Control of texture in alumina by colloidal processing in a strong magnetic field

Tohru S. Suzuki *, Tetsuo Uchikoshi, Yoshio Sakka

Fine Particle Processing Group, Nano Ceramics Center, National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan

Received 29 December 2005; received in revised form 18 January 2006; accepted 19 January 2006

Available online 6 May 2006

Abstract

Electrical, mechanical and other properties of ceramic materials can be controlled by designing their microstructures. It had generally been difficult to utilize a magnetic field for tailoring the microstructure in feeble magnetic ceramics, such as Al₂O₃; however, the possibility of controlling the microstructure by a magnetic field occurred with the development of superconducting magnets. In this review paper, we introduce a novel processing for the microstructural design in ceramics by colloidal processing in a strong magnetic field and an electric field. We demonstrate that the textured alumina can be fabricated by slip casting in a strong magnetic field and the production of alumina/alumina laminar composites with different crystalline-oriented layers can be achieved by electrophoretic deposition in a strong magnetic field. 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. The degree of orientation depends on the processing factors, such as heating temperature, viscosity of suspension, etc. And the grain growth in Al₂O₃ matrix enhances crystallographic texture development. The bending strength of the laminar composite depended on the direction of the multilayered microstructure with alternate crystalline-oriented layers. Crack propagation and fracture mode depend on the direction of microstructure in the laminar composite with controlled crystalline orientation.

© 2006 NIMS and Elsevier Ltd. All rights reserved.

Keywords: Alumina; Slip casting; EPD; Texture; Orientation; Grain growth; Laminar composite

1. Introduction

The controlled development of texture in polycrystalline materials is effective in improving their electrical, piezoelectric, mechanical, and other properties. Many studies have been reported for production of the textured ceramics such as hot forging [1], templated grain growth method [2,3], the reaction bonding of aluminum oxide (RBAO) technique [4], etc.

Ceramics with asymmetric unit cells have anisotropic susceptibility, but it is very small in case of diamagnetic and paramagnetic ceramics such as Al₂O₃, TiO₂, AlN and ZnO; therefore, it is generally difficult to utilize magnetic influence for controlling the texture of these ceramics. Recently, the development of superconducting magnet technologies has expanded the application of a strong magnetic field to various academic and industrial fields. The interesting phenomena on the strong magnetic field have been reported [5,6], and magnetic fields have been used to produce a textured microstructure [7–12]. Therefore, texture even in feeble magnetic materials is believed to be controlled by a strong magnetic field [13].

The dispersion of each particle in a suspension is essential to control the texture by effective utilization of a magnetic field, because strong agglomeration prevents each particle from rotating in a magnetic field. Colloidal processing, used in this study, is very effective in consolidating fine particles to break heterogeneous agglomerates by using repulsive surface charge potential [14].

A strong magnetic field was applied to the particles in stable suspensions during colloidal processing. The particles were rotated to an angle minimizing the system energy by a magnetic torque generated from the interaction between the anisotropic magnetic anisotropy and the applied magnetic field (Fig. 1). The magnetic torque, \( T \), attributed to the interaction between the anisotropic susceptibility and a magnetic field is estimated from Eq. (1) [15].

\[
T = -\frac{\Delta \chi V R^2}{2\mu_0} \sin 2\theta
\]
where $\Delta \chi_c(=|\chi_\parallel - \chi_\perp|)$ is the anisotropy of the susceptibilities which are measured for the direction of parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the $c$-axis, $V$ is the volume of each particle, $\mu_0$ is the permeability in a vacuum, $B$ is the applied magnetic field and $\theta$ is the angle between an easy magnetization axis in a crystal and imposed magnetic field direction. This is the driving force for magnetic alignment.

We review in this paper that the development of the texture in alumina can be controlled by the colloidal processing in a strong magnetic field.

### 2. Experimental

The starting material was high purity spherical $\alpha$-Al$_2$O$_3$ powder with average particle size of 0.20 $\mu$m. The Al$_2$O$_3$ powder was dispersed in distilled water with appropriate amount of dispersant to ensure dispersion by mutual electrosteric repulsion. The amounts of dispersant were determined from viscosity measurements. The suspensions were mixed with a magnetic stirrer, and ultrasonicated for 10 min to break agglomerates [16,17]. The suspensions were consolidated by slip casting or electrophoretic deposition [18] (Figs. 2 and 7). A strong magnetic field in the range of 0–10 T was applied to the suspension during consolidation process at room temperature. The green compacts before sintering were further densified without disturbing the particle orientation by cold isostatic pressing (CIP) at 392 MPa for 10 min. The green bodies were heated isothermally at each temperature in air, outside of the magnet.

