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Grain oriented titania ceramics made in high magnetic field

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Abstract

Microstructure with grain orientation has a high potential for greatly improving characteristics of ceramics. This paper shows a very promising approach for developing the structure of grain orientation through para- and dia-magnetic interaction of ceramics particles in an extremely strong magnetic field. We used titania as a raw material. Grain oriented titania ceramics of high density was successfully developed through a processing in a high magnetic field. X-ray diffraction shows that the *c*-axes of particles of fine powder particles were oriented parallel to the applied magnetic field. The orientation factor is 0.05 as determined using the Lotgering method. High density was achieved by the subsequent sintering. Relative density is 98% of theoretical density.

Keywords: Suspension; Microstructure; X-ray method; TiO_2

1. Introduction

Single-crystalline materials have big merits in splendid properties, but have disadvantages, such in high price and limitation in shape and size, etc. Poly-crystalline ceramics have an outstanding merit in price, but their properties are often inferior to those of single-crystalline materials. Grain oriented ceramics may have merits of both single- and poly-crystalline materials. The structure of grain orientation has been developed through a variety of processes relying on the external stresses such in hot pressing and tape casting.[1,2] Recently, a novel method was developed in which the interaction between a material and a high magnetic field is used for orientation of particles.[3] This method relies on the anisotropic para- and dia-magnetic property of "non-magnetic" non-cubic materials in a very strong magnetic field of super-conducting magnet. Merit of this technique is that regular powders having an isotropic shape can be oriented. Conventional method requires plate-like particles to develop a driving force through interaction between the particle and the stress field. Plate-like particle often prevents the achievement of high density on sintering.

Resent study reported that alignment of titania whisker can be controlled in the colloidal filtration under a high magnetic field.[4] The report also showed that textured rutile ceramics could be obtained through the anatase to rutile transformation after solidification of anatase suspension by slip casting in the high magnetic field.[5] Although textured rutile ceramics have been formed, the relative density attained only 96%.

This study applies the use of a magnetic field to develop the grain oriented titania ceramics of high sintered density. A fine rutile powder having an isotropic particle shape will be used to accomplish the high sintering density.

2. Experiment

A commercial titania powder (PT301, Ishiharasanngyo Ltd.) was used as a raw material. The titania particles consist of mainly rutile phase. The powder was placed in a planetary ball mill with dispersant, distilled water, and zirconia balls, and mixed for 10 min to prepare a slurry with solid loading 20 vol.%. Flow characterization of the slurry was evaluated by a concentric viscometer (VT550, HAAKE, Switzerland). In the measurement, the shear rate was increased from 0 to 250 s^{-1} in 3 min, and then returned to 0 s^{-1} in 3 min. After the slurry was left still for 3 min, the flow characteristics were measured by increasing and then decreasing the shear rate in 10 min over the same range of

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shear rates. Temperature of the slurry was kept constant at 20 °C during this measurement.

After passing through a mesh with the opening of 60 μm, the prepared slurry was poured into a mold made of TEFLON. The mold was placed in a magnetic field 10 T in a super-conducting magnet (TM-10VH10, Toshiba, Japan), and kept for more than overnight at the room temperature for drying. The direction of the magnetic field applied was horizontal to the mold. For comparison, slurry was also dried in a mold without magnetic field at room temperature.

The dried compact was heated at 5 °C/min to 1600 °C for 2 h, and cooled to the room temperature. The grain orientation was examined with X-ray diffraction analysis (MO3XHF22, MacScience) by the Lotgering method. Measurement condition were, Cu Kα radiation at an acceleration voltage 40 kV, a current of 40 mA, scan step 0.02° and scan speed of 2°/min. To examine the microstructure with Scanning Electron Microscope (JEOL 5300LV), the sintered specimen was polished and thermally etched at 1550 °C for 1 h. The density of sintered specimen was measured by the Archimedean method with a distilled water as a medium.

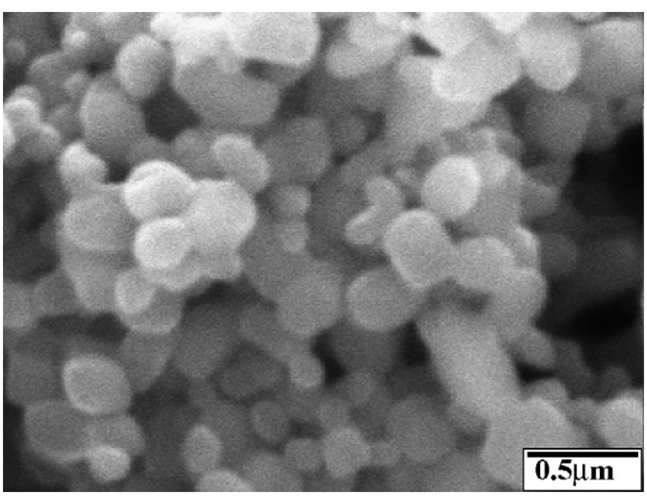

Fig. 1. SEM micrograph of titania raw powder.

