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Microstructural changes in sintered Al_2O_3 by acid treatment of compacts produced by slip casting in gypsum molds

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Abstract

Slip casting in gypsum molds is one of the important forming methods industrially. Sintering compacts which were produced by slip casting using gypsum molds showed abnormal grain growth. The grain size of the compacts sintered at 1350 °C was in the range of 0.2–2 μm. The grain size of the compacts sintered at 1450 and 1550 °C were in excess of 2 μm and the sintered compacts showed discontinuous grain growth. Calcined bodies produced by slip casting using gypsum molds were washed with acid to remove the contamination from the bodies. The grains of these sintered compacts grew normally. The mean grain sizes were about 0.8, 5 and 8 μm respectively after sintering at 1350, 1450, and 1550 °C. The microstructure became more homogeneous. The relative densities of the sintered compacts were higher than those of the sinteried compacts. Grain-growth activation energy was calculated from experimental data. The activation energy was 4.8×10^3 J/mol.

Keywords: A. Grain growth; A. Slip casting; D. Alumina; Gypsum

1. Introduction

Fine grained and uniform microstructures are desirable for structural ceramics. Forming processes have been investigated intensively [1,2].

Slip casting [3–15] has been used in the forming of traditional ceramics. It is cost efficient, and can produce large and dense green bodies of complicated shape. Slip casting is an important colloidal processing method for the ceramic industry. In general, gypsum is used for the slip casting molds because gypsum is cost efficient and molds for complicated shapes can be produced. However the dissolution of gypsum contaminates the green bodies with calcium and sulfate. It has been reported [14] that impurities can cause a lower performance of the sintered ceramics. It is known that sintered compacts of pure Al_2O_3 can be translucent. It has been reported that Al_2O_3 compacts, which were slip cast in gypsum molds and sintered at 1350 °C did not show the transmittance. After removal of the impurities the necessary transmittance was obtained. This property was influenced by the grain growth.

In this work, it is reported that grain size and relative density of the compacts which were sintered at various temperatures are influenced by the acid treatment of the compacts produced by slip casting in a gypsum mold.

2. Experimental

2.1. Materials

High-grade Al_2O_3 (99.99% purity, Taimicron TM-DAR, Taimei Chemicals Co. Ltd., Japan) and low-soda Al_2O_3 (AES-11C, Sumitomo Chemical Co. Ltd., Japan) were used in the present work. The particle size distribution was determined by light scattering and laser diffraction (particle size analyzer, E-900, Horiba, Ltd., Kyoto, Japan). The high-grade Al_2O_3 consisted of ultrafine particles averaging 0.157 μm in diameter. The low-soda Al_2O_3 consisted of fine particles averaging 0.417 μm in diameter.

2.2. Preparation of Al_2O_3 slurry and slip casting

For the preparation of the mold, gypsum was added to water (70:30 mass%), and the gypsum slurry was

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stirred for 1.5 min, then degassed for 3 min under vacuum. The gypsum slurry was then poured into an acrylic-resin mold adjusted to a height of 4 cm and a diameter of 5 cm, and the gypsum mold of the shape of the column was made. This gypsum mold was dried in air at 40 °C before slip casting. The rheological characteristics of the slurry were measured using a viscometer (Type E, Tokyoseiki Co. Ltd., Tokyo, Japan). A commercially available deflocculant (Aron A6114, Toagousei Chemical Industry, Japan) which is an ammonium salt of poly(methacrylic acid) was used to obtain a well-dispersed slurry. The composition of the slurry, which yielded a low viscosity at a high solid content, is shown in Table 1. The slurry was mixed for 16 h in a ball-mill with both mill and balls of high-grade Al_2O_3. The slurry was degassed for 10 min before slip casting. Slip casting was performed in gypsum molds on which an acrylic-resin mold (diameter 3 cm) was put. Thus, the slurry penetrated in one direction. The Al_2O_3 green bodies were dried in air after slip casting and removed from the gypsum mold.

