Densification Behavior of Ti-Doped Polycrystalline Alumina in a Nitrogen-Hydrogen Atmosphere

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The densification behavior during sintering of 0.1 mol% TiO₂-doped Al₂O₃ was measured in either an air or N₂ + 5%H₂ gas atmosphere at the sintering temperature of 1573–1673 K. The grain boundary diffusivity was evaluated from the densification rate. High-resolution transmission electron microscopy (HRTEM) and nano-probe energy-dispersive X-ray spectroscopy (EDS) analyses revealed that the doped Ti cations segregate in the vicinity of the grain boundaries in the Al₂O₃. An electron energy loss spectroscopy (EELS) investigation indicated that the valence state of Ti in the Al₂O₃ sintered in the reducing atmosphere was close to +3. The grain boundary diffusivity in undoped Al₂O₃ was insensitive to the atmosphere, but was enhanced by the grain boundary segregation of Ti⁴⁺. The grain boundary diffusivity of alumina in the reducing atmosphere was, however, retarded by the Ti³⁺-doping. The retarded diffusivity by Ti³⁺-doping must be related to the lack of aluminum vacancies and the large ionicity of Ti-O compared to Al-O. [doi:10.2320/matertrans.MC200829]

(Received November 5, 2008; Accepted January 19, 2009; Published April 25, 2009)

Keywords: alumina, titanium-doped alumina, sintering, grain boundary, diffusivity

1. Introduction

High-temperature matter transport phenomena, such as densification during sintering in fine-grained, polycrystalline Al₂O₃, is often rate-controlled by grain boundary diffusion.^{1–4)} For example, in the hot-isostatic pressing diagram of Al₂O₃ constructed by Ashby's group,¹⁾ the grain boundary diffusion is the predominant process over a wide range of temperatures and pressures. In addition, it is well-known that the sintering behavior in alumina is sensitive to small levels of doping of various cations and the atmosphere during sintering;^{2–7)} for instance, the translucent alumina polycrystal is generally fabricated by sintering in a H₂ atmosphere.⁷⁾ The dependence of the grain boundary diffusivity on the dopant cations and the sintering atmosphere is therefore important information for fabricating high-performance Al₂O₃ ceramics. In fact, many studies have been conducted on the effect of sintering aids on the sintering of alumina. In contrast, only a few studies have been conducted on the effect of the sintering atmosphere on the sintering behavior.

The grain boundary diffusivity in Al₂O₃ has been previously estimated from neck growth during the initial stage of sintering,⁸⁾ creep deformation^{9,10)} and densification rate during the final stage of sintering^{2,11)} owing to the difficulties in the direct measurement of the grain boundary diffusivity by the tracer method.¹²⁾ Our group has recently measured the grain boundary diffusivity of various kinds of cation-doped alumina from the densification rate during the sintering experiment by using a scanning-laser micrometer system.⁶⁾ This study aims to measure the densification behavior of 0.1 mol% TiO₂-doped Al₂O₃ during sintering in either an air or N₂ + H₂ atmosphere as the first step of elucidating the effect of atmosphere on the sintering of alumina. The microstructure and valence state of Ti in the present materials were also investigated.

2. Experimental Procedure

The materials used in this study were undoped, high-purity Al₂O₃ and 0.1 mol% TiO₂-doped Al₂O₃. Commercially available α -Al₂O₃ powder with a purity of 99.99% and average particle size of 130 nm (TM-DAR; Taimei Chemistry) was used as the base material. The dopant was titanium oxide (nano-powder; Aldrich) with a particle size of 25–70 nm and purity of 3N. The Al₂O₃ powders and the dopant oxide were ball-milled using alumina balls in ethanol for 24 h, dried and sifted through a 60 mesh sieve for granulation. The green compacts were prepared by pressing the mixed powders into a cylindrical shape at a pressure of 30 MPa, and then isostatically pressed at a pressure of 400 MPa. The dimensions of the samples were about 15 mm in diameter and about 18 mm in length.

