Fabrication and optical characterization of high-density Al_2O_3 doped with slight MnO dopant

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Effects of manganese oxide (MnO) addition on the densification of Al_2O_3 during sintering were studied. Although MnO is commonly used as a sintering aid for Al_2O_3 , it has not been used as a sintering aid to produce transparent alumina. High-density Al_2O_3 doped with slight MnO (> 99.5%) was obtained using a conventional powder processing method, with sintering at 1250°C for 24 h. The Al_2O_3 -0.05 mass% MnO exhibited optical total transmittance of 42% at 600 nm wavelength and three-point bending strength of 528 MPa. The transmittance was further improved to greater than 70% at 600 nm through hot isostatic pressing (HIP) after conventional sintering. The possibility of high-strength transparent alumina was demonstrated.

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1. Introduction

Transparent alumina (Al_2O_3) can be fabricated either in single-crystal (sapphire) or polycrystalline forms. Sapphire is used as a highly transparent material for many industrial and military applications, such as optical windows for lasers, spectrometers, armor parts, and IR-domes for infrared missile guidance systems. Polycrystalline transparent alumina has been increasingly available for optical applications since the early 1960s, when Coble¹⁾ invented transparent alumina. It has become a key material for high-pressure sodium vapor lamps and other optical instruments manufactured all over the world. The cost of manufacturing polycrystalline transparent alumina is much lower than that for sapphire because the former is easier to produce in large quantities.

Polycrystalline transparent alumina is normally produced through powder processing using high-purity and fine-particle-size alumina powder with the addition of a small amount of magnesium oxide (MgO); sintering is the key process to obtain a pore-free, highly transparent material. For this purpose, extremely high sintering temperatures, as high as 1900°C, and long holding times of several hours are applied under a high-vacuum or pure hydrogen atmosphere. Recently, various researchers attempted the fabrication of transparent alumina using new methods: slip-casting method, hot isostatic pressing (HIP), and microwave sintering.^{2)–4)}

In fact, MnO is commonly used as a sintering aid for Al_2O_3 . Doping of MnO^{5),6)} increased the densification rate. Recently, the dopant effect on grain boundary diffusivity in Al_2O_3 has been reported as related to the ionicity: the grain boundary diffusivity of Mn-doped Al_2O_3 is higher than that doped with Mg, Sr, Lu, Ti, Zr, or Pt.⁷⁾ In this study, the fabrication of transparent alumina was attempted using MnO as a dopant to improve densification during sintering. This study is intended to examine fabrication of transparent alumina by doping MnO.

2. Experimental procedure

Commercial α - Al_2O_3 powder (TM-DAR; Taimei Chemicals Co., Ltd., Japan) with an average grain size of 200 nm and MnO powder (Kojundo Chemicals Co., Ltd., Japan) with an average grain size of 500–1000 nm were used as starting materials. The α - Al_2O_3 powder was mixed with 0–0.4 mass% MnO powder using a conventional ball mill in ethanol for 24 h. Ball milling was carried out using a polyethylene pot (600 ml) and 350 g of high-purity Al_2O_3 balls. After drying, the milled powder mixture was pressed uniaxially at 20 MPa and cold isostatically pressed (CIPed) at 200 MPa. The compacts were sintered at a temperature between 1200 and 1400°C for 2 h.

The densities of sintered samples were measured using Archimedes' method, and the relative densities were obtained by normalizing with the theoretical density of α - Al_2O_3 , i.e. 3.99 Mg/m³.⁸⁾ Microstructures were examined using scanning electron microscopy (SEM). The average grain size of Al_2O_3 was determined according to the linear intercept method.⁹⁾

The sintered samples were cut and their flat surfaces were polished to 0.5-mm thickness for optical-transmittance measurement. The optical total transmittances were measured for wavelengths of 200–800 nm using an ultraviolet/visible-spectrum spectrometer.

The sintered samples were cut, then ground using diamond wheels for flexural tests. The dimensions of all specimens were 3 × 4 × 40 mm. The flexural strength was evaluated using a three-point bending test with a 30 mm span and cross-head speed of 0.5 mm/min.

3. Results and discussion

Figure 1 shows the variation of the relative density with sintering temperature for Al_2O_3 doped with 0–0.4 mass% MnO. The density of sintered samples increased markedly with the amount of MnO dopant and sintering temperature. At sintering temperatures higher than 1300°C, the densities were higher than 99.5%, except for that of pure Al_2O_3 . From the nearly full density, we inferred the possibility of fabricating transparent alumina by

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doping MnO. The density was further examined at a low sintering temperature and a long holding time. **Figure 2** shows the relative density with holding time for Al_2O_3 doped with 0–0.4 mass%MnO at 1250°C. At this temperature, all samples except

Fig. 1. Variation of the relative density with sintering temperature for Al_2O_3 doped with 0–0.4 mass%MnO.

Fig. 2. Variation of the relative density with holding time for Al_2O_3 doped with 0–0.4 mass%MnO, sintered at 1250°C.

Fig. 3. Variation of the average grain size with the amount of MnO dopant after sintering at 1250°C for 24 h.

for pure Al_2O_3 were densified to greater than 99.5% after 24 h. These data indicate that the densification rate was markedly accelerated by the doping of MnO at low sintering temperatures.