2.3. Calcining and sintering

The green bodies were dried and calcined at 800 °C for 2 h in air to remove the deflocculant. The calcined compacts were immersed in 0.9 N HCl for 1 h to remove gypsum that had penetrated into the compacts. Then, the compacts were washed with water until HCl was removed. The absence of HCl was confirmed using $AgNO_3$ until no chloride ions could be detected. The existence of gypsum components ($CaSO_4$) was found with EDX apparatus (EDAX, DX-4, USA). The calcined bodies were sintered after no detection of $CaSO_4$ with EDX. The bodies were sintered at 1350, 1450 and 1550 °C.

2.4. Measurements of density and SEM images

The densities of the sintered Al_2O_3 compacts were determined by Archimedes method. After the surface of the sintered Al_2O_3 compacts was polished, the specimens were thermally etched at 1330, 1430 and 1530 °C for 5 min. The microstructures were observed by scanning electron microscopy (SEM, S-3500N, Hitachi, Japan).

Table 1
Composition of the slurry

Generic	Specific	Composition (wt.%)
Alumina	TMDAR	80
	AES-11C	80
Water		20
Deflocculant	NH_4^+ salt of poly(methacrylic acid)	2.61 (TMDAR) 0.7 (AES-11C)

3. Results

Fig. 1 shows the relation between relative density and sintering rate relating to the high-grade Al_2O_3 compacts which were washed with acid. The sintering temperature was 1350 °C for 2 h. The relative density was 98.5±0.15% at a sintering rate of 50 °C/h. The relative densities were 99.5±0.15 and 99.4±0.16% at a sintering rate of 100 and 200 °C/h, respectively. The relative density had its maximum when the sintering rate was 100 °C/h.

Fig. 2 shows the relation between relative density and sintering time at 1350 °C, relating to the high-grade Al_2O_3 compacts which were washed with acid. The relative densities of the bodies sintered at 1, 2 and 5 h were 99.2±0.15, 99.5±0.15 and 99.1±0.16%, respectively. The relative density had its maximum after sintering for 2 h. Therefore sintering of the green bodies by slip casting was performed at a rate of 100 °C/ h for 2 h.

Figs. 3–5 show the microstructures of the high-grade Al_2O_3 compacts sintered at 1350, 1450 and 1550 °C. Figs. 3a–5a show the microstructures of the high-grade Al_2O_3 compacts which were sintered without previous acid treatment. On the other hand, Figs. 3b–5b show the microstructures of the high-grade Al_2O_3 compacts which were sintered after the calcined bodies had been treated with acid. At all sintering temperatures, the grain size of the compacts with acid treatment became more homogeneous than without acid treatment. However, the compacts which were sintered at 1350 °C had a more homogeneous microstructure. The grain size of the compacts with acid-treatment was 0.4–1.2 μm, and the grain size of the compacts without acid treatment was 0.2–2 μm. The range of the grain size was larger in the case of the compacts without acid treatment. The

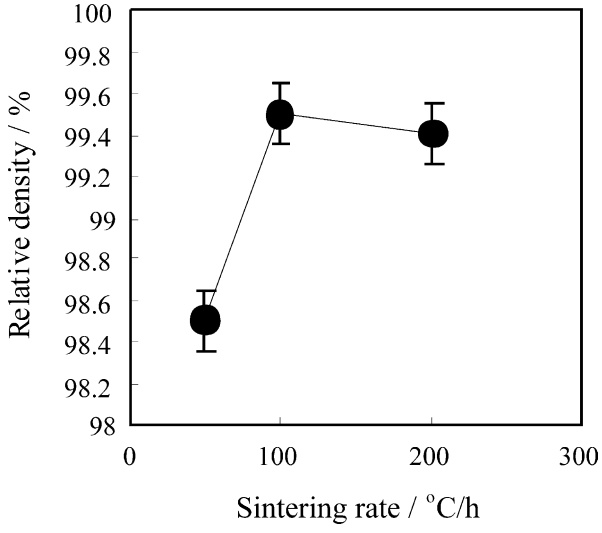

Fig. 1. Relation between relative density and sintering rate for high-grade Al_2O_3.

grains of the compacts, which were produced from the calcined bodies without acid treatment, showed a discontinuous microstructure at 1450 and 1550 °C. In case of the sintered compacts with acid treatment, the grains grew more homogeneous.

