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Effect of crystallite size of boehmite on sinterability of alumina ceramics

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Abstract

Alumina ceramics were prepared by heating γ-Al_2O_3 powders obtained from boehmites with a variety of crystallite sizes to elucidate effect of the crystallinity on the sinterability of alumina derived from boehmite. Boehmite powders were prepared both by precipitation and by hydrothermal treatment of a commercial boehmite powder. The crystallite sizes of these boehmites were ranged from 0 (in a gel) through 2.9 to 24.4 nm while those of the γ-Al_2O_3 powders formed by heating the boehmites at 600 °C for 1 h were 4.0, 4.6 and 8.0 nm, respectively. The powders were ground in a planetary mill to 1.4–1.5 μm and their sinterability was examined by forming them into pellets and heating at 1400–1600 °C for 3 h. The sinterability increased in the γ-Al_2O_3 from boehmite of larger crystallite size. The difference in sinterability is suggested to originate in the difference in agglomeration hardness of fine boehmite particles.

Keywords: A. Sintering; B. Grain size; B. Microstructure; D. Alumina

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1. Introduction

Alumina is one of the most widely used ceramics in various industries as refractories, mechanical parts, abrasives, insulators, etc [1]. A great number of papers have been published on various aspects, including sintering of alumina, its enhanced densification by seeding [2], control of microstructure by additives [3], and the packing and densification of bimodal mixed powders [4].

Boehmite (γ-AlOOH) is an important starting material for preparing both γ-Al_2O_3 and α-Al_2O_3. Since boehmite can be synthesized under a wide variety of preparation conditions, its crystallinity can be varied widely. We are interested in the effect of boehmite crystallinity on its properties and those of γ-Al_2O_3 and α-Al_2O_3 prepared from it. The porous properties of boehmite were found to be strongly influenced by its crystallinity, the highest specific surface area being obtained when the crystallite size was several nm [5]. Boehmites with this crystallite size were found to show higher thermal stability than those other crystallite sizes [6]. The crystallinity of the boehmite was also found to be related to its conversion temperature to γ-Al_2O_3 and the phase transition temperatures of γ-to-α-Al_2O_3. In boehmites of higher crystallinity, the formation temperature of γ-Al_2O_3 and the temperature of the θ-to-α-Al_2O_3 phase transition were found to increase while the temperature of the γ-to-θ-Al_2O_3 transition decreased [7].

In this paper, the effect of boehmite crystallite size on sinterability of alumina ceramics was investigated as part of a series of studies on the effect of boehmite crystallite size.

2. Experimental

The three γ-Al_2O_3 powders G-1, G-4 and G-5 used as the starting materials were prepared by heating boehmites and boehmite gel at 600 °C for 1 h. The boehmite precursor of G-1 was prepared by hydrothermal treatment of a commercial boehmite powder (Condea Chemie GmbH, Hamburg, Germany) in 1 M NaOH solution at

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150 °C for 72 h. The precursor for G-4 was prepared by precipitation from a solution of aluminium nitrate nonahydrate and sodium aluminate (0.5 M) using 5 M NaOH at 80 °C, pH 9 and an aging time of 15 min. The boehmite gel for G-5 was prepared by precipitation from the same solution at 22 °C (pH 5) aged at 60 °C for 20 h. Since these powders were prepared using sodium aluminate and/or sodium hydroxide the Na component is expected to be constant in all the samples. The bulk and surface Na contents were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP; SPS1500VR, Seiko Instruments, Tokyo, Japan) and X-ray photoelectron spectroscopy (XPS; 5500MC, Perkin–Elmer, Physical Electronics, Eden, Prairie, MN, USA), respectively. The crystalline phases in the samples and their crystallite sizes were examined by XRD (Geigerflex, Rigaku, Tokyo, Japan) using monochromated Cu Kα radiation. The crystallite sizes of boehmite and γ-Al_2O_3 were calculated using the Scherrer equation from the *020* and *440* reflections, respectively. The specific surface area (S_{BET}) was calculated by the BET method from the N_2 gas adsorption isotherms (Autosorb-1, Yuasa Ionics, Tokyo, Japan).

