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Improvement of translucency in Al_2O_3 ceramics by two-step sintering technique

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Abstract

Pure, 140, 500, and 2500 ppm MgO-doped Al_2O_3 specimens were sintered at 1700 °C in a vacuum with and without pre-sintering heat treatment (HT) at 800 °C for 50 h in air. Pre-sintering HT improved the transmittance in the visible (400–700 nm) range significantly. This enhanced transmittance was explained in terms of the removal of residual pores and the homogenization of the microstructure due to the lowering of the boundary mobility as a result of the MgO addition and the suppression of local densification through a pre-coarsening step.

Keywords: Sintering; Optical properties; Al_2O_3; Lamp envelopes

1. Introduction

Translucent polycrystalline Al_2O_3 ceramics is being used in high-pressure sodium lamp envelopes due to its high translucency, gas-impermeable properties, chemical stability, mechanical strength, and cost-effectiveness. The high transmittance, which is the primary goal of lamp-envelope application, requires special efforts to eliminate any light scattering centers such as residual pores, grain boundaries, secondary phases, and rough surfaces.[1–3] The main approaches for obtaining translucency are full densification and grain-size control.[4] In addition, uniformity of the microstructure should be taken into account as another key factor when one considered that the transmittance is a sensitive function of the grain sizes.[3]

Thus far, the addition of trace concentrations of MgO is known to suppress abnormal grain growth (AGG)[5] and the MgO concentration needed to prevent AGG depends critically on other impurities such as CaO and SiO_2.[5–7] The homogeneity of the microstructure and densification can be enhanced by adding MgO. It was reported that a two-step sintering technique can be also used as an efficient route to attain a homogeneous microstructure and to decrease the number of closed pores.[8] This study combined these two efficient approaches to improve the translucency of polycrystalline Al_2O_3 ceramics. The pure and 140, 500, and 2500 ppm MgO-doped Al_2O_3 specimens were sintered at 1700 °C in a vacuum with and without pre-sintering heat-treatment (HT) at 800 °C for 50 h and their microstructure and transmittance were compared. The translucency was improved to a significant extent by pre-sintering HT. The reason for the enhanced transmittance was examined and discussed in terms of the grain-size distribution, porosity and MgO concentration.

2. Experimental

High purity α-Al_2O_3 (SM-8, 99.99%, average particle size = 340 nm, Baikowski Co., Ltd., Japan) powder was used as the raw material. The quoted impurity concentrations of Si, Ca, Na, K, Fe were 17, 2, 8, 12, 4 ppm, respectively. From the preliminary study, it was found that the addition of Mg_2SiO_4 rather than that of MgO induced more uniform microstructure. Thus, the sintering agent, MgO, was added in the form of $MgAl_2O_4$ (Yeeyoung Cerachem. Co. Ltd., Seoul, Korea) powder. The doping concentration of MgO was varied from 140 to 2500 ppm. The mixture of Al_2O_3 powder, $MgAl_2O_4$ powder, and C_2H_5OH was ball-milled for 24 h. The solvent was removed by rotatory evaporation. The soft aggregation was pulverized and the green compact was isostatically pressed at 173 MPa. A set of

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specimens were sintered in a vacuum furnace (vacuum level: 10^{-4} torr) at 1700 °C for 3 h. The heating and cooling rates were 3.3 and 14 °C/min, respectively. In order to investigate the effect of pre-sintering HT on the microstructural evolution, another set of specimens were pre-sintered at 800 °C for 50 h (heating and cooling rate: 10 °C/min) in air and then sintered at 1700 °C for 3 h in a vacuum. The apparent density of the sintered body was measured using the Archimedes method in deionized water. The sintered microstructure was observed by scanning electron microscopy (XL-30 FEG, FEI) after thermal etching at 1600 °C for 1 h. For grain size and grain-size distribution, ∼500 grains were analyzed using image analyzer software (Image-Pro Plus, MediaCybernetics, Inc., MD, USA). The transmittance was determined after polishing both sides of the sintered specimen using 1 μm Al_2O_3 until there was a mirror finish. The specimen thickness was fixed at 0.8 mm. The transmittance was measured in the 200–800 nm range using a UV–vis spectrophotometer (Lamba 19, Perkin-Elmer). The distance between the light source and the specimen was 7.5 cm and the distance between the specimen and detector was 4.5 cm.

