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Control of Microstructure in Textured Alumina Based Ceramics Prepared by Colloidal Processing in a High Magnetic Field

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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 using a magnetic field. We have demonstrated, however, that textured microstructures in alumina, titania, zinc oxide can be prepared by slip casting in a high magnetic field followed by sintering. We applied this processing technique to alumina based composites. After the suspension was molded in a high magnetic field, a green body with a slight degree of crystallographic orientation of alumina matrix was obtained. The degree of crystallographic texture increased during densification and depended on the grain size of alumina matrix. The grain size can be controlled by the content of zirconia particle as a second phase, sintering temperature, annealing temperature, annealing time and so on.
Key words: crystalline orientation, grain growth, ZrO_2, TiO_2, MgO

1. INTRODUCTION

The development of superconducting magnets is extending the potential applications of strong magnetic fields. Interesting phenomena associated with strong magnetic fields have been reported [1, 2] and magnetic fields have been used to produce a textured microstructure in the diamagnetic and paramagnetic ceramics which show the anisotropy of the magnetic susceptibility because of asymmetric unit cells, such as hexagonal and tetragonal structures [3-9]. A crystal with an anisotropic magnetic susceptibility will rotate to an angle minimizing the system energy when placed in a magnetic field. The reduction of the magnetic energy on the rotation is the following equation

$$\Delta E = -\frac{\Delta\chi V B^2}{2\mu_0} \qquad (1)$$

where $\Delta\chi = \chi_{a,b}-\chi_c$ is the anisotropy of the magnetic susceptibility, V is the volume of each particle, μ_0 is the permeability in a vacuum and B is the applied magnetic field. This is the driving force for magnetic alignment.

α-Al_2O_3 with a rhombohedral structure shows the anisotropy of the magnetic susceptibility, however, it is generally difficult to utilize a magnetic field for controlling the texture in diamagnetic and paramagnetic materials even if a high magnetic field is used, because this anisotropic susceptibility is extremely small and fine particles agglomerate spontaneously. The dispersion of powder in a suspension is necessary for effective utilization of the magnetic field, because a strong interaction between the agglomerated particles in a suspension prevents each particle from rotating under the application of a magnetic field. In order to rotate the particles, Colloidal processing was used in this study because the processing is very effective in developing consolidated fine particles, thereby avoiding heterogeneous agglomerates, by using repulsive surface forces [10].

In previous reports, we have pointed out that the green compact with a slight degree of crystalline orientation was obtained just after slip casting in a high magnetic field, and the degree of crystalline orientation increased with the increasing temperature, and we have suggested that the crystalline orientation seems to be inseparably related to the microstructure. In this study we discuss the development of the crystalline orientation in consideration of microstructure in Al_2O_3 based ceramics prepared by a slip casting in a high magnetic field of 10 T followed by heating.

2. EXPERIMENT PROCEDURE

Starting powders were high purity spherical α-Al_2O_3, 3 mol% Y_2O_3 stabilized tetragonal ZrO_2, TiO_2 and MgO with average particle sizes of 0.15μm, 60nm, 30nm and 0.1μm, respectively. Aqueous suspensions containing 30 vol% solids of Al_2O_3 containing various amounts of ZrO_2, Al_2O_3 containing 0.25 mass% TiO_2 or Al_2O_3, containing 0.03 mass% MgO were prepared. When suspensions consist of particles of different size and density, segregation occurs because of differences in the sedimentation rate during slip casting [11, 12]. Segregation has been shown to be inhibited by hindering sedimentation if the solid content exceeds 30 vol% in suspension [13]. The suspensions were ultrasonicated for 10 minutes and stirred for more than 8 hours to disperse the powder [14, 15]. Electrosteric stabilization was used to disperse the fine particles and was achieved by polyelectrolyte adsorption on the surface of the particles. The adsorbed polyelectrolyte is ionized, and the negative charge on the surface is sufficiently large to cause stable particle dispersion due to strong mutual electrostatic and steric repulsion [16, 17]. The amounts of polyelectrolyte for maximum dispersion for each powder were determined from viscosity experiments done previously. After elimination of air bubbles, the suspensions were compacted by slip casting. A high 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 a high 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.