The γ-Al_2O_3 powders were ground in ethanol by planetary ball mill (LA-P01, Itoh, Tokyo, Japan) using 5 mmϕ Al_2O_3 balls with 200 ppm MgO added as $Mg(NO_3)_2 6H_2O$. Milling was carried out for 1–5 h, producing an average particle size of 1.4–1.5 μm measured by a Microtrac (Nikkiso, Tokyo, Japan). After drying at 60 °C, the powders were sieved to #100 and pelletized by uniaxially pre-pressing at 24.5 MPa and CIPing at 98 MPa to form 10 mmϕ pellets. Two pellets were heated at 1400, 1500 and 1600 °C for 3 h at each temperature. The apparent density of the pellets was measured by the Archimedes method using water and the values averaged. The relative density was calculated assuming a true density of 3.987 g/cm^3 for α-Al_2O_3.

The heated pellets were polished using diamond paste (4 μm) and thermally etched at a temperature 100 °C lower than the heating temperature. The microstructures of the samples were observed by SEM (S-2050, Hitachi, Tokyo, Japan). The average grain sizes of the samples were calculated by the intercept method counting about 200 grains.

3. Results and discussion

3.1. *Properties of γ-Al_2O_3 powders*

The various properties of the starting powders and resulting γ-Al_2O_3 powders are listed in Table 1 which also includes a reference γ-Al_2O_3 powder (AKP-G015, Sumitomo Chemicals, Osaka, Japan). The XRD patterns of the γ-Al_2O_3 powders are shown in Fig. 1. As apparent from Fig. 1, the crystallinity of the γ-Al_2O_3 powders differs from sample to sample. The reference powder is seen to have been calcined at >600 °C because the XRD pattern shows the partial formation of θ-Al_2O_3. The crystallite size of the γ-Al_2O_3 increased with increasing crystallite size of the precursor boehmite. The S_{BET} values of γ-Al_2O_3 also showed a good correlation with crystallite size except for G-4. Since the three powders were prepared using sodium aluminate and/or sodium hydroxide, they contained significant Na contamination (230–460 ppm). This contaminating Na was found to be concentrated at the surfaces of powders which showed by XPS much higher Na contents (900–

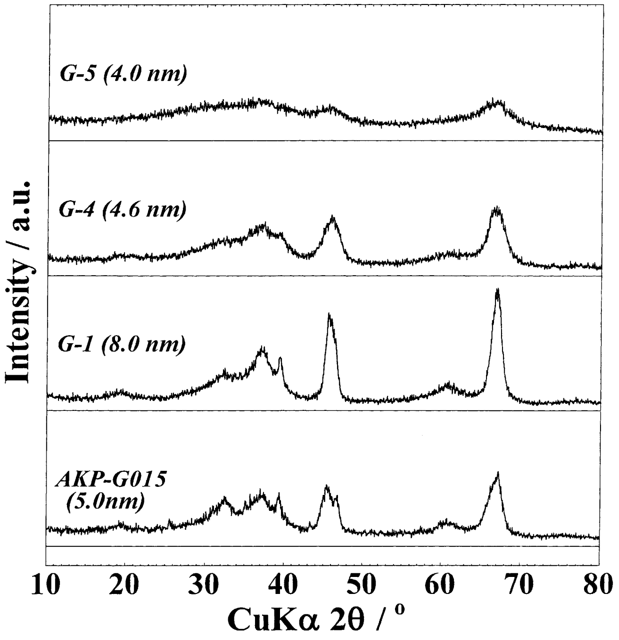

Fig. 1. XRD patterns of the powder samples.

Table 1
Various properties of samples

Sample	As-prepared			γ-Al_2O_3 (600 °C 1 h)				
	Phase	Crystallite size (nm)	S_{BET} (m^2/g)	Crystallite size (nm)	S_{BET} (m^2/g)	Bulk Na (ppm)	Surface Na (ppm)	Particle size (μm)
G-1	Boehmite	24.4	32	8.0	75	330	1200	1.37
G-4	Boehmite	2.9	340	4.6	232	460	1400	1.49
G-5	Gel	0	2.7	4.0	200	230	890	1.38
AKP-G015	–	–	–	5.0	150	tr	tr	1.38

1400 ppm). This surface contamination by Na is suggested to influence the sintering of the present powders.