Figure 3 shows the variation of the average grain size for Al_2O_3 doped with 0–0.4 mass%MnO sintered at 1250°C for 24 h. The average grain size increased concomitant with the increase of the dopant, but remained less than 3.5 μm , even for the sample doped with 0.4 mass%MnO. SEM micrographs of some samples are shown in **Fig. 4**. Abnormal grain growth was not observed in any of the samples doped with 0–0.4 mass%MnO. The flexural strengths for pure Al_2O_3 and those doped with 0.05, and 0.2 mass%MnO sintered at 1250°C for 24 h are shown in **Table 1**. The measurement was limited to the specimens doped up to 0.2 mass%MnO, because, as will be

Fig. 4. SEM micrographs of Al_2O_3 doped with (a) 0, (b) 0.05, and (c) 0.2 mass%MnO sintered at 1250°C for 24 h.

Table 1. Flexural Strength of Al_2O_3 Undoped and Doped with MnO, Sintered at 1250°C for 24 h

Dopant Content (mass%)	0	0.05	0.2
Flexural strength (MPa)	636 ± 81	528 ± 82	465 ± 34

shown later, further doping considerably decreased the optical total transmittance. The flexural strength of Al_2O_3 decreased gradually with increased amounts of MnO. The result seems to be explained mainly by the grain growth of Al_2O_3 , although grain boundary segregation of Mn and the effect of slight pore coarsening may be partly in effect.

Although the strength was decreased by doping MnO, the Al_2O_3 doped up to 0.2 mass% MnO retained a strength higher than 450 MPa, which is still considerably stronger than commercial products (200 MPa) obtained by conventional sintering processes.¹⁰⁾ The high strength also seems to arise from the finer grains ($< 3.3 \mu\text{m}$), attributable to the low sintering temperature, than those of commercial products ($20 \mu\text{m}$).

Figure 5 shows photographs of Al_2O_3 doped with 0–0.4 mass%MnO sintered at 1250°C for 24 h. In contrast with the white color of pure Al_2O_3 , the sample became slightly pink when 0.05 mass%MnO was doped. The depth of the red color of samples increased concomitant with increasing dopant content. As shown in Fig. 5, pure and slightly doped samples (< 0.1 mass%) were translucent. The optical total transmittances were measured using an ultraviolet/visible-spectrum spectrometer for the 200–800 nm range. As shown in Figs. 6(a) and 6(b), all samples except for pure Al_2O_3 , showed no transmittance between 200 and 300 nm. With increasing dopant content, the transmittance decreased at all wavelengths. The MnO doping was characterized by the transmittance drop at wavelengths of $500 \text{ nm} \pm 50 \text{ nm}$. Furthermore, such a trend became stronger with increasing dopant contents. Except for wavelengths of $500 \text{ nm} \pm 50 \text{ nm}$, the transmittance for the sample doped with 0.05 mass%MnO was the highest among all samples: its value was about 42% at 600 nm, as shown in Fig. 6(a).

However, the transmittance of highly doped samples was lower than that of pure Al_2O_3 because these increased the depth of the red color with increasing dopant content. Finally, hot isostatic pressing (HIP) treatment after conventional sintering processes was performed to explore the possibility of fabricating transparent MnO-doped Al_2O_3 . Figure 6(b) shows the total trans-

Fig. 5. Photographs of Al_2O_3 doped with 0–0.4 mass%MnO, sintered at 1250°C for 24 h. From left, 0, 0.05, 0.1, 0.2, 0.3, and 0.4 mass%MnO doped samples; all are 0.5 mm-thick.

Fig. 6. Optical total transmittances of (a) Al_2O_3 undoped and doped with 0–0.4 mass%MnO sintered at 1250°C for 24 h and (b) Al_2O_3 doped with 0.05 mass%MnO fabricated by HIP processing at 1400°C for 2 h at 100 MPa after sintering at 1250°C for 24 h.

mittances for Al_2O_3 doped with 0.05 mass%MnO fabricated by HIP processing at 1400°C for 2 h at 100 MPa after sintering at 1250°C for 24 h. At all wavelengths, except for those under 300 nm, the transmittance increased by 30% and attained a transmittance that was higher than 70% at 600 nm. The result suggests that the elimination of smaller pores by HIP is effective to improve the transparency, although it was difficult to clarify the evidence by the SEM micrographs and the variation of the relative densities in this study. Although the transparency of the present material must be further improved for commercial use, the possibility of high-strength transparent alumina was demonstrated.

4. Conclusions

Effects of manganese oxide (MnO) addition on the densification of Al_2O_3 during sintering were studied. The densification rate was markedly accelerated by doping a small amount of MnO through conventional powder processing and sintering at 1250°C for 24 h. The optical transmittance of Al_2O_3 was improved by MnO doping; the highest transmittance was obtained with 0.05 mass%MnO. The optical total transmittance was 42% at 600 nm wavelength. The three-point bending strength was 528 MPa. The transmittance was further improved to greater than 70% at 600 nm through hot isostatic pressing (HIP) after conventional sintering. The possibility of high-strength transparent alumina was demonstrated.

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