3. Results and discussion

Fig. 1 shows the SEM microstructures of the pure and MgO-doped Al_2O_3 specimens sintered at 1700 °C with and without pre-sintering HT at 800 °C for 50 h. From the microstructures, the grain-size distribution and average grain size were calculated. The results are shown in Figs. 2 and 3, respectively. Coarse grains larger than 50 μm could be observed in the pure Al_2O_3 without pre-sintering HT (Fig. 1(a) and Fig. 2(a)). Note that many pores are located both on the grain boundaries and within the grains (see circled regions). No significant removal of the residual pores by HT was noted. In contrast, the pore size tends to increase slightly (see the arrows in Fig. 2(b)).

When the Al_2O_3 was doped with 140 ppm MgO, the grains larger than 40 μm disappeared and the grain-size distribution became narrower (Fig. 1(a) and (c) and Fig. 2(a) and (c)). In addition, the average grain size decreased from 15.63 to 13.05 μm (Fig. 3). Note that the scale bars in Fig. 1(a) and (c) are different. The addition of 500 and 2500 ppm of MgO narrowed the grain-size distribution and decreased the grain size further (Fig. 1(e) and (g) and Fig. 2(e) and (g)). The tendency of narrowing the grain-size distribution and decreasing the grain size by the addition of MgO was also valid for the specimens with pre-sintering HT (Fig. 1(b), (d), (f), (h), Fig. 2(b), (d), (f), (g), and Fig. 3).

Despite the intensive research, the role of MgO in the sintering of Al_2O_3 is unclear. However, it is generally acknowledged that the microstructure becomes more homogeneous and densification can be promoted by the addition of MgO. Moreover, the prevention of AGG[5] and a decrease in the grain size have been reported to be related to the decrease in the boundary mobility. This is important in the prevention of pore trapping within grains caused by rapid grain growth. Indeed, regardless of the pre-sintering HT process, it was very difficult to find the pores trapped within the grain in the MgO-doped specimens (Fig. 1(c)–(h)). The lowering of the boundary mobility by the addition of MgO can be also verified by the decrease in the grain size with increasing MgO concentration. Slow grain growth will be more advantageous in the removal of intergranular pores. In this respect, the decrease in boundary mobility by the addition of MgO will help the removal of residual pores as well as the homogenization of microstructure.

