured by Archimedes method using water immersion. Pore size distributions of green bodies were evaluated by high-pressure porosimetry measurement (CARLO ERBA STRUMENTAZIONE porosimeter 2000 series). The microstructures of sintered bodies were observed by thermal etching polished sections at 1600°C for 15 min using scanning electron microscopy (SEM) after gold coating. The average grain size, G , in the polycrystalline alumina was evaluated by the linear-intercept method. G is equal to $1.5L$, where L is average linear intercept length of grains. Intercepts of 500 grains were counted for each sample.

4. Results and discussion

4.1 Slip casting test

The following equation has been established between the cast layer thickness of a green compact, L , and casting time, t , in slip casting process.¹⁰⁾

$$L^2 = kt \quad (3)$$

where k is a constant, and represents the rate constant of cast layer thickness. Figure 3 shows the relationship between L^2 and t for slurries of alumina powders with various σ . L^2 increases linearly with respect to t . The value of k increases with decreasing σ . k value of $\sigma=1.2$ is $0.058\text{mm}^2/\text{s}$, and this is twice or more the value of $\sigma=2.0$.

Sobue et al.¹¹⁾ derived

$$k = \frac{L^2}{t} = \frac{2\kappa\Delta P}{\eta} \cdot \frac{f_1}{f_2 - f_1} \quad (4)$$

where κ , η , f_1 , f_2 and ΔP are the water penetration rate of cast layer, the viscosity of water, the particle volume fraction of slurry, the particle volume of cast layer, and the penetration pressure, respectively. If the penetration phenomenon is due to external pressure ΔP and the wettability with liquid then:

$$\Delta P = \frac{2\gamma_L \cos \theta}{r} + \Delta P \quad (5)$$

where γ_L is surface energy of liquid, θ contact angle and r the average pore radius. When no external pressure is applied, i.e., Δp is null, ΔP depends on the penetration pressure by the

Fig. 3. Relationship between square of cake thickness, L^2 , and casting time, t , for slurries of alumina powders with various σ .

Fig. 4. Relationship between relative density of green compacts and σ of alumina powders.

water wettability of the mold, namely a capillary pressure. In this study, η , f_1 and ΔP are constant, as a result k is governed by κ and f_2 . Here, κ is proposed as following equation.^{11),12)}

$$\kappa = \frac{(1-f_2)^3}{f_2^2 S_0^2 \kappa'} \quad (6)$$

where S_0 is specific surface area (The value in which surface area is divided by volume) of cast layer and κ' Kozeny constant κ depends on f_2 and S_0 . Therefore, increasing k value with decreasing σ in Fig. 3 is due to decreasing f_2 and S_0 . In other words, it is thought that the average pore diameter decreases and density of the cast layer increases as σ increases.

4.2 Characteristics of green compact

Figure 4 shows relationship between relative density of green compacts and σ of alumina powders. Relative density increases linearly with increasing σ . Densities of $\sigma=1.2$, 1.7 and 2.0 powder are 55.25%, 60.38% and 62.96%, respectively. Figure 5 is relationship between pore diameter and cumulative pore volume of green compacts with various σ . Total pore volume and pore diameter decrease as σ increasing. Pore diameter of $\sigma=1.2$, 1.7 and 2.0 powders are 0.21, 0.17 and

Fig. 5. Relationship between pore diameter and cumulative pore volume of green compacts with various σ .

Fig. 6. Typical SEM photographs of green compacts with (a) $\sigma=1.2$ and (b) $\sigma=2.0$.

0.15 μm , respectively. This is because the number of small particles increases with σ , and these particles are packed into the space made between big particles. The typical SEM photographs of green compacts with $\sigma=1.2$ and 2.0 are shown in Fig. 6.

On the other hand, Konokawa et al.¹³⁾ reported the highest relative density was achieved by compacting the powder with σ

Fig. 7. Relationship between relative densities of sintered bodies and σ in various sintering temperature.

of 1.7 in lognormal particle number-size distributions with same median diameter. Kondo et al.¹⁴⁾ also showed a high density compact was obtained by using powders with small average particle number-size and the same σ in lognormal distributions. In this study, though mass median diameter of all powders is the same, number median diameter decrease with increasing σ , and caused the compact density to increase.