Although the S_{BET} values of the primary particles of the γ-Al_2O_3 powders suggested that they are small, the SEM shows them to be agglomerated to several μm or more. This agglomeration is rather difficult to break down, since no decrease of particle size was observed by particle size analysis even after grinding for a considerable time. An average particle size of about 1.4–1.5 μm was therefore adopted for all the samples in order to compare their sinterability.

3.2. Sinterability

The fractured surfaces of the green bodies were observed by SEM. As shown in Fig. 2, the microtextures of G-1 and G-015 appear to be smooth, consisting of very fine particles of much smaller size than the apparent particle size of these powders. The particle agglomerates in these samples must therefore collapse during forming. On the other hand, the microstructures of G-4 and G-5 are rough, with many large pores and a variety of particle sizes. Many large particles of irregular shape are observed, especially in G-5. The large particles are relics from the agglomerated starting powders which did not collapse during forming. It is apparent that the microtextures of the green bodies G-1 and G-015 are more uniform than in G-4 and G-5, with the uniformity decreasing in the order G-1 > G-015 > > G-4 > G-5.

Fig. 3 shows the densities and water absorption of the fired bodies as a function of heating temperature. In the samples heated at 1400 °C, the relative densities of G-4 and G-5 (73 and 76%) were very much lower than both G-1 and the reference sample G-015 (89%). The water absorption values of G-4 and G-5 were therefore higher than those of G-1 and G-015. The sinterability of G-015 was higher than G-1. Only G-015 was sintered at this temperature. When heated at 1500 °C, G-4 and G-5 densified significantly, especially G-4. G-1 sintered and its density became higher than G-015 at this temperature. At 1600 °C, the samples G-1, G-4 and G-015 sintered but G-5 did not. The resulting densities decreased in the order G-1 > G-015≈G-4 > G-5. This order of sinterability correlates strongly with the order of uniformity of the green bodies, which also shows strong correlation with the crystallinity of the starting powder. Thus, the uniformity of the green body strongly influences the sinterability of the resulting alumina ceramics.

Photographs of the microtextures of bodies heated at 1600 °C are shown in Fig. 4. The grain sizes of the present three samples smaller than G-015, the microtexture of G-1 is observed to be uniform and dense, whereas those of G-4 and G-5 are less uniform and contain many pores. The microtextures of G-4 and G-5 show regional differences, some areas appearing dense and some grain growth but other appearing rather porous. These non-uniform microtextures in the green bodies strongly influence the microtextures of fired bodies. The average grain size was determined by the intercept