### 3. Texture control by slip casting in a strong magnetic field

The degree of orientation was evaluated by X-ray diffraction, neutron diffraction and electron backscatter...
diffraction (EBSD) measurements [19]. Fig. 3 shows typical EBSD mapping of the surfaces perpendicular and parallel to a magnetic field and the sample not exposed to a magnetic field. Fig. 3(c) indicates that the sample prepared without applying a magnetic field has a randomly-oriented polycrystalline structure. By comparison, the sample prepared by a strong magnetic field clearly shows that the preferential texture of each grains and (001) planes are perpendicular to the magnetic field. As regards the microstructure, we confirmed that the c-axis of the platelet grains aligned perpendicular to the magnetic field in the specimen prepared using the strong magnetic field and heating.

The degree of crystalline texture was estimated using Eq. (2) from the intensities of the X-ray diffraction measurement.

\[
P = \frac{I_{006}}{I_{006} + I_{110}}
\]

where \(I_{006}\) and \(I_{110}\) are the intensities from the 006 and the 110 reflections on the surface perpendicular to the direction of the magnetic field, respectively. The number of grains with the c-axis orientation increases as the value of \(P\) approaches unity. Fig. 4 illustrates the degree of crystalline texture together with the densities and the grain sizes as a function of heating temperature for the specimens prepared by slip casting in 10 T and the specimens prepared without applying a magnetic field. For the specimens not subjected
to a magnetic field, the value of $P$ is approximated to 0.025 in agreement with that calculated from the International Center for Diffraction Data (ICDD) value. The specimens prepared without a magnetic field were confirmed to be a crystalline untexured material. By comparison, the value of $P$ for the specimens prepared in a strong magnetic field increased with increasing temperature above 1600 K.

Fig. 5 shows the inverse pole figures calculated for the z-axis direction (parallel to the magnetic field) by neutron diffraction data. These illustrate a major (001) component. Linear density scale, equal area projection.

Fig. 6 shows effect of dispersion state on the degree of orientation of alumina prepared by slip casting in 10 T and sintering at 1873 K, where each suspension was prepared by different amounts of dispersant. The alignment of particle strongly depends on the degree of dispersion. It is clear that the sample prepared from the well-dispersed, low-viscosity suspension showed superior textured orientation.

To clarify the effect of solids content on crystalline texture, three kinds of alumina suspensions with different solid contents of 30, 40 and 45 vol.% were prepared. Fig. 7 shows the effect of solids content of alumina and the applied magnetic field on the degree of crystalline orientation after heating at 1873 K for 2 h. The degree of orientation improved above at a certain magnetic field. It is probably that higher magnet torque is required for the rotation of the particles in viscous suspensions.

In order to control the microstructure of $\text{Al}_2\text{O}_3$, it is possible that $\text{TiO}_2$ and $\text{MgO}$ are doped and 3 mol% $\text{Y}_2\text{O}_3$ stabilized tetragonal $\text{ZrO}_2$ (YTZ) particles are dispersed as a second phase. During sintering of $\text{Al}_2\text{O}_3$, the addition of $\text{TiO}_2$ in small amount is known to enhance densification and promote grain growth [23–25]. By contrast, it is recognized that the addition of $\text{MgO}$ in small amount effectively suppress the abnormal grain growth of $\text{Al}_2\text{O}_3$ [26] and YTZ.
particles also prevent the Al₂O₃ grain growth by the pining effect [27,28]. Fig. 8 shows the value of P together with the densities and the grain size as a function of the sintering temperature for TiO₂-doped, MgO-doped and YTZ-dispersed Al₂O₃. 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 TiO₂-doped Al₂O₃ sifted toward lower temperature than that of pure Al₂O₃. Contrary to this, the temperature ranges of the MgO-doped Al₂O₃ and the YTZ dispersed Al₂O₃ sifted toward higher temperature than that of pure Al₂O₃. Fig. 9 shows SEM images of the textured Al₂O₃ containing various additives and the textured YTZ-dispersed Al₂O₃ composite prepared by slip casting in 10 T and sintered at 1873 K for 2 h. From these results, it is clear that the grain
Fig. 10. Schematic illustration of the apparatus for EPD in a superconducting magnet.