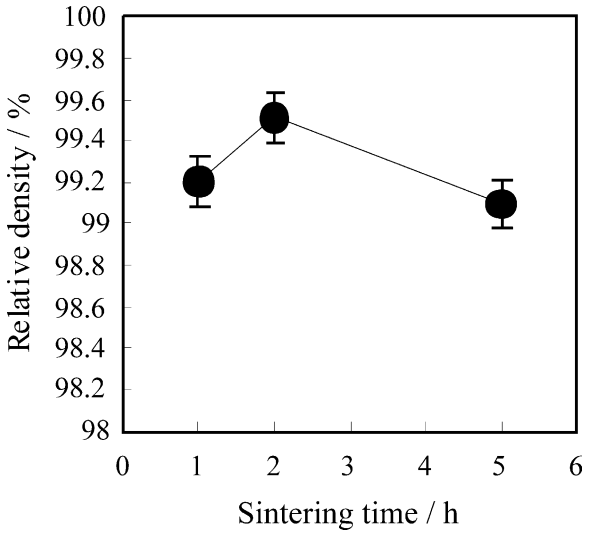

Fig. 2. Relation between relative density and sintering time for high-grade Al_2O_3.

Fig. 6 shows the grain size range of the sintered compacts when calcined bodies were used with and without acid treatment. As shown in Figs. 3–5, the grains of the compacts with acid treatment grew more homogeneous at all sintering temperatures. The ranges of the grain size 0.2–2, 3–7, and 5–10 μm. In the case of the sintered compacts without acid treatment, the grain grew discontinuous with exception of the compacts sintered at 1350 °C. The range of the grain size was over 2 μm and was considerably wide. It is possible that the grain growth was controlled by the treatment with acid.

Fig. 7 shows the relation between relative density and sintering temperature for the high-grade Al_2O_3 compacts. The relative density was at its maximum when the calcined bodies with or without acid-treatment were sintered at 1350 °C. With increasing sintering temperature, the relative densities decreased. The tendency in the density decrease was larger in the compacts without acid treatment than in those with acid treatment because the grains grew more heterogeneous with increasing sintering temperature.

Similar experiments were performed with low-soda Al_2O_3 compacts. The green bodies were sintered at 1600 °C. Fig. 8a shows the microstructure of the sintered compacts without acid treatment and Fig. 8b the microstructure of the sintered compacts with acid treatment. As in the case of the high-grade Al_2O_3 compacts

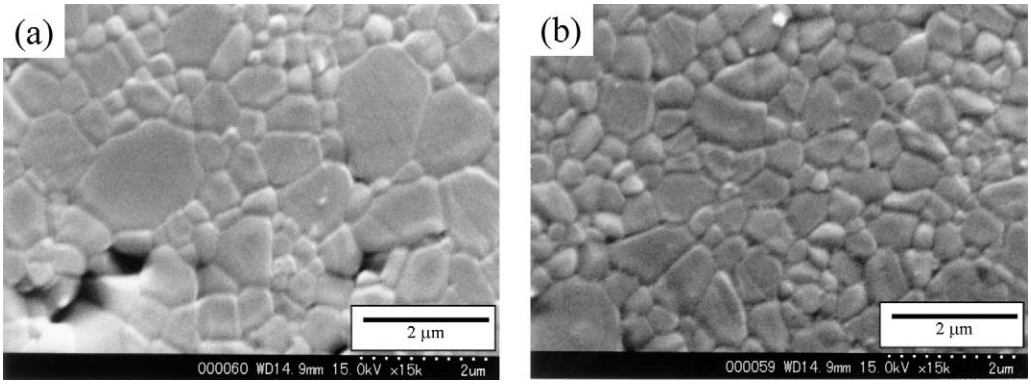

Fig. 3. Microstructure of the bodies sintered at 1350 °C. (a) without acid-treatment, (b) with acid-treatment.

