Texture Development in Alumina Composites by Slip Casting in a Strong Magnetic Field

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強磁場中スリッキャストにより作製したアルミナコンポジットにおける配向の発達

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Magnetic susceptibility is very small in feeble magnetic ceramics such as alumina, consequently, it had been very difficult to develop a textured microstructure in these ceramics by using a magnetic field. We have demonstrated, however, that textured microstructures in alumina, titania, zinc oxide can be prepared by colloidal processing in a high magnetic field followed by sintering. We applied this processing technique to alumina based composites. The degree of crystallographic texture was small in specimen sintered at the low temperature. The degree of orientation increased rapidly with increasing sintering temperature and depended on the grain size of alumina matrix. The grain size can be controlled by the content of YTZ particle as a second phase, the kind of dopant, sintering temperature, annealing temperature and annealing time.

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1. Introduction

The controlled development of texture has recently become a topic of interest in materials processing, because it allows improved tailoring of the properties of a material. Many studies have been reported for production of textured ceramics such as by hot forging,¹⁾ the Templated Grain Growth method,^{2),3)} the RBAO (reaction bonding of aluminum oxide) technique⁴⁾ and an extrusion process.⁵⁾ A magnetic field has been used for controlling the texture in ferromagnetic materials. A crystal possessing magnetic susceptibility anisotropy, when placed in a magnetic field, will rotate by the magnetic torque generated from the interaction between the anisotropic susceptibility and a magnetic field. The reduction of the magnetic energy on rotation is the driving force for magnetic alignment.

On the other hand, it has been generally difficult to apply a magnetic field to diamagnetic ceramics such as Al_2O_3 , TiO_2 and ZnO , because their susceptibility is extremely small. Recently, the development of superconducting magnet technologies has enhanced the application of strong magnetic fields to various academic fields. Some interesting phenomena in strong magnetic fields have been reported,^{6),7)} and magnetic fields have been used to produce a textured microstructure.⁸⁾⁻¹⁰⁾ We also demonstrate that a texture in diamagnetic ceramics can be controlled by colloidal processing with a high magnetic field.¹¹⁾⁻¹⁴⁾ Colloidal processing is very effective for consolidating fine particles by using repulsive surface forces to avoid heterogeneous agglomerates.¹⁵⁾ In order to control the texture using a magnetic field, a good dispersion of powder in a suspension is necessary because a strong attractive force between the agglomerated particles prevents each particle in a suspension from rotating in the magnetic field. Thus, a strong magnetic field was applied to dispersed particles in stable suspensions during slip casting, to cause the particles to rotate during consolidation.

In previous reports, we have pointed out that the degree of crystalline orientation increased during sintering, and we have

suggested that the crystalline orientation seems to be inseparably related to the microstructure.¹¹⁾⁻¹⁴⁾ This report studies the process of texture development in Al_2O_3 composites formed in a magnetic field and tries to clarify its relation to their microstructures with the controlled grain size.

In order to control the grain size of Al_2O_3 , it is possible that TiO_2 and MgO are doped and YTZ particles are dispersed as a second phase. During sintering of Al_2O_3 , the addition of TiO_2 in small amount is known to enhance densification and promote grain growth.¹⁶⁾⁻¹⁸⁾ By contrast, it is recognized that the addition of MgO in small amount effectively suppress the abnormal grain growth of Al_2O_3 ¹⁹⁾ and YTZ particles also prevent the Al_2O_3 grain growth by the pinning effect.^{20),21)}

2. Experimental procedure

A commercially available α - Al_2O_3 powder with average particle sizes of $0.15\ \mu\text{m}$, spherical and high purity was used as a starting material. 3 mol% Y_2O_3 stabilized tetragonal ZrO_2 (YTZ) spherical powder with an average particle size of 60 nm was used as the dispersed particle. TiO_2 and MgO spherical powders with average particle sizes of 30 nm and $0.1\ \mu\text{m}$, respectively, were used as additives. Aqueous suspensions containing 30 vol% solids of pure Al_2O_3 , Al_2O_3 to which various amounts of YTZ was added, Al_2O_3 with 0.25 mass% TiO_2 addition, and Al_2O_3 with 0.03 mass% MgO addition were prepared. Polyelectrolyte (poly(ammonium acrylate)) was suitably added at a ratio of 8.76×10^{-6} kg per weight of Al_2O_3 powders and 9.29×10^{-6} kg per weight of ZrO_2 powders into the suspension²²⁾ as a dispersant. The dispersant for TiO_2 and MgO is so little as to be neglected, because the amounts of them were too small. When suspensions consist of particles with different size and density, segregation occurs because of differences in the sedimentation rate during slip casting.^{23),24)} Segregation has been shown to be inhibited by hindering sedimentation if the solid content exceeds 30 vol% in suspension.²⁵⁾ The suspensions were ultrasonicated for 10 min and stirred for more than 8 h to disperse the powder.^{26),27)} Elec-

