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Effects of heating rate on microstructure and transparency of spark-plasma-sintered alumina

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Abstract

Commercial alumina powder was densified by spark plasma sintering (SPS) at 1150 °C. During SPS processing, the effects of the heating rate were examined on microstructure and transparency. With decreasing heating rate, the grain size and the residual porosity decreased, while the transparency increased. At a heating rate of 2 °C/min, the grain size was 0.29 μm, and the in-line transmission was 46% for a wavelength of 640 nm. The mechanisms for the fine microstructure and low porosity at slow heating, which are conflicting with some existing results, were explained by considering the role of defect concentration and grain-boundary diffusion during densification.

Keywords: Grain growth; Sintering; Porosity; Optical properties; Al_2O_3

1. Introduction

For attaining transparency in fine-grained alumina ceramics, a full density or an extremely low porosity is indispensable. Since residual pores have a significant negative effect on light transmission, for transparent alumina, porosity should generally be reduced to less than 0.05%.[1] Low porosity also allows good mechanical properties such as strength, wear resistance and hardness. In order to achieve such dense and fine microstructures in alumina, hot isostatic pressing (HIP) has widely been used, which effectively eliminates residual pores at low temperatures (1200–1300 °C).[1–4] By using HIP, Krell et al.[1] and Apetz and Bruggen[4] obtained a transparent alumina with an in-line transmission of 50–70%. Their grain sizes are 0.4–0.7 μm and porosities are less than 0.05%. Until quite recently, HIP has been the only way to obtain a transparent alumina with submicrometer grains.

On the other hand, spark plasma sintering (SPS) has recently been paid attention as an alternative method to obtain dense and fine-grained ceramics at low temperatures. Owing to the advantage of rapid heating, the alumina ceramics obtained by SPS have a grain size and density comparable to those of HIPed ones.[5–9] For example, a fully dense (a relative density of ∼100%) alumina with a grain size of 0.5 μm was obtained at 1200 °C by SPS.[8] During SPS of the alumina ceramics, the heating rate was very high (≥150 °C/min) and the holding time at sintering temperature was short (3–10 min). The short heating time at low temperatures significantly suppresses grain growth, and in the case of alumina (a non-conductor), rapid densification can proceed by easy shear-sliding between small powder particles under applied mechanical pressure. By using SPS, Dobedoe et al.[10] obtained a transparent alumina at 1200 °C, although the heating rate and the sintering time were not described in their research paper.

On the other hand, we recently reported that a transparent alumina can be obtained at a low heating rate (2 °C/min), not at a high heating rate (100 °C/min) during SPS.[11] This is the result opposite to the existing researches, although the reason is unclear. For understanding the mechanism, in the present study, we examined the effects of the heating rate on the microstructures and transparency during SPS of alumina. By investigating the microsturctural changes depending on the heating rate, we aimed to understand the phenomena which occur during the sintering process.

2. Experimental procedure

Commercial α-Al_2O_3 powder (TM-DAR, Taimei Chemicals Co. Ltd., Japan), with a purity of 99.99% and an average particle size of 0.15 μm, was used in this study. As-received powder was heated directly, without special treatment or additives, to

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1150 °C under a uniaxial pressure of 80 MPa using a Spark Plasma Sintering machine (SPS-1050, Sumitomo) with a pulse duration of 3.4 ms. Heating was conducted using a sequence consisting of twelve DC pulses (40.8 ms) followed by zero current for 6.8 ms. The heating rate from 600 °C to 1150 °C was varied between 2 °C/min and 100 °C/min. The temperature was measured with an optical pyrometer focused on the non-through hole (1 mm in diameter and 2 mm in depth) of a graphite die. After holding for 20 min at the sintering temperature and subsequent annealing at 1000 °C for 10 min, we obtained a sintered disk with a diameter of 30 mm and a thickness of 3 mm. In addition, for a heating rate of 8 °C/min and 50 °C/min, the sintering time was varied between 0 h and 5 h, in order to examine the grain growth behavior. The mechanical pressure was unloaded before annealing.