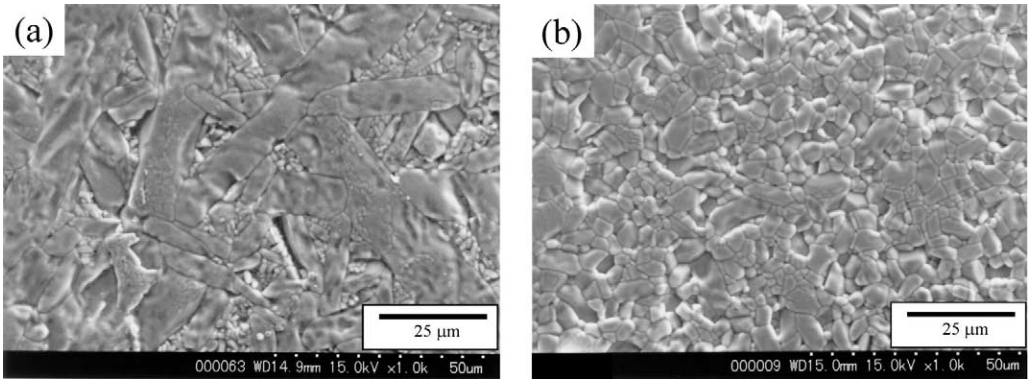

Fig. 4. Microstructure of the bodies sintered at 1450 °C. (a) without acid-treatment, (b) with acid-treatment.

(Figs. 3–5), the grains of the sintered compacts without acid treatment grew discontinuously, and the grains of the sintered compacts with acid treatment grew homogeneously. The grain size of the compacts with acid treatment was about 3.4–13 μm. The mean grain size was about 7 μm. The grain size of the sintered compacts with acid-treatment was smaller than of the samples without acid treatment. These results are the same as the case of the sintered compacts prepared from high-grade Al_2O_3. Thus, it is possible that the grain growth can be controlled by treating with acid.

4. Discussion

The control of grain size and grain growth is of importance for producing advanced ceramics because abnormal grain growth and grain size influence the characteristics of the ceramic product. It was described in a previous report [14] that impurities penetrated into the green bodies during the slip casting process using gypsum molds. The treatment of the calcined compacts with HCl removed the $CaSO_4$ from the compacts, according to the following reaction.

$$CaSO_4(s) + 2HCl(l) \rightarrow Ca^{2+} + 2Cl^- + 2H^+ + SO_4^{2-}$$

The sintered Al_2O_3 compacts showed the required transmittance after such acid treatment because the impurity ($CaSO_4$) was removed from the green bodies [14]. As shown in Fig. 6, the mean grain size of the sintered compacts with acid treatment increased proportional to the sintering temperature, and the grain grew more homogeneously. On the other hand, the grains of the sintered compacts without previous acid treatment grew heterogeneously with increasing sintering temperature. During the sintering process without previous acid treatment, impurities from the gypsum molds penetrated and accumulated in the boundaries. It was suggested that abnormal grain growth occurs because the boundary moves faster in one direction caused by the presence of impurities [16]. Therefore, the removal of