trosteric stabilization was used to disperse the fine particles and was achieved by polyelectrolyte adsorption on the surface of the particles.^{28),29)} The amounts of polyelectrolyte for maximum dispersion for each powder were determined from viscosity experiments done previously. The suspensions were then consolidated by slip casting after a vacuum desiccator was used to remove as many air bubbles as possible. A strong magnetic field of 10 T was applied to the suspension during slip casting at room temperature. The direction of the magnetic field was parallel to the casting direction. After slip casting in the magnetic field, the green compacts were further densified by cold isostatic pressing (CIP) at 392 MPa without disturbing the particle orientations. The green bodies were fired isothermally at the desired sintering temperature in air without a magnetic field.

Density measurements were made in kerosene by Archimedes method. The samples were polished and then thermally etched for microstructural analysis using a scanning electron microscope (SEM). Grain size measurements were made on the surface parallel to the magnetic field using the linear intercept method. And the average Al_2O_3 grain size perpendicular to a magnetic field was measured, because the anisotropic grain shape during grain growth was taken into consideration. The degree of crystalline texture was determined using the intensities of X-ray diffraction measurements and Eq. (1) below.

$$P = \frac{I_{006}}{I_{006} + I_{110}} \quad (1)$$

where I_{006} and I_{110} are the intensities from the 006 and the 110 reflections of Al_2O_3 phase on the surface perpendicular to the magnetic field, respectively. The degree of crystalline texture increases as the value of P approaches unity. The number of the grains with the basal plane completely perpendicular to the magnetic field is regarded as the orientation when we use Eq. (1).

3. Results and discussions

Figure 1 illustrates the XRD profiles of a specimen which was compacted by slip casting in a strong magnetic field of 10 T and sintered at 1873 K for 2 h. The profile of the random Al_2O_3 prepared without applying a magnetic field is shown in the bottom of Fig. 1. For comparison, in the surface perpendicular to the magnetic field (T -plane) of other textured Al_2O_3 , the intensities of the 00/ reflection peaks were very large and the intensity of the (1010) peak at an angle of 17.5° with the basal plane was also large. It was clear that even in Al_2O_3 with various additives addition the development of crystalline orientation could be controlled by the strong magnetic field and the basal plane of Al_2O_3 were perpendicular to the applied magnetic field. That is, the c axis was parallel to the magnetic field.

For the YTZ-dispersed Al_2O_3 shown in **Fig. 2**, in the surface perpendicular to the magnetic field (T -plane), the (006) and (0012) peaks appeared and the intensity of the (1010) peak was large. According to the International Center for Diffraction Data (ICDD), the relative intensity of 006 reflection is only hundredth part of that of 113 reflection which is main peak in Al_2O_3 , thus this (006) peak is hardly observed in general. In contrast with the T -plane, in the surface parallel to the magnetic field (S -plane), the intensities of (110) and (300) peaks were large. Accordingly, orientation of the Al_2O_3 matrix with the c axis parallel to the magnetic field was also confirmed, but the degree of crystallographic orientation was smaller than that of other Al_2O_3 in Fig. 1 and the random

Fig. 1. X-ray diffraction profiles of Al_2O_3 prepared by slip casting in a magnetic field (10 T), followed by sintering at 1873 K for 2 h, in the plane perpendicular to a magnetic field, which is parallel to the casting direction. By comparison, the bottom of profile is the random Al_2O_3 prepared by slip casting without a magnetic field and sintered at 1873 K for 2 h.