The center of the sintered body was machined to a tile of 10 mm × 10 mm with a thickness of 1 mm, and mirror-polished carefully on both sides using diamond slurry. The final thickness of the sample is about 0.9 mm. The in-line transmission was measured in the wavelength range from 0.24 μm to 1.6 μm using a double-beam spectrophotometer (SolidSpec-3700DUV, Shimadzu). The distance between the sample and the detector is about 55 cm.

The microstructure was observed on the specimen surfaces, which had been polished and thermally etched at 1050 °C for 1 h, by using a scanning electron microscope (SEM) (JSM-6500, JEOL). The porosity was measured on the SEM images taken at a magnification of 10,000 times. We did not measure the absolute density because the conventional techniques such as the Archimedes method are insensitive to extremely low porosity. The grain size was measured by obtaining the average cross-section area per grain and assuming spherical grains. The measured grain size is an apparent one, so that it was multiplied by 1.225 to determine the true grain size.[4]

3. Results and discussion

3.1. Grain size

For the alumina sintered at 1150 °C for 20 min, the grain size was smaller at lower heating rates. The dependence of the grain size on the heating rate is shown in Fig. 1, where the grain size decreases with decreasing heating rate. The grain size was 0.55 μm at a heating rate of 100 °C/min, and it was decreased to 0.29 μm at 10 °C/min. Further decrease in the heating rate below 10 °C/min has no remarkable effect on the grain size. At a heating rate of 2 °C/min, a slight tendency toward increasing grain size was observed owing to the increased heating time. The microstructures of the sintered aluminas are shown in Fig. 2.

For the effect of the heating rate on the grain size, there have been conflicting results. Stanciu et al.,[6] Shen et al.[8] and Zhou et al.[9] reported that the grain size of alumina decreased with increasing heating rate, whereas Murayama and Shin[12] reported opposite results that are consistent with the present study. The origin of the conflicting results has been unclear. However, their respective SPS experiments were conducted under different sintering conditions with different Al_2O_3 powders, as shown in Table 1. Although the present Al_2O_3 powder is identical to that of Zhou et al.,[9] the pressure is different, which also has a significant effect on the sintered microstructure. The different sintering conditions may provide a clue for understanding the conflicting results.

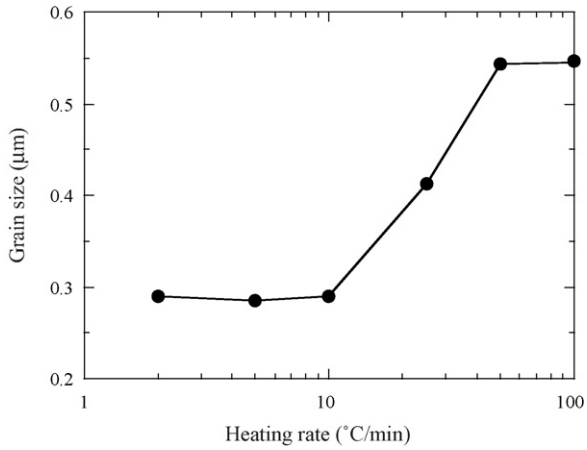

Fig. 1. Dependence of the grain size on the heating rate for sintering at 1150 °C for 20 min.