The sintering experiment was carried out in an alumina tube furnace that was externally heated by a molybdenum disilicide heater in either air or flowing N₂ + 5%H₂ gas (1atm) atmosphere; it has been reported that sintering in a N₂ + H₂ atmosphere with a H₂ content of 2–8% is feasible for the fabrication of translucent alumina polycrystals.⁷⁾ Specimen shrinkage was measured using a laser-scanning micrometer with a resolution of $\pm 3 \mu\text{m}$ (LS-7070; Keyence, Japan) from room temperature to the sintering temperature of 1573–1673 K. Figure 1 shows a schematic illustration of the furnace and attached laser-scanning system. The semiconductor laser generator projects a strip-shaped beam through the alumina tube to the detector at a wavelength of 520 nm with laser scans of 2400 scans/s. The specimen shrinkage was calculated from the time-dependent diameter of the cylindrical specimen L . The temperature of the specimen was measured by a Pt-PtRh thermocouple placed close to the specimen in the alumina tube. The specimen was heated to its sintering temperature at 10°C/min then held for 2 h.

The microstructures of the present materials were observed by scanning electron microscopy (SEM) and high-resolution

Fig. 1 A schematic illustration of the furnace and scanning-laser micro-meter used for the measurement of the densification behavior.

Table 1 Average grain size of undoped and 0.1 mol% TiO_2 -doped Al_2O_3 s sintered in either the air or $\text{N}_2 + \text{H}_2$ gas atmosphere.

Average grain size/(μm)					
Material		undoped-Al ₂ O ₃		Al ₂ O ₃ + TiO ₂	
Atmosphere		Air	N ₂ + 5%H ₂	Air	N ₂ + 5%H ₂
Sintering temperature/K	1573	0.83	0.73	1.20	0.61
	1623	1.70	1.96	1.97	1.45
	1673	3.17	2.26	4.67	2.08

Fig. 2 SEM micrographs of undoped Al_2O_3 s sintered in the (a) air and (b) $\text{N}_2 + 5\%\text{H}_2$ atmosphere and 0.1 mol% TiO_2 -doped Al_2O_3 sintered in the (c) air and (d) $\text{N}_2 + 5\%\text{H}_2$ atmosphere. The sintering temperature was 1573 K.

transmission electron microscopy (HRTEM). The average grain sizes of the present materials were measured by the linear intercept method based on more than 300 grains in the SEM photographs. The TEM specimens were prepared using standard techniques involving mechanical grinding to a thickness of less than 0.1 mm, and ion beam milling to an electron transparency at about 4 kV. For analysis of the Ti distributions in the Al_2O_3 , an energy-dispersive X-ray spectroscopy (EDS) analysis was also performed using the Noran Voyager system attached to a Topcon EM-002BF field emission microscope with a focused beam size of about 1 nm. The electron energy loss spectrometry (EELS; Enfina spectrometer, Gatan Co., Ltd.) measurements were carried out in the HRTEM at twelve different grain boundaries in each sample with the probe size of about 1 nm. The full width at half maximum of the zero-loss peak was 1.4 eV under the present condition, and the energy resolution of the EELS was 0.2 eV.

3. Results and Discussion

Figure 2 shows SEM images of the undoped Al_2O_3 s sintered in (a) air and (b) $\text{N}_2 + \text{H}_2$ atmosphere and of the 0.1 mol% TiO_2 -doped Al_2O_3 s sintered in (c) air and (d) $\text{N}_2 + \text{H}_2$. The sintering temperature was 1573 K for the

undoped and TiO_2 -doped Al_2O_3 s. The as-sintered materials consist of equiaxed alumina grains without any abnormal grain growth. In addition, the relative density of the sintered samples reached more than 99% for the examined sintering conditions. Table 1 shows the average grain size of the present materials sintered at 1573–1673 K. The grain sizes were in the range of 1–5 μm . In the Al_2O_3 s sintered in air, the grain size is increased by the Ti-doping at the examined sintering temperatures. In contrast, the grain sizes in the undoped and TiO_2 -doped Al_2O_3 s sintered in the $\text{N}_2 + \text{H}_2$ atmosphere are smaller than those in the materials sintered in air. The sintering in the reducing atmosphere can effectively suppress the grain size of the alumina.

The HRTEM observations indicated that no second phase particle or amorphous layer exists at the grain boundary of the TiO_2 -doped Al_2O_3 s sintered in the air and $\text{N}_2 + \text{H}_2$ gas atmospheres. Figure 3 shows the EDS spectra obtained at a grain boundary, at 5 nm and 10 nm from the grain boundary, and at the grain interior in the TiO_2 -doped Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$ at 1573 K. The size of the electron beam was about 1 nm. Ti cations can be detected at the grain boundary and slightly detected 5 nm from the grain boundary, but cannot be observed at 10 nm from the grain boundary and the grain interior. These results indicate that the doped Ti cations

Fig. 3 EDS spectra obtained at the grain boundary, at 5 nm and 10 nm from the grain boundary, and the grain interior in the Ti-doped Al_2O_3 sintered in the $\text{N}_2 + \text{H}_2$ atmosphere at 1573 K.