Fig. 11. The variation in the XRD patterns and the supposed texture of the alumina monolithic layers deposited at various $\phi_{B-E}$. 
growth in Al₂O₃ matrix enhances crystallographic texture development [29].

4. Microstructure control in layers by electrophoretic deposition (EPD) in a strong magnetic field

The combination of the orientation and lamination is one of the possible ways of tailoring the microstructure to improve the mechanical properties and other properties due to the superposition effect. Hence, we attempted to produce alumina/alumina laminar composites with different crystalline-oriented layers by EPD in a strong magnetic field. A schematic illustration of the apparatus of EPD in a strong magnetic field is shown in Fig. 10. The head of the support for fixing the electrodes is variable to alter the direction of the electric field relative to the magnetic field (the angle between the vectors \( E \) and \( B, \phi_{B \cdot E} \)). The crystalline-textured alumina/alumina laminar composites were prepared by alternately changing \( \phi_{B \cdot E} \) layer by layer during EPD in a magnetic field. A palladium sheet was used as the cathodic substrate to absorb hydrogen produced by electrolysis of the aqueous solvent [30].

---

**Fig. 11** shows the variation in the XRD patterns of the alumina monolithic layers deposited at various \( \phi_{B \cdot E} \). To characterize the XRD peaks, the interplanar angles \( \phi_{hkl} \) between the planes \( (hkl) \) and the basal plane \( (00l) \) were calculated for a hexagonal unit cell of \( \alpha \)-alumina \((a = 0.4758 \text{ nm}, c = 1.2991 \text{ nm}) \) [31]. The standard XRD data of \( \alpha \)-alumina from ICDD [32] with the \( \phi_{hkl} \) have been described in the previous paper [33]. When the \( \phi_{B \cdot E} = 0^\circ \), the dominant diffraction peaks were from the planes \((006)(\phi_{006} = 0^\circ)\), \((0012)(\phi_{0012} = 0^\circ)\) and \((1010)(\phi_{1010} = 17.5^\circ)\). The interplanar angles \( \phi_{hkl} \) of these planes were close to 0\(^\circ\). When the \( \phi_{B \cdot E} \) was changed to 45\(^\circ\), the \( \phi_{hkl} \) of the dominant refraction planes were close to 45\(^\circ\). And the \( \phi_{B \cdot E} \) changed to 90\(^\circ\), the \( \phi_{hkl} \) of all the dominant refraction planes are 90\(^\circ\). In the other cases, the \( \phi_{hkl} \) of all the dominant refraction planes was also agree with \( \phi_{B \cdot E} \). These results indicate that the crystalline orientation in alumina can be controlled regardless of compaction techniques in a strong magnetic field.

**Fig. 12** illustrates the microstructure control in laminar composite prepared by EPD in a strong magnetic field. These show the cross-sectional microstructures of laminar composites prepared by alternately changing \( \phi_{B \cdot E} = \pm 45^\circ \) layer by layer (Fig. 12(a)) and \( \phi_{B \cdot E} = 0^\circ/45^\circ/0^\circ/\sim 45^\circ \) layer by layer (Fig. 12(b)). Microstructures well-reflect the alternation of \( \phi_{B \cdot E} \) during the deposition.

The mechanical property of these laminar composites with differently crystalline-oriented layers is unique since cleavage planes \((c\)-planes\) are highly controlled. The bend strength was determined using the three-point bending test for the samples with alternately changing \( \phi_{B \cdot E} = \pm 45^\circ \) layer by layer in which the tensile surface was either parallel or perpendicular to the plane defined by the

---

**Fig. 13**. Bending strength for laminate alumina composite with alternate oriented layer, depending on the crack-growth direction. And schematic illustrations of crack growth and bend-bar geometries for alumina specimens with alternate oriented layer.
deposition direction. Schematic illustrations of the orientation of the crack-growth direction relative to the samples are shown in Fig. 13. Two types of samples were tested: (a) laminate alumina composite with the deposition direction parallel to the crack-growth direction, and (b) laminate alumina composite with the deposition direction perpendicular to the crack-growth direction. The bending strengths for specimens with CIP and without CIP are shown in Fig. 13. The strength for the crack-growth direction perpendicular to the deposition direction was higher than that parallel to the deposition direction even with or without CIP treatment.