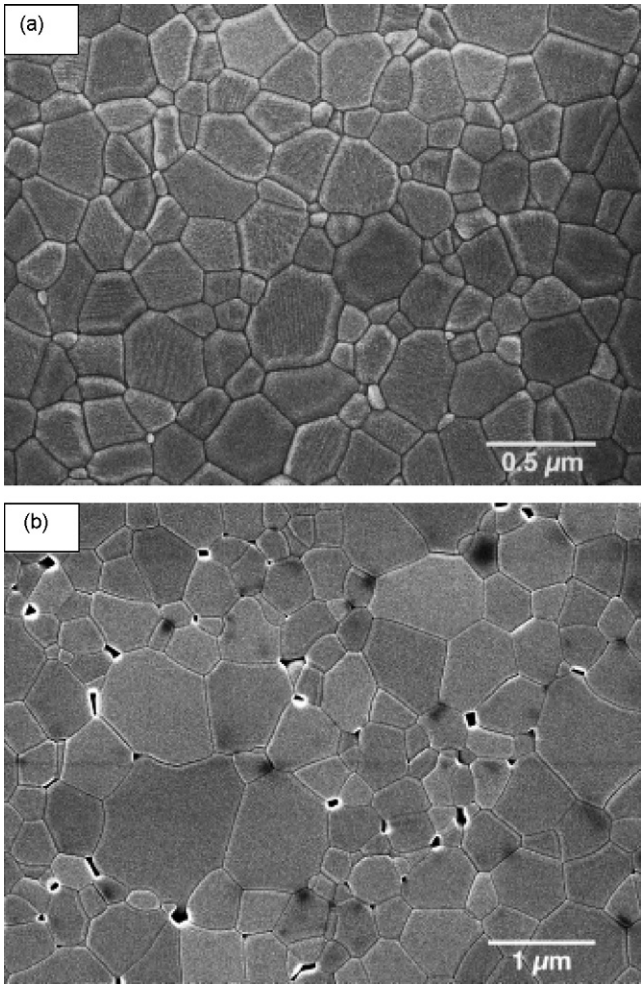

Fig. 2. Microstructures of the alumina sintered at a heating rate of (a) 2 °C/min and (b) 100 °C/min.

Table 1
SPS condition for alumina reported with varying heating rate

Powder (average size)	Temperature (°C)	Dwelling time (min)	Pressure (MPa)	Heating rate (°C/min)	
Sumitomo Chemical (0.1 μm)	1100	2	45	50, 250, 700	Stanciu et al.[6]
Ceralox APA0.5 (0.4 μm)	1300, 1400	0	50	50–600	Shen et al.[8]
Taimei Chemical (0.15 μm)	1000–1400	0	47	50, 300	Zhou et al.[9]
Undefined (0.22 μm)	1190, 1250	1–20	50	5, 500	Murayama and Shin[11]
Taimei Chemical (0.15 μm)	1150	20	80	2–100	Present study

First, in order to compare the present SPS results with the existing ones, we focus on the sintering in a temperature range of 1100–1250 °C. In this temparature range, Zhou et al.[9] and Murayama and Shin[12] obtained a result consistent with the present one, that is, large grain size for rapid heating. In the study of Zhou et al.,[9] the grain size at 1150 °C was 0.17 μm and 0.31 μm at a heating rate of 50 °C/min and 300 °C/min, respectively. The grain size examined by Murayama and Shin[12] after sintering at 1250 °C for 4 min, was about 0.42 μm and 0.55 μm at a heating rate of 5 °C/min and 500 °C/min, respectively. For the reason of the larger grain size at higher heating rate, Murayama and Shin[12] explained by assuming that a high defect concentration is produced by rapid heating and associated rapid deformation during densification. Large DC current for rapid heating is considered to assist the defect formation owing to high-temperature plasma generated on particle surfaces, and the deformation-induced defect is well known to induce dynamic grain growth.[13,14] The defect produced by both heating and deformation may therefore accelerate the grain growth during SPS processing.

The accelerated grain growth for high heating rates was confirmed in the present study, as illustrated in Fig. 3. For a heating rate of 8 °C/min and 50 °C/min, the grain size 0.21 μm is almost identical when the temperature reached 1150 °C. The grain growth rate during sintering, however, is higher for the more rapidly heated alumina. The grains heated at a rate of 50 °C/min grew to 0.99 μm for 2 h, whereas those heated at 8 °C/min grew to 0.34 μm for 5 h. A quite similar result was reported by Murayama and Shin,[12] and also during HIP by Besson and Abouf.[14] Although we did not quantitatively investigate the defect concentration, the defect related mechanism seems to be the rationale for the above heating-rate dependence of the grain size.