Fig. 4 An EELS spectrum acquired at the grain boundary in the Ti-doped Al_2O_3 sintered in the $\text{N}_2 + \text{H}_2$ atmosphere at 1573 K.

segregate in the vicinity of the grain boundaries in Al_2O_3 . Our previous studies revealed that a small amount of doped cations tends to segregate in the vicinity of the grain boundaries in polycrystalline Al_2O_3 sintered in air.^{13–17} The present result of the TiO_2 -doped Al_2O_3 sintered in the reducing atmosphere is consistent with the previous reports for that sintered in air.

Figure 4 shows an EELS spectrum for the TiO_2 -doped Al_2O_3 s sintered in the $\text{N}_2 + \text{H}_2$ atmosphere at 1573 K. The $\text{Ti-L}_{2,3}$ and O-K edges can be seen in the spectrum, though the intensity of the $\text{Ti-L}_{2,3}$ edge is fairly weak compared to the O-K edge. Figure 5(a) shows the typical electron energy-loss near-edge fine structure (ELNES) of the $\text{Ti-L}_{2,3}$ edges obtained from the TiO_2 -doped Al_2O_3 s sintered in the air and $\text{N}_2 + \text{H}_2$ atmospheres at 1573 K. For comparison, the

Fig. 5 (a) $\text{Ti-L}_{2,3}$ ELNESs acquired at the grain boundaries in the Ti-doped Al_2O_3 s sintered in the air and $\text{N}_2 + \text{H}_2$ atmospheres at 1573 K. (b) The reference data of $\text{Ti-L}_{2,3}$ ELNESs of Ti_2O_3 and Ti^{4+} in the octahedral crystal field.¹⁷⁾

reference data of $\text{Ti-L}_{2,3}$ edge ELNESs for Ti_2O_3 (Ti^{3+}) and Ti^{4+} in octahedral crystal field are shown in Fig. 5(b).¹⁸⁾ A previous study of the TiO_2 -doped Al_2O_3 single crystal indicates that annealing in air converts the titanium to a valence state of Ti^{4+} .¹⁹⁾ Therefore, the Ti in the present Al_2O_3 sintered in air must be in the quadrivalent state. The $\text{Ti-L}_{2,3}$ edge of the Al_2O_3 sintered in air in Fig. 5(a) probably reflects the Ti^{4+} state, though the present $\text{Ti-L}_{2,3}$ edge ELNES for the Al_2O_3 sintered in air is observed at about 1 eV higher energy than the reference data of Ti^{4+} . On the other hand, the $\text{Ti-L}_{2,3}$ edge in the TiO_2 -doped Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$ is observed at 2–3 eV lower energy in comparison to the TiO_2 -doped Al_2O_3 sintered in air. The $\text{Ti-L}_{2,3}$ edge in the Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$ has a tendency to be observed at 1–3 eV lower energy for all the examined grain boundaries. In addition, a small additional peak at 459–461 eV (indicated by the black inverted triangle in Fig. 5(a)) is more apparent in the $\text{Ti-L}_{2,3}$ edge of the Al_2O_3 sintered in air. The differences in the ELNESs are perhaps attributed to the valence state of Ti. It has been pointed out that the $\text{Ti-L}_{2,3}$ edge in Ti_2O_3 shifts to the low energy side compared to the $\text{Ti-L}_{2,3}$ ELNES of Ti^{4+} .¹⁸⁾ In addition, the first peak at 458 eV (indicated by the black inverted triangle in Fig. 5(b)) is prominent in Ti^{4+} in comparison with Ti_2O_3 .¹⁸⁾ From the differences in the

Fig. 6 The change in the relative density during sintering in the undoped, high-purity Al_2O_3 and Ti-doped Al_2O_3 sintered in either the air or $\text{N}_2 + \text{H}_2$ atmosphere at 1573 K. The temperature of the specimen is also depicted.

reference Ti- $\text{L}_{2,3}$ ELNESs, the valence state of Ti in the TiO_2 -doped Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$ is probably closer to +3, rather than +4.