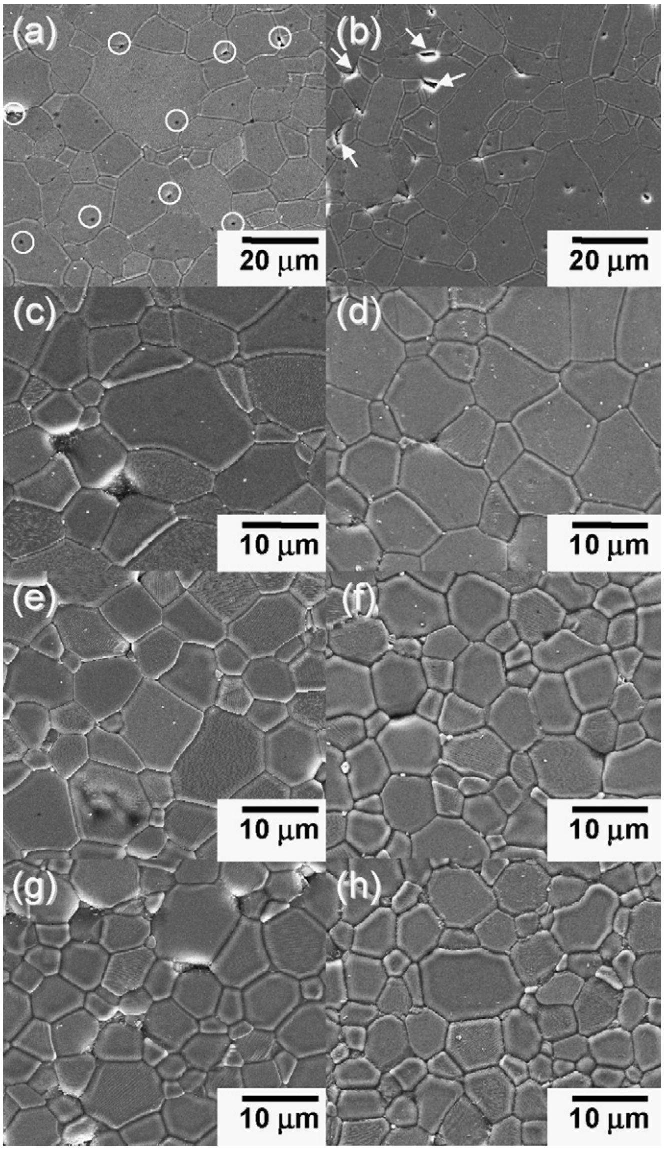

Fig. 1. SEM microstructures of pure and MgO-doped Al_2O_3 specimens sintered at 1700 °C in a vacuum with and without pre-sintering heat treatment (HT) at 800 °C for 50 h in air: (a) pure Al_2O_3, no HT, (b) pure Al_2O_3, HT, (c) 140 ppm MgO-doped Al_2O_3, no HT, (d) 140 ppm MgO-doped Al_2O_3, HT, (e) 500 MgO-doped Al_2O_3, no HT, (f) 500 MgO-doped Al_2O_3, HT, (g) 2500 MgO-doped Al_2O_3, no HT, and (h) 2500 MgO-doped Al_2O_3, HT.

SEM showed that the porosity decreased significantly with MgO addition (Fig. 1). However, a quantitative comparison of the amount of residual pores solely from the SEM microstructure was difficult. Moreover, the apparent densities were similar, 3.91 g/cm^3, for all specimens without HT, and 3.90, 3.91, 3.90 and 3.89 g/cm^3 for the pure, 140, 500, and 2500 ppm MgO-doped specimens after pre-sintering HT, respectively. This suggests that the change in the open porosity by HT is not remarkable and/or is difficult to estimate using the Archimedes

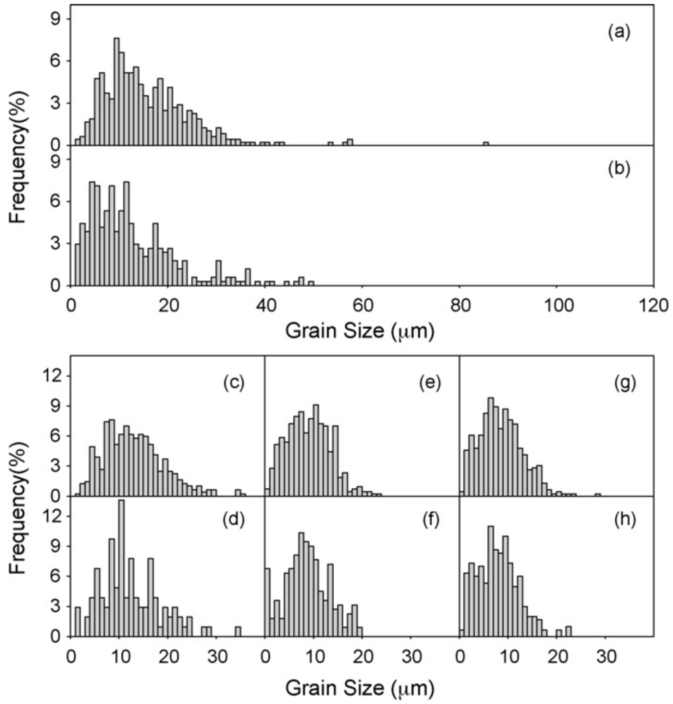

Fig. 2. Grain-size distribution of pure and MgO-doped Al_2O_3 specimens sintered at 1700 °C in a vacuum with and without pre-sintering heat treatment (HT) at 800 °C for 50 h in air: (a) pure Al_2O_3, no HT, (b) pure Al_2O_3, HT, (c) 140 ppm MgO-doped Al_2O_3, no HT, (d) 140 ppm MgO-doped Al_2O_3, HT, (e) 500 MgO-doped Al_2O_3, no HT, (f) 500 MgO-doped Al_2O_3, HT, (g) 2500 MgO-doped Al_2O_3, no HT, and (h) 2500 MgO-doped Al_2O_3, HT.