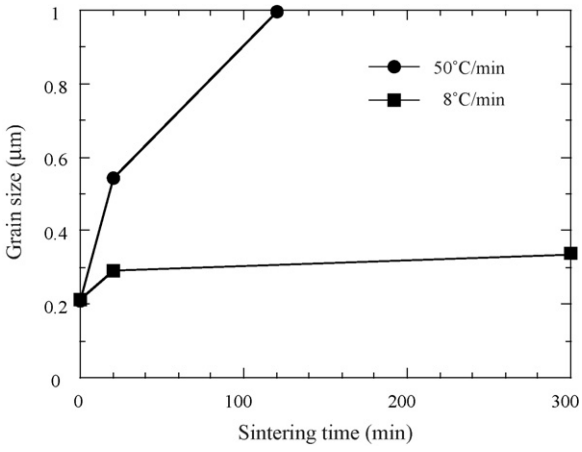

Fig. 3. Grain growth behavior at 1150 °C for two different heating rates.

Alternatively, the overheating of the alumina during SPS may be considered for the reason of the rate dependence. In actual, owing to its large volume, the graphite die was temporarily overheated up to 1155 °C and 1177 °C at a heating rate of 8 °C/min and 50 °C/min, respectively. However, the temperature difference between the two is only 22 °C and the overheated time is only about 2 min, which seems to be insignificant to affect the grain growth. Furthermore, the difference in the grain growth rate persists after 20 min, where the overheating effect should be vanished. Hence, it is difficult to attribute entirely the rate dependence of the grain growth to the overheating.

On the other hand, Stanciu et al.[6] reported a small grain size at rapid heating for the alumina sintered at 1100 °C for 2 min, which is opposite to the results of Zhou et al.[9] and Murayama and Shin,[12] and to the present study. They explained their results using the conventional equation of grain growth. However, the following consideration indicates that re-examination is necessary on their data and explanation. The ratio of the final grain size to the initial particle size of powder is 30–40 at a heating rate of 250 °C/min and 60–90 at 50 °C/min, which are too large compared to other results. In other SPS studies of alumina, under the condition of the heating energy less than 1200 °C × 20 min, the ratio does not exceed 7 in general, regardless of the heating rate and the initial particle size.[5,7–9,12] The largest ratio 7 was reported by Zhan et al.[7] for an initial particle size of 50 nm. A grain size of 6–9 μm at 1100 °C reported by Stanciu et al.[6] is generally obtained at temperatures of ≥1400 °C.

In conclusion, we consider that the heating-rate dependence of the grain size at 1150 °C can be attributed to the defect concentration produced by both heating and deformation. With increasing temperature, however, the effect of the defect concentration on grain growth becomes gradually vanished, so that the kinetic grain growth becomes to prevail. As a result, the grain size at ≥1300 °C is generally small for rapid heating.

3.2. Porosity

The size and the number of residual pores were decreased with decreasing heating rate. For low heating rates, fine pores smaller than 100 nm sparsely remained, whereas for high heating rates, numerous pores larger than 100 nm were frequently observed. The porosity also decreased with decreasing heating rate (Fig. 4), as in the case of the grain size (Fig. 1). The porosity was 0.59% at a heating rate of 100 °C/min, and decreased to

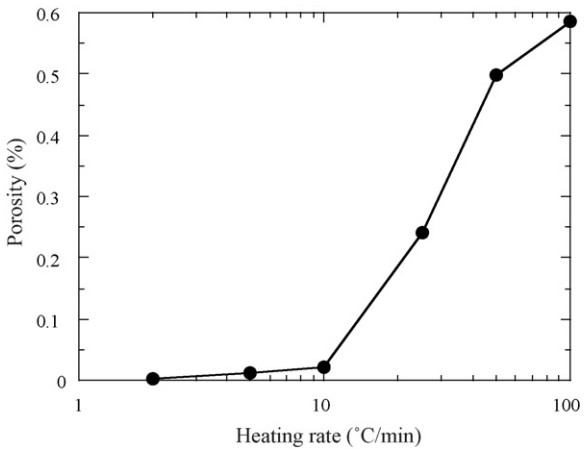

Fig. 4. Dependence of the porosity on the heating rate for sintering at 1150 °C for 20 min.