Figure 6 shows the change in the relative density during sintering of the undoped and 0.1 mol% TiO_2 -doped Al_2O_3 s in either the air or $\text{N}_2 + \text{H}_2$ at the sintering temperature of 1573 K. The temperature of the specimens is also depicted by the dotted line in Fig. 6. Rapid densification begins at the temperature of around 1273–1373 K in all of the materials, and the relative density becomes greater than 99% after the sintering. The densification of the undoped and TiO_2 -doped Al_2O_3 s is enhanced by the sintering in the reducing atmosphere. The densification rate of Al_2O_3 seems to be retarded by the doping of TiO_2 in both the air and $\text{N}_2 + \text{H}_2$ atmospheres. It has been reported that the grain boundary diffusion dominates the densification rate in Al_2O_3 for a grain size of less than $10\text{ }\mu\text{m}$.²⁰⁾ Since the densification is rate-controlled by the grain boundary diffusivity, and since the doped Ti cations tend to segregate at the grain boundaries, the origin of the TiO_2 -doping effect on the densification behavior must result from a change in the grain boundary diffusivity. However, because the grain size of the present materials depends on the TiO_2 -doping and other sintering conditions, it is necessary to examine the grain boundary diffusivity from the densification rate.

Final-stage sintering, in which residual pores are at multiple junctions,²¹⁾ can be theoretically described by the rate equation proposed by Ashby's group;^{1,22)}

$$\dot{\rho} = \frac{54\Omega(\delta D_{\text{gb}} + rD_{\text{l}})}{kTd^3} 5(1 - \rho)^{1/2} \left(P_{\text{e}} - P_{\text{i}} + \frac{2\gamma}{r} \right) \quad (1)$$

where ρ is the relative density of the specimen, Ω is the atomic volume, δ is the boundary thickness, D_{gb} is the grain boundary diffusion coefficient, D_{l} is the lattice diffusion coefficient, r is the pore radius during the final stage of sintering, d is the grain radius, γ is the surface energy, P_{e} is the atmospheric pressure, P_{i} is the internal pore pressure, k is the Boltzmann constant and T is the absolute temperature. For pressure-less sintering, however, $P_{\text{e}} - P_{\text{i}}$ in the external pressure term ($P_{\text{e}} - P_{\text{i}} + 2\gamma/r$) is negligible, and the densification rate of high-purity Al_2O_3 takes place mainly by grain boundary diffusion.¹¹⁾ Taking into account the actual dis-

Fig. 7 An Arrhenius plot of the grain boundary diffusivity versus the inverse temperature in the undoped and Ti-doped Al_2O_3 s sintered in either the air or $\text{N}_2 + \text{H}_2$ atmosphere.

tribution of residual pores and decreasing number of pores during sintering, the densification rate eq. (1) has been modified as follows:¹¹⁾

$$\dot{\rho} = \left(\frac{0.3}{1 - \rho} \right)^{-4/3} \frac{54\Omega\delta D_{\text{gb}}}{kTd^3} 5(1 - \rho)^{1/2} \frac{2\gamma}{r}. \quad (2)$$

As such, for the present analysis, the modified densification rate eq. (2) was then used. The value of δD_{gb} can be estimated by minimizing the sum of the residue least squares of the densification curves using eq. (2). For the calculation, Ω of $4.25 \times 10^{-29} \text{ m}^3$,²²⁾ and γ of 1 J m^{-2} were used, and the values of d and r were approximated by those measured from the SEM micrographs of the as-sintered materials.

Figure 7 shows an Arrhenius plot of the estimated δD_{gb} versus the inverse temperature for the undoped and 0.1 mol% TiO_2 -doped Al_2O_3 s sintered in the air and $\text{N}_2 + \text{H}_2$ atmospheres. The grain boundary diffusivity in the undoped Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$ is slightly lower than that in the undoped Al_2O_3 sintered in air. It has been pointed out that the high-temperature creep rate in high-purity polycrystalline Al_2O_3 is insensitive to the oxygen partial pressure.⁵⁾ Therefore, it is possible that the grain boundary diffusivity is only slightly changed by the reducing atmosphere. On the other hand, the diffusivity in the TiO_2 -doped Al_2O_3 sintered in air is greater than that in the undoped Al_2O_3 s. The previous studies revealed that the Ti^{4+} (TiO_2) addition enhances the grain boundary diffusivity in alumina.^{6,16,23)} In addition, it has been reported that the addition of Ti^{4+} in Al_2O_3 is likely accommodated by the formation of aluminum vacancies.^{24,25)} According to the theoretical study on the energy of the point defects in the Ti^{4+} -doped Al_2O_3 ,²⁴⁾ the following process for dissolution of Ti^{4+} into Al_2O_3 should take place;