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. Density measurements were made in kerosene by Archimedes method. The degree of crystalline texture was determined using the intensities of X-ray diffraction measurements and equation (2) below.

$$P = \frac{I_{006}}{I_{006} + I_{110}} \qquad (2)$$

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 equation (2).

3. RESULTS AND DISCUSSION

Figure 1 illustrates the XRD profiles of the specimen which was compacted by slip casting without a magnetic field, followed by sintering at 1873K for 2 h. Both of the profiles measured on the surfaces parallel and perpendicular to the casting direction were the same. The specimen prepared without applying a magnetic field was confirmed to have a randomly oriented polycrystalline structure.

Figures 2 illustrates the XRD profiles of the specimen which was compacted by slip casting in a high magnetic field of 10 T, followed by sintering at 1873 K for 2 h. In the surface perpendicular to the magnetic field (VT plane), the intensity of the $10\underline{1}0$ reflection at an angle of 17.5° with the basal plane was high, the intensities of the *hk*0 reflections at an angle of 90° with the basal plane were extremely small, and the 00*l* reflections were appeared. By contrast, in the surface parallel to the magnetic field (VS plane), the intensities of *hk*0 reflections were high. In view of these results, it is clear that the control of a crystalline orientation in Al_2O_3 matrix can be achieved by a high magnetic field and the *c* axis parallel to the applied magnetic field is developed for ZrO_2-dispersed Al_2O_3. This is analogous to the case of the undoped Al_2O_3 [3], but the degree of crystalline orientation is smaller than that of the undoped Al_2O_3 and the random orientation of ZrO_2 phase can be observed.

Figure 3 shows the degree of crystalline texture calculated using Equation (2) together with the densities and the grain sizes as a function of sintering temperature for Al_2O_3, 15mass% ZrO_2-dispersed Al_2O_3 and TiO_2-doped Al_2O_3 prepared by slip casting in 10 T and the specimens prepared without applying a magnetic field. TiO_2 dopant enhanced the densification of Al_2O_3 composites, conversely, ZrO_2 particles as a second phase inhibited the densification, and it could be considered that there was no effect of a magnetic field on the sinterability when the densities of the specimens prepared using a magnetic field (open plots) and those of the specimens without a magnetic field (closed plots) were compared. For those specimens without applying a magnetic field (closed plots), the degree of crystalline texture approximated to 0.025, which is in agreement with that calculated from the value of the International Center for Diffraction Data (ICDD) cards. By comparison, in

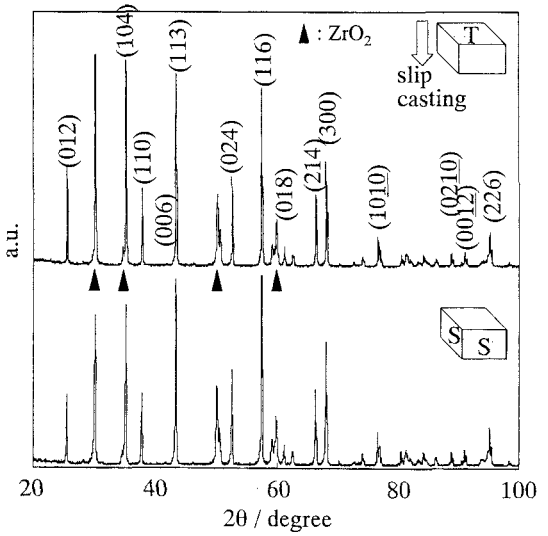

Fig. 1 X-ray diffraction patterns of 15 mass% ZrO_2-dispersed Al_2O_3 sintered at 1873 K in the plane perpendicular and parallel to the casting direction prepared without applying a magnetic field.