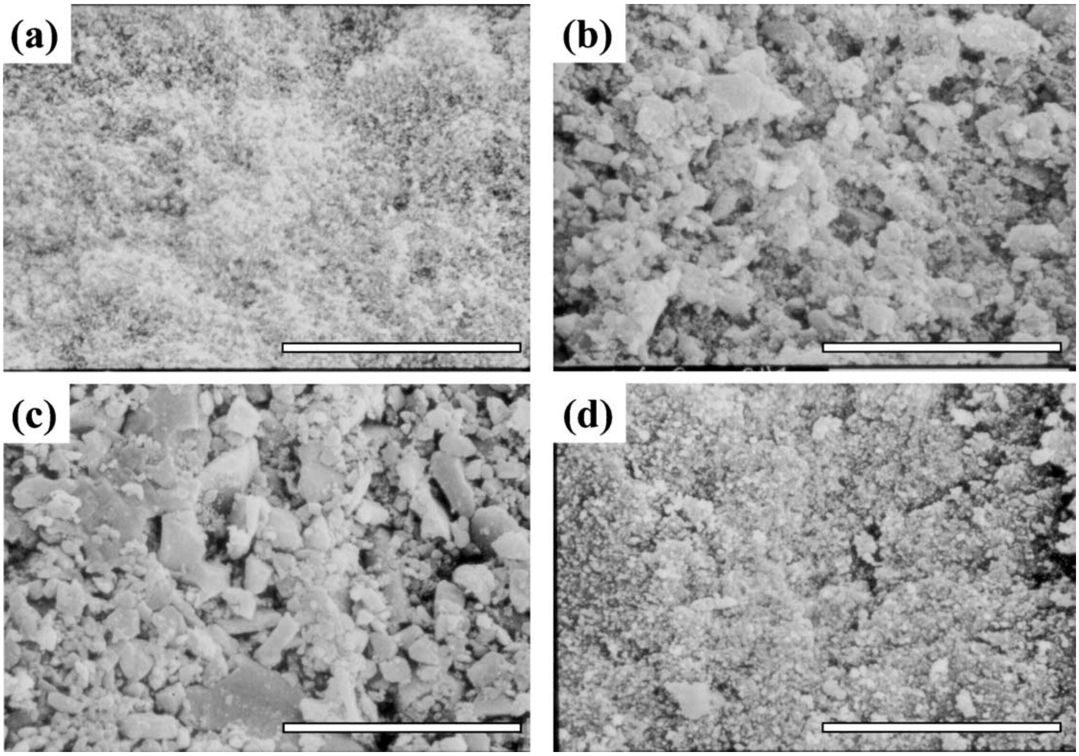

Fig. 2. Fracture surfaces of the green bodies. (a): G-1, (b): G-4, (c): G-5 and (d): G-015. The scale bars are 10 μm.

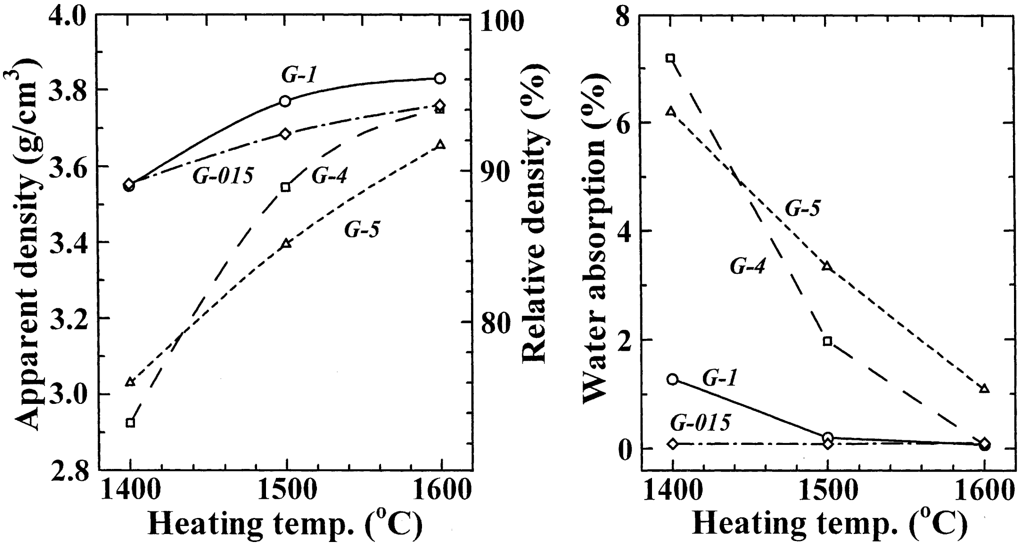

Fig. 3. Changes of apparent and relative densities (a) and water absorption (b) as a function of heating temperature.