Fig. 14 (a) and (b) are macroscopic views of the specimens after the bending test. A crack was propagated by bending in a zigzag path along the aligned grains when the crack-growth direction was parallel to the deposition direction (Fig. 14(a)). In Fig. 14(b), the crack changes to the direction perpendicular to the initial crack-growth.

The scanning electron micrographs shown in Fig. 15 reveal two distinct crack morphologies on the fracture surfaces after the bending test. A complete intergranular mode of fracture was observed when the crack-growth direction was parallel to the deposition direction (Fig. 15(a)). In contrast, the fracture surface was dominated by the transgranular mode when the crack-growth direction was perpendicular to the deposition direction.

5. Conclusions

The processing (slip casting and EPD in a strong magnetic field) can control the crystalline orientation and the grain orientation in Al₂O₃, when the particle dispersion in suspension is optimized for rotating by a magnetic field. And the interesting microstructural design was achieved by this processing technique. To fabricate textured ceramics, our processing technique can be applied to various non-cubic ceramics with asymmetric unit cells. Some demonstrations for the materials of hexagonal AlN, hexagonal ZnO, tetragonal TiO₂, etc. have been shown elsewhere [34–43].

Acknowledgements

The authors acknowledge the fruitful discussion with Prof. K. Kitazawa, Prof. S. Asai, Prof. T. Kimura, Prof. K. Uematsu and Dr N. Hirota. And we thank Dr H. Okuyama for setting up of the apparatus for EPD in a magnetic field. We also thank Dr. E. Guilmean for the measurement of the neutron diffraction and the analysis. This study was supported in part by the Budget for Nuclear Research and the Grant-in-Aid for Scientific Research.
of the Japanese Ministry of Education, Culture, Sports, Science and Technology, to whom we are deeply indebted.