Fig. 2. X-ray diffraction profiles of 15 mass% YTZ-dispersed Al_2O_3 prepared by slip casting in a magnetic field (10 T), followed by sintering at 1873 K for 2 h, in the plane perpendicular and parallel to a magnetic field, which is parallel to the casting direction. The subscript of "z" indicates the peaks of YTZ.

orientation of ZrO_2 with tetragonal phase was observed.

Figure 3 shows the degree of crystalline texture calculated using Eq. (1) together with the densities as a function of the

Fig. 3. Effect of temperature on the degree of crystalline texture and density in textured TiO_2 -doped, MgO -doped and TZP-dispersed Al_2O_3 .

sintering temperature for the specimens prepared by slip casting in a strong magnetic field of 10 T (the open plots), and the specimens prepared without applying a magnetic field (the closed plots). Both TiO_2 and MgO enhanced the sinterability of Al_2O_3 , and YTZ particles inhibited the sinterability of Al_2O_3 composites. For the specimens without an applied magnetic field, the degrees of crystalline texture, P , agreed with the value of 0.025 that was calculated from the ICDD. The specimen prepared without a magnetic field was confirmed to have a randomly oriented polycrystalline structure. By comparison, when a strong magnetic field was applied, the value of P was greater than 0.025 in all specimens, but the difference was small at low sintering temperature from 1073 K to 1473 K. The temperature ranges in which the value of P increased rapidly were observed in the specimens with applying a magnetic field and the temperature ranges depended on the specimens. The temperature range of the TiO_2 -doped Al_2O_3 sifted toward lower temperature than that of pure Al_2O_3 . Contrary to this, the temperature range of the MgO -doped Al_2O_3 sifted toward higher temperature than that of pure Al_2O_3 . For YTZ-dispersed Al_2O_3 , the temperature range was found to be wide and the value of P was the lowest.

Figure 4 shows SEM images of the textured Al_2O_3 containing various additives and the textured YTZ-dispersed Al_2O_3 composite prepared by slip casting in 10 T and sintered at 1873 K for 2 h. It can be seen that the platelet grains are oriented perpendicularly to the magnetic field in pure Al_2O_3 shown in Fig. 4(a). In TiO_2 -doped Al_2O_3 shown in Fig. 4(b), the grain size was larger than that of pure Al_2O_3 because TiO_2 enhanced the grain growth of Al_2O_3 and equiaxed grains were observed.^{16)–18)} In MgO -doped Al_2O_3 shown in Fig. 4(c), the grain growth of Al_2O_3 was suppressed by MgO and equiaxed grains were also observed.¹⁹⁾ Moreover in YTZ-dispersed Al_2O_3 , shown in Fig. 4(d), the Al_2O_3 grain size was the

Fig. 4. Microstructures of crystalline oriented Al_2O_3 sintered at 1873 K for 2 h. (a) undoped, (b) TiO_2 -doped, (c) MgO -doped, (d) 15 mass% YTZ-dispersed.

smallest because suppression of the Al_2O_3 grain growth was controlled by the pinning effect of YTZ particles.^{20),21)} It should be noted that the scale in Fig. 4(d) is different from the others.

In TiO_2 -doped Al_2O_3 , grain growth was enhanced and the temperature range in which the value of P increased rapidly shifted toward lower range than that of pure Al_2O_3 . On comparison, in both MgO -doped and YTZ-dispersed Al_2O_3 the grain growth was suppressed and the temperature range in which P increased sifted toward higher range than that of pure Al_2O_3 . Therefore, the development of texture in Al_2O_3 seems to require grain growth. The dependence of P on the grain size is shown in Fig. 5. In the case of the starting Al_2O_3 powder having the same particle size, all experimental data plots were approximately on a curve. The degree of orientation depended on the grain size even if other factors, such as the kind of dopant, the amount of the second phase, sintering temperature, annealing temperature, annealing time, controlled the Al_2O_3 grain growth.

Fig. 5. Al_2O_3 grain size dependence for the degree of orientation in the textured specimens.

4. Summary

This processing technique for the development of a texture can be applied to Al_2O_3 based composites, such as ZrO_2 -dispersed Al_2O_3 , TiO_2 -doped Al_2O_3 , MgO -doped Al_2O_3 . The degree of crystalline orientation can be controlled by the Al_2O_3 grain size. The development of the microstructure can be controlled by many factors, such as the amount of a second phase, various additives, sintering temperature and annealing time.

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