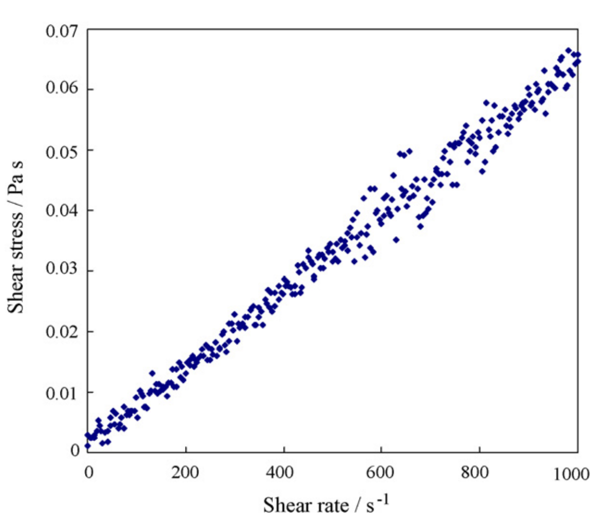

Fig. 2. Flow curve of slurry with 20 vol.%.

3. Results and discussion

Fig. 1 shows SEM micrograph of the raw powder used in this study. Particle has a nearly spherical shape. Mean particle size is about 0.2 μm. Agglomerates of particles are noted in the raw powder.

Fig. 2 shows the rheological behavior of the slurry. The shear stress increases linearly with increasing shear rate. This slurry showed the Newtonian flow, which indicates only little attractive force present to form a particle network structure in the slurry. Each particle must be rotate freely in the applied magnetic field in this slurry.

Fig. 3 shows microstructures of sintered specimens observed from the direction parallel and perpendicular to the magnetic field. The relative density after sintering is 98% of theoretical density. This high density was expected for a compact prepared from the fine powder. Microstructure has an isotropic structure, and this apparent absence of grain orientation is very interesting.

Fig. 4 shows X-ray diffraction pattern taken from specimens made in high magnetic field 10 T and followed by sintering at 1600 °C for 2 h. The surfaces for examination are parallel and perpendicular to the applied magnetic field. The figure also shows the diffraction pattern for a sintered body prepared without the magnetic field. In surface perpendicular to the magnetic field (Fig. 3a), intensity of the peak (1 0 1) is very strong. Diffraction peak of *c*-plane of crystal such as (0 0 2) is also strong. Inter-planar angle between the plane (1 0 1) and basal plane (0 0 2) is 32.8° for the tetragonal cell of rutile (a = 0.4593 nm, c = 0.2959 nm). The plane (1 0 1) is nearly parallel to the *c*-plane of the crystal. It also seems that there is such influence on (1 1 2)

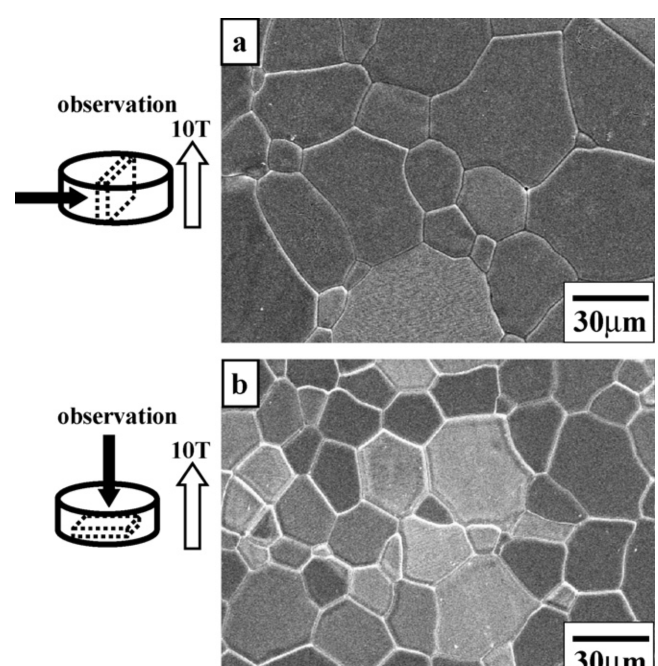

Fig. 3. Microstructure of grain oriented titania (a) perpendicular to the applied magnetic field, and (b) parallel to the field.