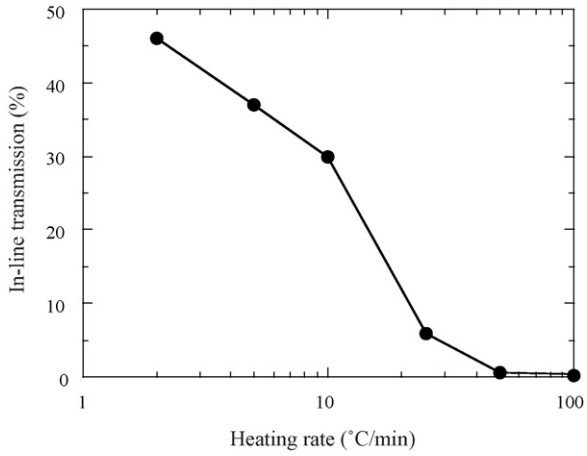

Fig. 6. Dependence of the in-line transmission on the heating rate for sintering at 1150 °C for 20 min.

0.02% at 10 °C/min and 0.002% at 2 °C/min. The heating-rate dependence of the porosity in Fig. 4 is quite similar to that of the grain size in Fig. 1. Low heating rates resulted in small grain size and high density in the present study.

In order to understand the effect of the heating rate, we only consider the final stage sintering. When the temperature reached 1150 °C, the porosity was 2.4% and 6.3% for a heating rate of 8 °C/min and 50 °C/min, respectively. After sintering for 20 min, the porosity decreased to 0.01% and 0.5%, and the initial grain size 0.21 μm (at zero sintering time) increased to 0.29 μm and 0.54 μm, respectively. During sintering at 1150 °C, the grain size were throughout smaller for 8 °C/min, as shown in Fig. 4, probably owing to a low defect concentration. Since a small grain size means a large grain-boundary area, the large boundary area along with the low porosity for slow heating may enhance grain-boundary diffusion and eventually densification. In addition, the small grain size lowers the flow stress for grain boundary sliding, and hence, deformation-induced densification can also be activated.

3.3. Transparency

As mentioned above, low heating rates resulted in small grain size and low porosity. Since transparency is inversely proportional to the grain size (in submicrometer grains) and the porosity,[4] the transparency of the present alumina increased with decreasing heating rate, as shown in Fig. 5. The alumina changed gradually the appearance from opaque to transparent with decreasing heating rate. All samples with a thickness of about 0.9 mm in Fig. 5 are 24 mm above the text, and the samples sintered at a heating rate of ≤10 °C/min satisfy the definition of transparency 'objects on the other side may be distinctly seen'.

The heating-rate dependence of the in-line transmission for a wavelength of 640 nm is shown in Fig. 6. The in-line transmission increases from 0.2% at a heating rate of 100 °C/min to 30% at 10 °C/min, and to 46% at 2 °C/min. From the increasing tendency of the in-line transmission with decreasing heating rate in Fig. 6, further heightened transparency may be anticipated at heating rates lower than 2 °C/min. We consider, however, that the in-line transmission 46% is around the maximum obtainable in the present SPS processing, because the transmission after sintering for 5 h was slightly increased but did not exceed 50%. In order to obtain an in-line transmission of ≥50% by SPS, a special pre-treatment of powder or mixing with additives may be necessary.