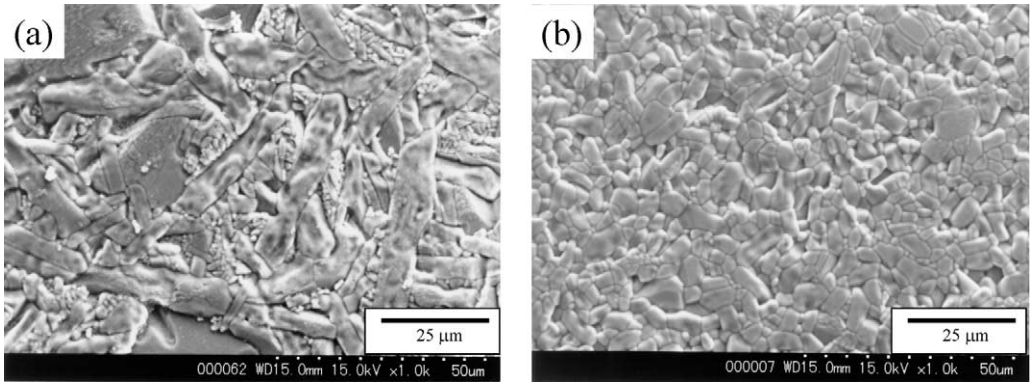

Fig. 5. Microstructure of the bodies sintered at 1550 °C. (a) without acid-treatment, (b) with acid-treatment.

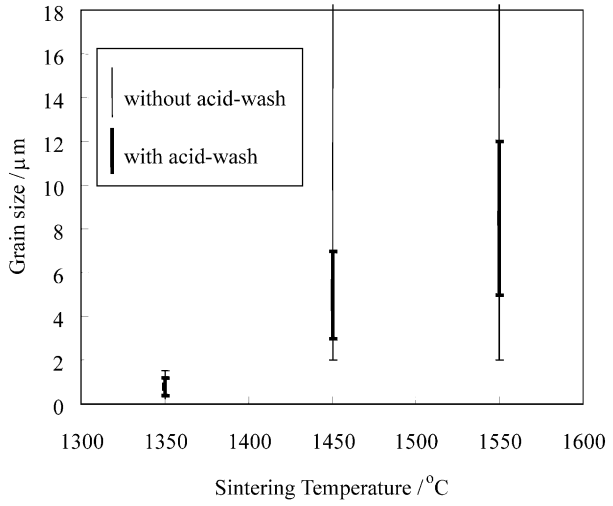

Fig. 6. Relation between grain size and sintering temperature for high-grade Al_2O_3.

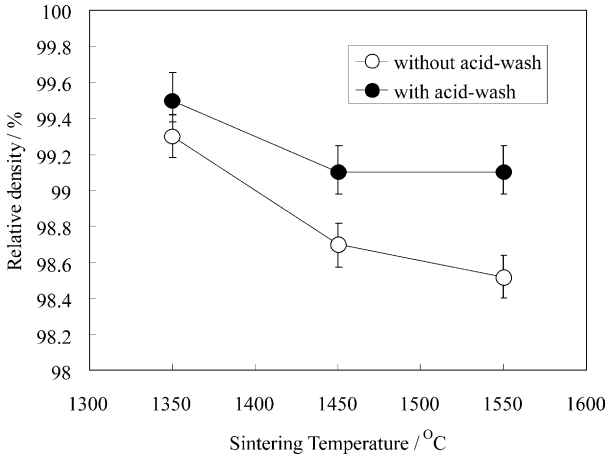

Fig. 7. Relation between relative density and sintering temperature for high-grade Al_2O_3.

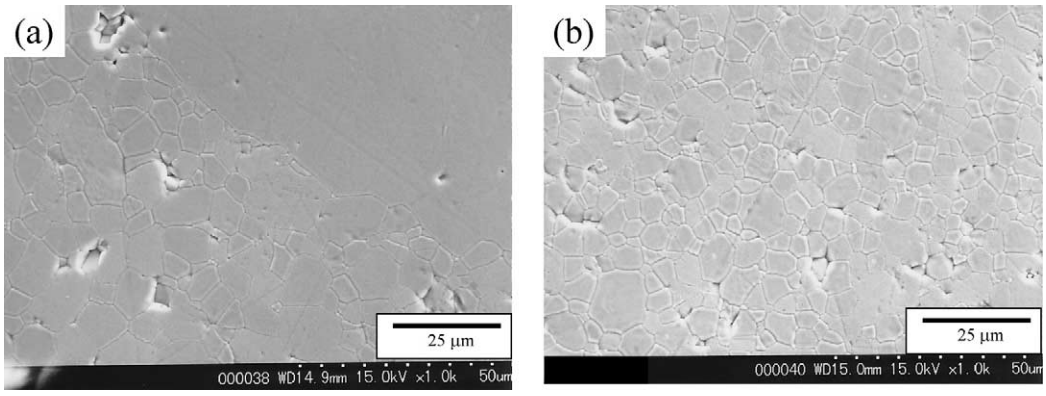

Fig. 8. Microstructure of low-soda Al_2O_3 compacts sintered at 1600 °C. (a) without acid-treatment, (b) with acid-treatment.