4.3 Densification and grain growth behavior of sintered bodies

The relationship between relative densities of sintered bodies and σ in various sintering temperature is shown in Fig. 7. Relative densities of compacts sintered at up to 1300°C increase with increasing σ , this is due to influence of green density. At 1500°C or more, densities decrease with increasing σ .

Ikegami et al.¹⁵⁾⁻¹⁷⁾ proposed a model of densification with simultaneous grain growth during intermediate sintering stage shown in the following expression.

$$\log \left(\frac{\rho(1-\rho_0)}{\rho_0(1-\rho)} \right) = K \log \left(\frac{G}{G_0} \right) \quad (7)$$

where G_0 is the average number-particle size of the powdered compact before sintering starts, G is average number-particle/grain size, ρ_0 is relative density of green bodies, ρ is relative density after sintering, K is dimensionless parameter dependent on the spread of distribution of particle/grain size in the compact, the homogeneity of particle packing and the mass transfer. Figure 8 shows relationship between $\rho/(1-\rho)$ and G . The value of $\rho/(1-\rho)$ of each powder compact increases with G : the densifications of compacts proceed with simultaneous grain growth. The slope, K decrease with increasing σ . It was reported that K value became small as particle size distribution broadened. The result in this study showed a similar tendency with past studies.¹⁵⁾⁻¹⁷⁾ The rate of densification is faster when the σ of particles is smaller in the compact. When grain size, G becomes 1.5 μm or more, the slopes for all compacts become small. This is because it becomes the final sintering stage and the particle/grain size distribution changed. Equation (7) was theoretically derived under the assumption that the extent of spread of particle/grain size distribution remains constant until intermediate sintering stage.

Figure 9 shows SEM photographs of polished surfaces of alumina bodies sintered at 1700°C with various σ . Figure 10 also shows grain size distributions of those sintered bodies.

Fig. 8. Plot of $\rho/(1-\rho)$ versus G during sintering of various σ compacts.

Fig. 9. SEM photographs of polished surfaces of alumina bodies sintered at 1700°C with various σ . σ of starting powders are: a) 1.2, b) 1.4, c) 1.7 and d) 2.0.

Fig. 10. Grain size distributions of alumina bodies sintered at 1700°C with various σ .

A pore number increase as σ increases, and this result corresponds to relative densities of compacts in Fig. 7. Average grain size for all sintered bodies are almost the same and their size was about $9\text{ }\mu\text{m}$. Grain size distribution spreads with increasing σ of particles in the green compact. A lot of small particles still exist in the sintered body with large σ . Abnormal grains over $30\text{ }\mu\text{m}$ of the grain size generate at more than 1.7 of σ for alumina bodies sintered at 1700°C and those grains contained many pores. This abnormal grain growth is different from anisotropic grain growth such as platelike grain due to impurity.^{18)–20)} This result shows that some large particles in raw powders with large σ behave as nuclei of abnormal grain growth. In this study, a high dense sintered ceramics could be fabricated using powders with narrow distribution size, although green body with high density was prepared from powders with wide distribution. The results basically corresponded to that by Tin and Lin et al.^{1)–5)} The powder with narrow distribution in size is better to fabricate a translucent material. The powder with wide distribution in size is proper to require a dense green body.

5. Conclusions

Influence of particle size distributions with various geometrical standard deviations on slip-cast forming and sintering behavior in submicron alumina powder compacts under near-ideal preparing condition of alumina compacts were investigated in detail. The results are summarized as follows.

- (1) The value of rate constant of cast layer thickness, k , increases with decreasing σ in slip casting process.
- (2) Relative density of green compact increases linearly with increasing σ . Total pore volume and pore diameter decrease as σ increasing.
- (3) Relative densities of compacts sintered at up to 1300°C increased with increasing σ , and at 1500°C or more, densities decrease with increasing σ .
- (4) The rate of densification for grain growth is faster when the σ of particles is smaller in the compact.
- (5) The width of grain size distributions of compacts sintered at 1700°C increase with σ . Abnormal grains over $30\text{ }\mu\text{m}$ of the grain size generate at more than 1.7 of σ for alumina bodies.

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