References

[1] Y. Ma, K.J. Bowman, J. Am. Ceram. Soc. 74 (1991) 2941.
[2] D. Brandon, D. Chen, H. Chan, Mater. Sci. Eng. A195 (1995) 189.
[3] M.M. Seabaugh, I.H. Kersch, G.L. Messing, J. Am. Ceram. Soc. 80 (1997) 1181.
[4] E. Suvaci, G.L. Messing, J. Am. Ceram. Soc. 83 (2000) 2041.
[5] E. Beaugnon, R. Tournier, Nature 349 (1991) 470.
[6] N. Hirota, T. Homma, H. Sugawara, K. Kitazawa, M. Iwasaki, S. Ueno, H. Yokoi, Y. Kakadate, S. Fujiwara, M. Kawamura, Jpn. J. Appl. Phys. 34 (1995) L991.
[7] H. Morikawa, K. Sassa, S. Asai, Mater. Trans., JIM 39 (1998) 814.
[8] P. de Rango, M. Lees, P. Lejay, A. Sulpice, R. Tournier, M. Ingold, P. Germi, M. Pernet, Nature 349 (1991) 770.
[9] S. Stassen, R. Cloots, Ph. Vanderbemden, P.A. Godelaine, H. Bougrine, A. Rulmont, M. Ausloos, J. Mater. Res. 11 (1996) 1082.
[10] T.S. Suzuki, Y. Sakka, K. Kitazawa, Adv. Eng. Mater. 3 (2001) 490.
[11] C.Y. Wu, S.Q. Li, K. Sassa, Y. Sakka, T.S. Suzuki, S. Asai, ISIJ Int. 45 (2005) 997.
[12] T.S. Suzuki, Y. Sakka, K. Kitazawa, J. Ceram. Soc. Jpn 109 (2001) 886.
[13] Y. Sakka, T.S. Suzuki, J. Ceram. Soc. Jpn 113 (2005) 26.
[14] F.F. Lange, J. Am. Ceram. Soc. 72 (1989) 3.
[15] T. Sugiyama, M. Tahashi, K. Sassa, S. Asai, ISIJ Int. 43 (2003) 855.
[16] T.S. Suzuki, Y. Sakka, K. Nakano, K. Hiraga, J. Am. Ceram. Soc. 84 (2001) 2132.
[17] T.S. Suzuki, Y. Sakka, K. Nakano, K. Hiraga, Mater. Trans., JIM 39 (1998) 689.
[18] S. Doungdaw, T. Uchikoshi, Y. Noguchi, C. Eamchotchawaiwit, Y. Sakka, Sci. Tech. Adv. Mater. 6 (2005) 927.
[19] E. Guilmeau, C. Henrist, T.S. Suzuki, Y. Sakka, D. Chateigner, D. Grossin, B. Ouladdaf, Mater. Sci. Forum 495–497 (2005) 1395.
[20] E. Guilmeau, D. Chateigner, T.S. Suzuki, Y. Sakka, C. Henrist, Chem. Mater. 17 (2005) 102.
[21] K. Uematsu, N. Uchida, S. Tanaka, Sci. Tech. Adv. Mater. 6 (2005) 135.
[22] Y. Doshida, K. Suzuki, H. Kishi, A. Makiya, S. Tanaka, K. Uematsu, T. Kimura, J. Appl. Phys. 43 (2004) 6645.
[23] D.S. Horn, G.L. Messing, Mater. Sci. Eng. A195 (1995) 169.
[24] Y-M. Kim, S-H. Hong, D-Y. Kim, J. Am. Ceram. Soc. 83 (2000) 2809.
[25] A. Kebbede, J. Parai, A.H. Carim, J. Am. Ceram. Soc. 83 (2000) 2845.
[26] K. Ikegami, K. Eguchi, J. Mater. Res. 14 (1999) 509.
[27] K. Okada, T. Sakuma, J. Ceram. Soc. Jpn 100 (1992) 382.
[28] S. Hori, R. Kurita, M. Yoshimura, S. Somiya, J. Mater. Sci. Lett. 4 (1985) 1067.
[29] T.S. Suzuki, T. Uchikoshi, Y. Sakka, J. Ceram. Soc. Jpn 114 (2006) 59.
[30] T. Uchikoshi, K. Ozawa, B.D. Hatton, Y. Sakka, J. Mater. Res. 16 (2001) 321.
[31] B.D. Cullity, in: Elements of X-ray Diffraction, Addison Wesley, London, 1959, p. 460.
[32] ICDD (JCPDS) #10-173 [corundum].
[33] T. Uchikoshi, T.S. Suzuki, H. Okuyama, Y. Sakka, J. Mater. Res. 18 (2003) 254.
[34] T.S. Suzuki, Y. Sakka, Jpn. J. Appl. Phys. 41 (2002) L1272.
[35] T.S. Suzuki, Y. Sakka, Chem. Lett. (2002) 1204.
[36] T.S. Suzuki, Y. Sakka, Scripta Mater. 52 (2005) 583.
[37] Y. Sakka, T. Suzuki, N. Tanabe, S. Asai, K. Kitazawa, Jpn. J. Appl. Phys. 41 (2002) L1416.
[38] K. Inoue, K. Sassa, Y. Yokogawa, Y. Sakka, M. Okido, S. Asai, Mater. Trans. 44 (2003) 1133.
[39] S. Li, K. Sassa, S. Asai, J. Am. Ceram. Soc. 87 (2004) 1384.
[40] A. Makiya, D. Kasuno, S. Tanaka, N. Uchida, K. Uematsu, K. Kitazawa, Y. Doshida, J. Ceram. Soc. Jpn 111 (2003) 702.
[41] S. Hori, I. Matsubara, M. Sano, K. Fujie, M. Suzuki, R. Funahashi, M. Shikano, W. Shin, N. Murayama, J. Shimoyama, K. Kishio, Jpn. J. Appl. Phys. 42 (2003) 7018.
[42] T. Kumagai, S. Horii, T. Uchikoshi, T.S. Suzuki, Y. Sakka, T. Okamoto, J. Shimoyama, K. Kishio, J. Appl. Phys. 44 (2005) L1263.
[43] Y. Sakka, A. Honda, T.S. Suzuki, Y. Moriyoshi, Solid State Ionics 172 (2004) 341.