impurities from green bodies is of importance for the ceramic production with slip casting using gypsum molds. Such a phenomenon can occur not only in the high-grade Al_2O_3 but also in the low-soda Al_2O_3. It is considered that grain growth is controlled and almost the same grain growth takes place after acid treatment of compacts produced by slip casting in a gypsum mold.

The activation energy for the sintering process can be readily determined from the sintering data as described below. If the energy of the boundary between grains is equal, the boundaries cross at 120°. The grains have six sides. However, this does not actually occur. In general, grains with the various sides are present. Therefore, the energy difference (ΔG) is caused by the boundary curvature as shown in Figs. 9 and 10.

ΔG is represented in the following equation as

$$\Delta G = \gamma_b V_M (1/r_A + 1/r_B) \quad (1)$$

γ_b: surface energy
V_M: mole volume
r_A r_B: radius of curvature
ΔG: energy difference that derives from curvature

when $r_A = r_B = r$

$$\Delta G = \gamma_b V_m (2/r) \quad (2)$$

In Fig. 10, the frequency of atoms which moves from A to B, P_{AB}, and the frequency of atoms which move from B to A, P_{BA}, are represented as follows

$$P_{AB} = H\exp(-\Delta G/RT) \quad (3)$$

$$P_{BA} = H\exp\{-(\Delta G^* + \Delta G/RT)\} \quad (4)$$

H: constant (temperature dependent)
x: distance moved from A to B

Further, the rate of grain growth, U, is represented as follows

$$U = xP = x(P_{AB} - P_{BA}) \quad (5)$$

$$= Hx\exp(-\Delta G^*/RT)\{1 - \exp(-\Delta G/RT)\} \quad (6)$$

$1-\exp(-\Delta G/RT)$ approximates as $\Delta G/RT$. The Eq. (2) substituted in Eq. (6).

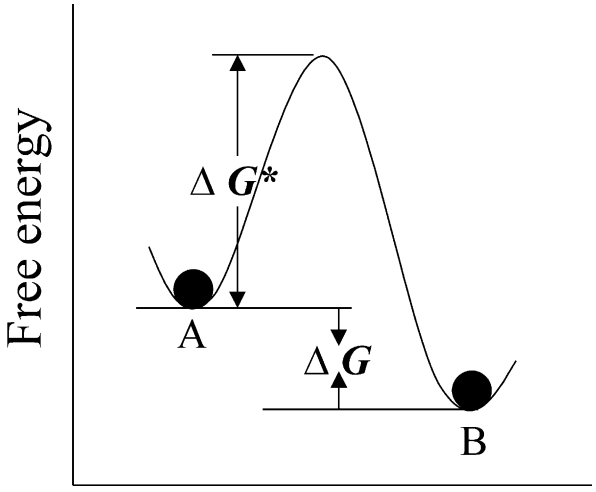

Fig. 9. Energy change for atom movement.

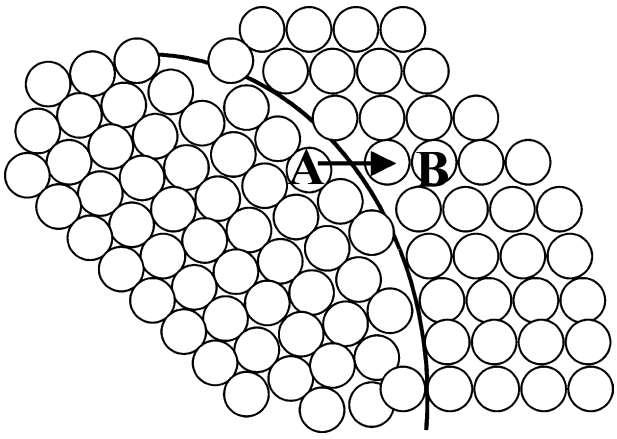

Fig. 10. Boundary model.