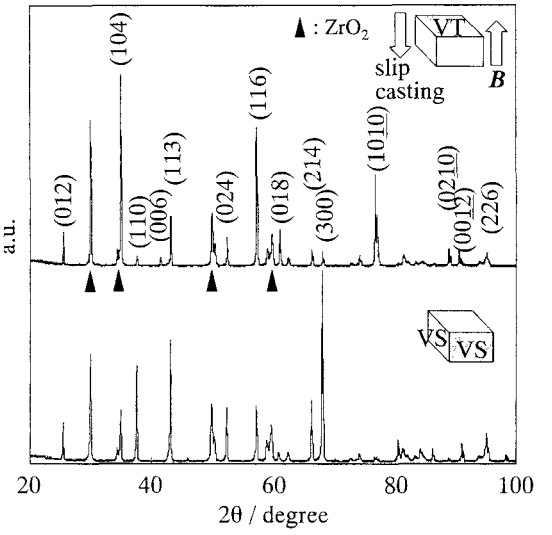

Fig. 2 X-ray diffraction patterns of 15 mass% ZrO_2-dispersed Al_2O_3 sintered at 1873 K in the plane perpendicular and parallel to a magnetic field, which is parallel to the casting direction.

the specimens exposed to a high magnetic field (open plots), the degree of crystalline orientation was very small just after slip casting, but it should be noted that this degree is larger than that of the untextured specimens. The degree of crystalline texture in the specimens prepared in a high magnetic field gradually increased from the point at which the densities were approximately 80% of the theoretical value. The crystallographic texture development occurred rapidly with the grain growth when the densities were more than 90%. The grain growth of Al_2O_3 decreased when ZrO_2 particles were dispersed, because suppression of the Al_2O_3 grain growth was controlled by the pinning effect of ZrO_2 particles [18]. Furthermore, the degree of crystalline orientation was smaller than that in undoped Al_2O_3. Conversely, TiO_2 dopant promotes the Al_2O_3 grain growth [19], and the degree of crystalline orientation was lager than that in the undoped Al_2O_3. From this comparison, it is clear that crystallographic texture development closely relates to the grain growth in Al_2O_3 matrix.

In order to increase the degree of crystalline orientation, Al_2O_3 containing various amounts of ZrO_2 were annealed at 1773K for various periods. The degree of crystalline orientation, the grain size perpendicular to the applying magnetic field, $d_\perp$, and the ratio of $d_\perp$ to $d_{//}$ during annealing are shown in Fig. 4. The degree of crystalline orientation and the ratio of $d_\perp$ to $d_{//}$ increased monotonously with the increasing annealing time, and the Al_2O_3 grain growth occurred during annealing. The degree of crystalline orientation and the ratio of $d_\perp$ to $d_{//}$ developed with the grain growth.

Figure 5 shows the degree of crystalline texture as a function of $d_\perp$ for the specimens prepared by slip casting in 10 T. As mentioned

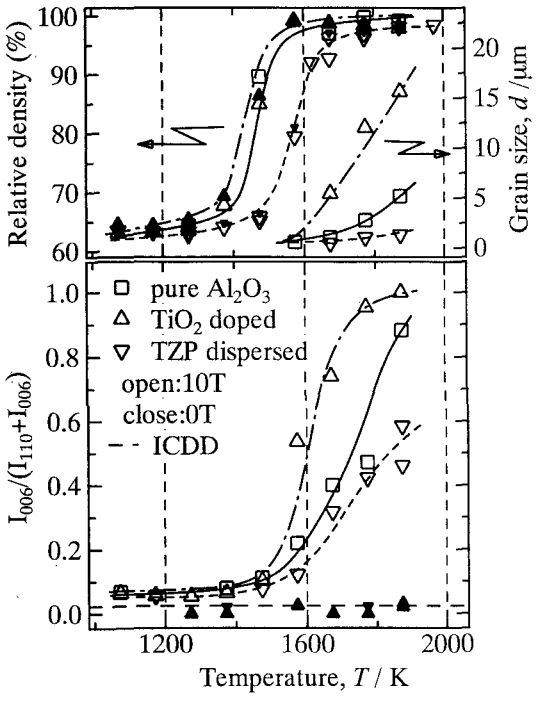

Fig.3 Effect of temperature on the degree of crystalline texture, density and grain size in textured Al2O3, 15mass%ZrO_2-dispersed Al_2O_3, TiO_2-doped Al_2O_3.