The dependence of the in-line transmission on the wavelength of light is shown in Fig. 7. As expected, the in-line transmission approaches the value of sapphire (86%) with increasing wavelength, whereas it decreases rapidly with decreasing wavelength. For a grain size of 0.29 μm (2 °C/min), the theoretical in-line transmission calculated by using the model of Apetz and Bruggen[4] for zero porosity is about 68%. Although the present in-line transmission (46%) lower than the theoretical value is mainly due to the residual porosity, it is comparable to the transmission of 40–57% obtained by using HIP for the alumina doped with 0.03 wt.% MgO.[1]

In order to achieve full density or extremely low porosity in alumina, Krell et al.[1,15] emphasized the importance of homogeneous powder dispersion before sintering. By homogenizing the powder using such techniques as stirring, ultrasonification

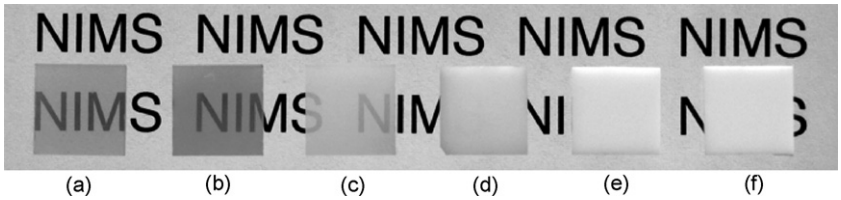

Fig. 5. Alumina ceramics sintered by SPS at a heating rate of (a) 2 °C/min, (b) 5 °C/min, (c) 10 °C/min, (d) 25 °C/min, (e) 50 °C/min and (f) 100 °C/min. The samples 0.9 mm thick are on the transparent polystyrene plate, and 24 mm above the text.

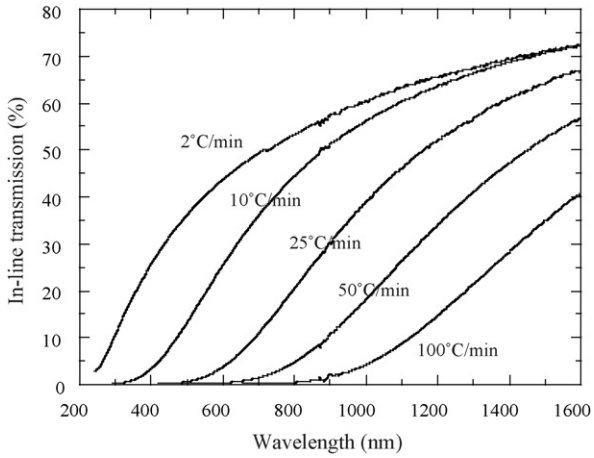

Fig. 7. In-line transmission of the alumina sintered at 1150 °C for 20 min. The sample thickness is about 0.9 mm.

and milling, they improved the final density and transparency. On the other hand, Chu et al.[16] found that the precoarsening of powder compact at low temperatures improves homogeneity, allows the powder to stay in the open porosity state longer, and inhibits grain growth during sintering. The microstructures resulting from the precoarsening + sintering were more uniform and finer than those resulting from the conventional sintering without precoarsening. By applying the precoarsening technique to hot pressing, Kim and Kishi[17] obtained a dense alumina with a four-point bending strength of 750 MPa. In the present study, we consider that in addition to the low defect concentration, an effect similar to the precoarsening may act on the powder during long-time (slow) heating at low temperatures, and the as-received alumina powder was homogenized by itself during SPS. Using the homogeneous powder dispersion together with the precoarsening may therefore improve the quality of the microstructure during SPS processing.

4. Conclusion

During SPS of alumina, low heating rates resulted in fine grain size, low porosity and high transparency: for sintering at 1150 °C for 20 min, a grain size of 0.29 μm, a porosity of 0.002% and an in-line transmission of 46% were obtained at a heating rate of 2 °C/min. The fine microstructure at low heating rates can be explained by using the assumption of low defect concentration, and the low porosity (high density) by the accelerated grain-boundary diffusion owing to a large gain-boundary area. We consider that slow heating also homogenized the powder during SPS, which should contribute to result in the fine microstructure and high density.

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