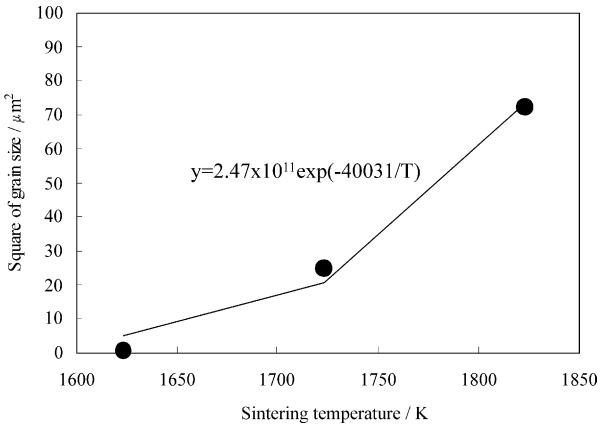

Fig. 11. Relationship between square of grain size and sintering temperature.

$$U = dr/\mathrm{d}t = Hx\gamma_b V_M(2/rRT)\exp(-\Delta G^*/RT)$$

$$= K_1/r \quad (7)$$

$$K_1 = Hx\gamma_b V_M(2/RT)\exp(-\Delta G^*/RT) \quad (8)$$

When the grain diameter is G

$$G = 2r \quad (9)$$

Eq. (9) substituted in Eq. (7) after integration:

$$G^2 - G_0^2 = Kt \quad (t = 0,\ \ G = G_0) \quad (10)$$

In general, $G >> G_0$
Thus,

$$G^2 = Kt \quad (11)$$

In this work, the sintering time was 2 h. The grain size is a function of K.

$$G^2 = 2K \quad (12)$$

In reaction kinetics, K is represented as follows;

$$K = (8x\gamma_b V_M/N_A h)\exp(-\Delta G^*/RT) \quad (13)$$

N_A: avogadoro's number
h: Planck's constant
As shown in Eqs. (12) and (13), the grain size is a function of the sintering temperature.

$$G^2 = (16x\gamma_b V_M/N_A h)\exp(-\Delta G^*/RT) \quad (14)$$

The relationship between the square of grain size and the sintering temperature using the compacts with acid-treatment relating to the high-grade Al_2O_3 is shown in Fig. 11. The graph was fitted with the equation, $Y = a\exp(-b/X)$., The fitting curve was calculated from the results.

$$Y = 2.47 \times 10^{11}\exp\left(-4.0 \times 10^4/T\right) \quad (15)$$

Eq. (15) corresponds with Eq. (14). The grain-growth activation energy is determined as follows in the present work.

$$\Delta G^* = 4.0 \times 10^4/R = 4.8 \times 10^3\ \mathrm{J/mol}$$

5. Conclusions

This paper shows that grain size and relative density of the sintered compacts produced by slip casting using gypsum molds were influenced by the effect of acid treatment. The microstructure of sintered compacts without acid-wash showed discontinuous grain growth. The heterogeneous grains became larger with increasing sintering temperature. On the other hand, the grains of the sintered compacts with acid-wash grew homogeneous, even at higher sintering temperature. The relative densities of the sintered compacts with acid-wash were higher than that of the sintered compacts without acid-wash. With increasing sintering temperature, the difference of the relative densities of the sintered compacts with and without acid-wash became larger. The grain-growth activation energy of the high-grade Al_2O_3 in the present work was calculated. The value was 4.8×10^3 J/mol. Not only in the case of high-grade Al_2O_3 but also the grains of sintered compacts of the low-soda Al_2O_3 produced by the acid treatment grow homogeneously at high temperature. It is possible that ceramic compacts with a fine grained and uniform microstructure, desirable for ceramic applications in producing a reliable structural part, are obtained easily by acid treatment of the slip-cast body.

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