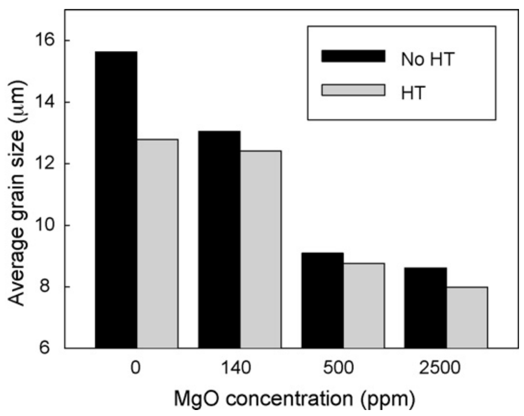

Fig. 3. Average grain size of pure and MgO-doped Al_2O_3 specimens sintered at 1700 °C in a vacuum with and without pre-sintering heat treatment (HT) at 800 °C for 50 h in air.

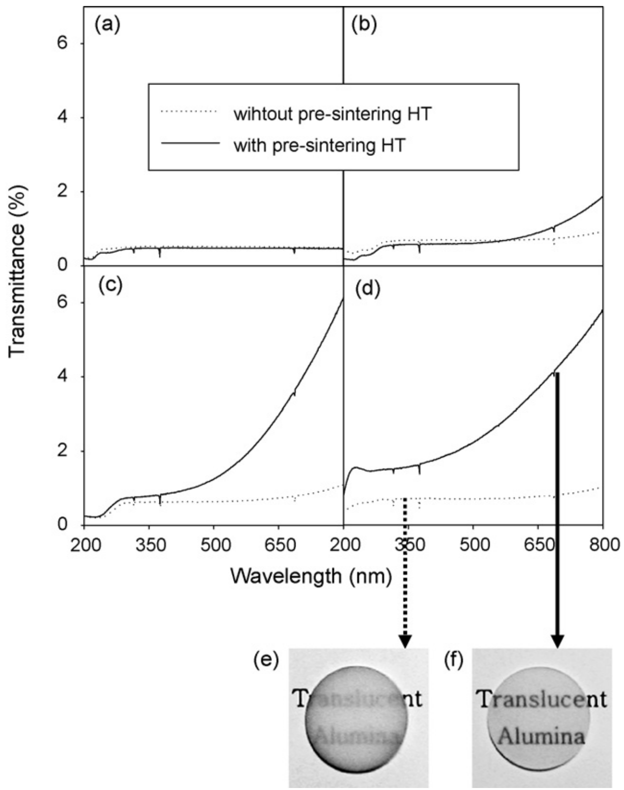

Fig. 4. Transmittance of pure and MgO-doped Al_2O_3 specimens sintered at 1700 °C in a vacuum with and without pre-sintering heat treatment (HT) at 800 °C for 50 h in air: (a) pure Al_2O_3, (b) 140 ppm MgO-doped Al_2O_3 (c) 500 MgO-doped Al_2O_3, and (d) 2500 MgO-doped Al_2O_3, (e) photograph of 2500 MgO-doped Al_2O_3 without HT, and (f) photograph of 2500 MgO-doped Al_2O_3 with HT.

method. Therefore, the transmittance was measured at wavelengths ranging from 200 to 800 nm (Fig. 4). In the pure Al_2O_3 specimen, almost no transmittance was observed in the visible range (400–800 nm), which was not improved by pre-sintering HT (Fig. 4(a)). In the 140 ppm MgO-doped Al_2O_3 specimen, HT increased the transmittance near 600–800 nm significantly. The HT improved the transmittance to a greater extent in the 500 and 2500 ppm MgO-doped specimens. Note that a transmittance of up to 6% can be attained at the ~800 nm range (in Fig. 4(c)). The improvement in transmittance at 600–800 nm was higher than that at 400–600 nm (in Fig. 4(c) and (d)). Note that the transmittances at 600 nm were 0.475%, 0.605%, 1.246%, and 2.223% for pure, 140, 500, and 2500 ppm MgO-doped specimens with a pre-sintering HT, respectively (Fig. 4(a)–(d)). This clearly shows that the addition of MgO plays another important role in improving the transmittance. In Fig. 4(e) and (f), it can be clearly seen that pre-sintering HT markedly improves the translucency of the 2500 ppm MgO-doped Al_2O_3 specimen.