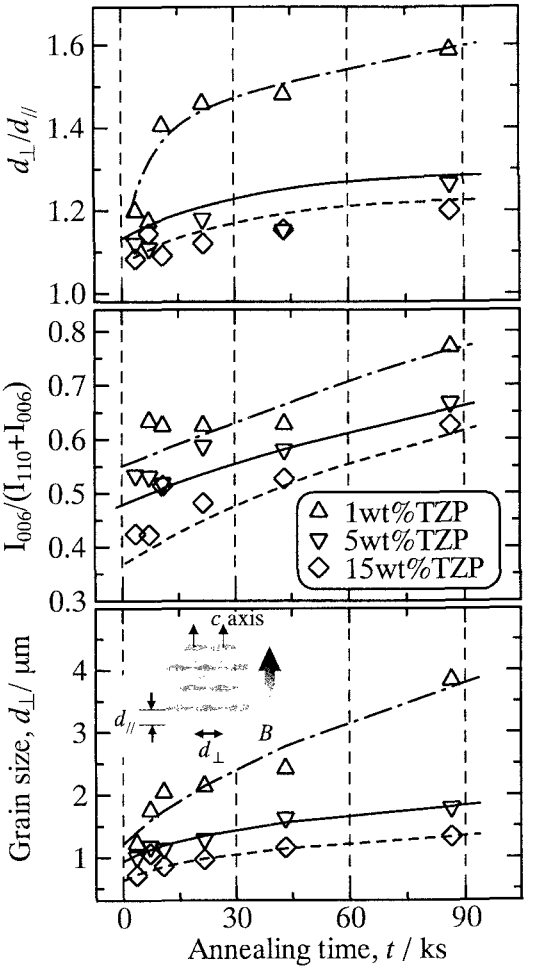

Fig.4 Effect of annealing time at 1773K on the degree of crystalline texture and grain size in textured ZrO_2-dispersed Al_2O_3

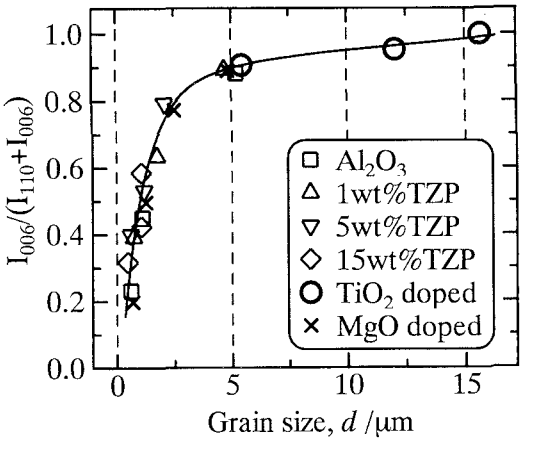

Fig.5 The Al_2O_3 grain size dependence for the degree of crystalline orientation in the textured specimens.

above, TiO_2 dopant enhances the Al_2O_3 grain growth, ZrO_2 particles prevent the Al_2O_3 grain from growing and MgO dopant also inhibits from the Al_2O_3 grain growth [19]. In case of the starting powder with same particle size, all experimental data points were approximately on a curve, even if any 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.

4. CONCLUSIONS

A processing technique (slip casting in a strong magnetic field and heating) 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 development of its microstructure, because the degree of crystalline orientation depends on the Al_2O_3 grain size perpendicular to the magnetic field. The control of the grain size can be provided by lots of factor, such as the amounts of the second phase, sintering temperature, annealing time and so on. In order to obtain specimens with fine grains and high orientation, it is assumed that we need a magnetic field higher than 10 T.

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