where $\text{Ti}_{\text{Al}}^{\bullet}$ is a titanium cation (Ti^{4+}) substituted for an aluminum cation (Al^{3+}) with a unit positive charge, V_{Al}''' is a vacant lattice site of Al^{3+} with three units of negative charge, and O_{O} is an oxygen anion (O^{2-}) on O^{2-} site. The formation of Al vacancies must increase the diffusivity of Al_2O_3 . The enhanced grain boundary diffusion due to the grain boundary

segregation of Ti^{4+} is consistent with the previous results. However, the grain boundary diffusivity in the TiO_2 -doped Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$ is lower than those of the undoped Al_2O_3 s. Assuming that the valence state of Ti is +3 in the TiO_2 -doped Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$, Ti^{3+} can segregate without any aluminum vacancies, and the grain boundary diffusivity should be almost unchanged. Therefore, the result in Fig. 7 indicates that another factor must influence the grain boundary diffusivity in alumina.

Our group has recently found out that the high-temperature creep rate and grain boundary diffusion coefficient in various kinds of cation-doped Al_2O_3 s correlate well with the ionicity that can be obtained by molecular orbital calculations.^{6,15,16} The previous results indicate that the high-temperature matter transport in Al_2O_3 increases with the decreasing absolute value of the effective ionic charge. The effective ionic valence in the Al cation and O anion must correspond to Coulomb's attractive force between the ions.²⁶ In addition, based on Pauling's electronegativity scale, the ionic bond is a major part of the binding force of Al_2O_3 .²⁶ It is therefore reasonable that the atomic diffusion in alumina is influenced by the ionic bonding strength. The Pauling electronegativity values of Al and Ti are reported to be 1.61 and 1.54, respectively.²⁷ The electronegativity is a semi-empirical index of the chemical bonding state, however, the low electronegativity of Ti suggests that a chemical bond between Ti and O gives rise to a large ionicity compared to the Al-O bond. The grain boundary segregation of Ti^{3+} may increase the ionicity and thereby decrease the grain boundary diffusivity of alumina.

It has recently been reported that the relative surface energy (normalized by surface energy of (0001) plane) in sapphire is increased by Ti-doping.²³ Because the surface and grain boundary energies must influence the densification behavior and related microstructural development during the sintering of alumina, the interfacial energies must be investigated in cation-doped polycrystalline alumina as a future study. In addition, further investigation into the chemical bonding state is necessary to provide more atomistic information on the high-temperature grain boundary diffusivity and to elucidate the effect of the atmosphere and cation-doping on the sintering of polycrystalline Al_2O_3 .

4. Conclusion

The densification behavior during sintering in 0.1 mol% TiO_2 -doped Al_2O_3 was measured in either an air or $\text{N}_2 + 5\%\text{H}_2$ gas atmosphere at the sintering temperatures of 1573–1673 K. In addition, the HRTEM-EDS analysis and EELS investigation were carried out to examine the distribution and valence state of Ti in Al_2O_3 . The results are summarized as follows:

- (1) Ti cations tend to segregate in the vicinity of the grain boundary in Al_2O_3 s sintered in air and $\text{N}_2 + \text{H}_2$ gas atmospheres.
- (2) The Ti- $L_{2,3}$ ELNES investigation suggests that the valence state of Ti in TiO_2 -doped Al_2O_3 sintered in $\text{N}_2 + \text{H}_2$ is close to +3, while the valence of Ti is +4 in Al_2O_3 sintered in air.
- (3) The grain boundary diffusivity in undoped Al_2O_3 was insensitive to the atmosphere, but was enhanced by the

grain boundary segregation of Ti^{4+} .

- (4) The grain boundary diffusivity of alumina was suppressed by Ti^{3+} -doping. The retarded diffusivity due to the grain boundary segregation of Ti^{3+} must be related to the lack of aluminum vacancies and the large ionicity of Ti-O compared to Al-O.

Acknowledgments

The authors wish to express their gratitude to the Ministry of Education, Culture, Sports, Science and Technology and the Japan Society for the Promotion of Science for the financial support by a Grant-in-Aid for Scientific Research on Priority Areas 474-19053008 and for Young Scientists (A)-19686042.

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