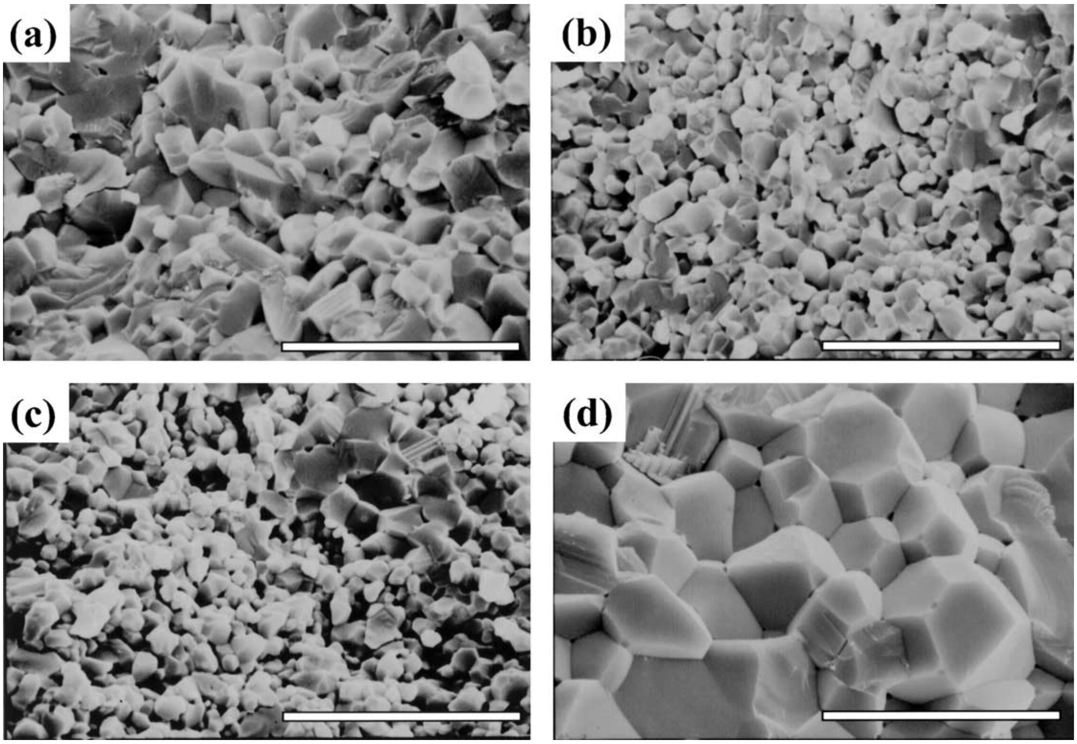

Fig. 4. Fracture surfaces of the bodies heated at 1600 °C. (a): G-1, (b): G-4, (c): G-5 and (d): G-015. The scale bars are 10 μm.

method using the thermally etched surfaces of the fired bodies. Fig. 5 shows the change in average grain sizes in all the samples as a function of their relative density. The average grain size of G-1 is smaller than that of G-015, this condition being maintained up to a relative density of 95–96%. The grains of G-4 and G-5 also show small average sizes though slightly larger than G-1. The smaller grain sizes in these three samples are suggested to be due to the Na contaminant. Since these samples contain high Na concentrations at the surface, even in the starting powders, this surface Na is thought to form a surface layer which suppresses diffusion in the alumina, resulting in a very different grain size by comparison with the reference sample.

4. Conclusions

The effect of boehmite crystallite size on the sinterability of alumina ceramics was investigated using samples with crystallite sizes ranging from 0 to 24.4 nm. This difference in the crystallite size of the boehmite

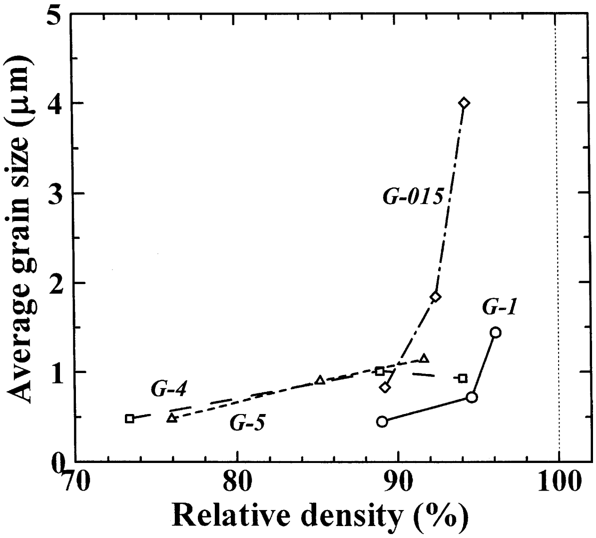

Fig. 5. Change of average grain size as a function of relative density.

starting material produced differences in the crystallite size of the γ-Al_2O_3 prepared by heating at 600 °C for 1 h, from 4.0 to 8.0 nm. Although the apparent particle size of these γ-Al_2O_3 powders was adjusted to a similar size of 1.4–1.5 μm by grinding, the microtextures of the resulting green bodies were different, the uniformity decreasing in the order G-1 > G-015 > > G-4 > G-5. The agglomeration of fine particles therefore appears to become more robust in G-5 than in G-1. This difference in the uniformity of the green bodies influences the relative density and microtexture of the fired bodies. It is concluded that the sinterability of alumina ceramics is greater in boehmite starting materials of larger crystallite size. The grain growth of alumina in these samples is suppressed by the presence of relatively high concentrations of impurity Na at the surfaces of the starting powders.

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