The effect of the pre-sintering HT on microstructural evolution was examined by Lin et al.[8] They found that the average pore size of a pre-sintered compact increases after the heat treatment at 800 °C for 50 h and the pore-size distribution becomes narrower. At the same sintered density, the specimen with the pre-coarsening step showed less closed porosity and a more homogeneous microstructure than that without. The key idea of pre-coarsening is to eliminate the finest particles that might induce local densification. When the finest particles densify faster, the pore size becomes uneven and some of the pores become trapped within the grains. In contrast, the pre-coarsened particles can delay the pinch-off of the continuous pore channel to a later stage of sintering. This leads to a significant decrease in residual porosity.

Indirect evidence for the delay of pinch-off of the continuous pores can be found in the change in the grain size. The use of HT at 800 °C for 50 h prior to sintering process provides more thermal energy. Accordingly it should increase the grain size. However, Lin et al.[8] observed a decrease in grain size by additional HT. From the later onset of densification, the higher final density, and lower closed porosity of the specimen with HT, they explained the decrease in the grain size in terms of the pore hindering grain-boundary motion. There are many reports showing that the pores can drag the grain boundary and decreases the grain size.[9] In order to check the above contribution, the change in the average grain size by HT was measured (Fig. 3). Indeed, the average grain size decreased with HT and this tendency was substantial. This suggests that the pinching-off of pores occurred at the later stage of sintering and more residual pores can be removed by pre-sintering HT. This is supported by marked increase in the transmittance by HT in Fig. 4(b)–(d). The higher improvement of transmittance at 600–800 nm is thought to be related with the pore removal.

In the pure Al_2O_3 specimen, the grain-size distribution becomes slightly narrower by HT. However, the reason for the appearance of elongated grains in the specimen with HT (Fig. 1(b)) is unclear. Although the detailed mechanism requires further study, the following can be suggested. Even in the highly pure Al_2O_3 specimen, the grain morphology tends to be elongated and AGG occurs frequently. Both grain elongation and AGG can be triggered by a trace concentration of CaO or SiO_2 impurities.[6,10] Accordingly, SiO_2 or CaO contamination of the compact during HT at 800 °C for 50 h from the furnace or crucible might be a possible reason. The MgO doping is known to prevent AGG and make the grain morphology more isotropic,[11] which explains the isotropic morphology of the MgO-doped specimens with HT (Fig. 1(d), (f), and (h)).

The above results show that a combination of MgO doping and two-stage sintering process can be used to attain a high degree of translucency in polycrystalline Al_2O_3. The advantageous aspect of MgO doping was the prevention of AGG and the decrease in the boundary mobility, which can help the removal of residual pores. In comparison, the pre-coarsening at 800 °C for 50 h suppressed local densification between the finest particles and the early pinch-off of closed pores. This decreased the number of closed pores and produced a uniform microstructure. Both MgO doping and two-step sintering decreased the grain size, which might be disadvantageous in obtaining a high translucency in the grain-size range of 10–20 μm. However, positive effects such as the removal of closed pores and homogenization of the microstructure are believed to play a larger role than the negative grain-boundary effect.

4. Conclusions

MgO doping and pre-sintering heat treatment (HT) were combined to accomplish a high translucency in polycrystalline Al_2O_3 ceramics. The pure Al_2O_3 specimen did not show any improvement in transmittance by pre-sintering HT, while the transmittance in the visible wavelength regime was greatly increased by pre-sintering HT in 140, 500, and 2500 ppm MgO-doped Al_2O_3 specimens. The suppression of local densification at the early stage of sintering by pre-sintering HT and the removal of residual pores at the later stage of sintering both by pre-sintering HT and MgO doping were suggested to be the primary reason for the enhanced transmittance.

Acknowledgements

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