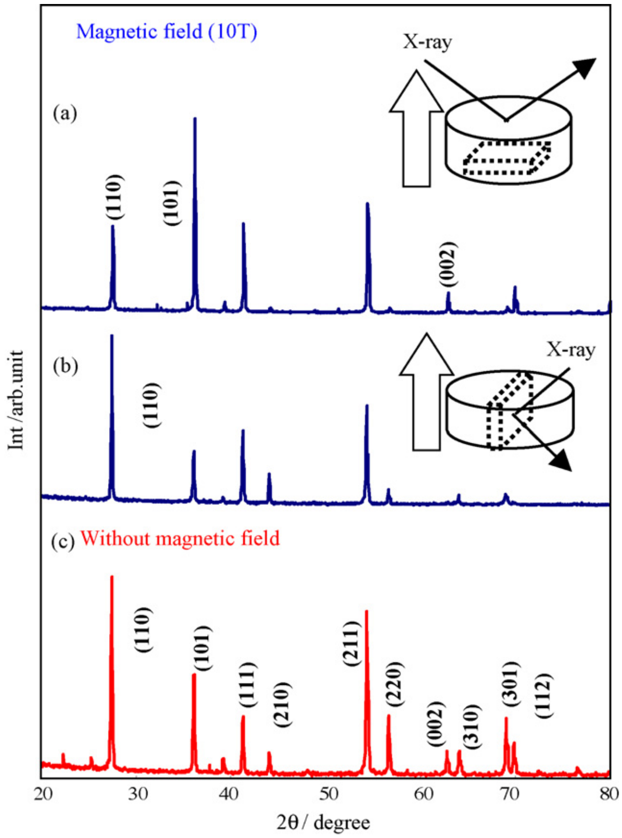

Fig. 4. X-ray diffraction patterns of (a) the grain oriented ceramics surface perpendicular to the applied magnetic field, (b) parallel to the field and (c) a randomly oriented specimen prepared without magnetic field.

diffraction whose inter-planar angle is 24.5°. In contrast, in the surface parallel to the magnetic field (Fig. 3b), the intensity of the (1 1 0) peak is strong. The peak (0 0 2) is almost absent on this surface. These results show that *c*-planes of particles orient perpendicular to the magnetic field. It notes that the orientation distribution is very wide, because particles in suspension cause Brownian motion due to thermal energy kT and particle–particle interaction (Van Der Waals interaction). Particles interaction may be most important in this system. Theses effect may induce accidentally (1 0 1) texture as shown in Fig. 4(a). Titania has diamagnetic property, and the magnetic susceptibility is the largest in the *c*-axis.[6] Results in this study support the previous work.

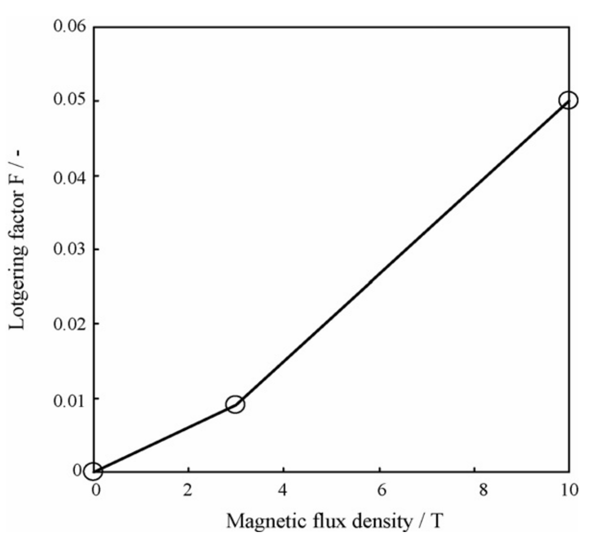

Fig. 5. Relationship between Lotgering factor and applied magnetic intensity.

Fig. 5 shows the Lotgering factor as a function of the magnetic field. The Lotgering factor F was determined from the intensity of X-ray diffraction pattern, as follows[7]:

$$F = \frac{P - P_0}{1 - P_0}$$

where $P = I_{(0\,0\,2)}/\Sigma I_{(h\,k\,l)}$, and $P_0 = I_{0(0\,0\,2)}/\Sigma I_{0(h\,k\,l)}$. I and I_0 are diffraction intensities of oriented and randomly oriented specimens, respectively. $\Sigma I_{(h\,k\,l)}$ and $\Sigma I_{0(h\,k\,l)}$ are sum of peak intensities in the diffraction patterns range of $20° < 2\theta < 80°$. The Lotgering factor increased with increasing magnetic field. Orientation factor achieved was 0.05 at 10 T. The factor calculated from data of Ref.4 is about 0.6 at 10 T. The orientation factor in this study is smaller than that of the previous work. A possible source of difference is the agglomerates shown in Fig. 1, which prevent particle orientation, because agglomerates have no net anisotropy in the magnetic property. The force for rotating the particle is weak in the present system. It is necessary to fully deflocculate the agglomerates in the slurry for achieving highly oriented structure.

4. Conclusion

Dense, grain oriented titania ceramics have been produced using a high magnetic field. The *c*-axes of the titania particles are oriented parallel to the applied magnetic field. Orientation factor of specimens depended on magnetic intensity. Orientation factor of sintered body is 0.05 as determined by Lotgering method. Sintering density achieved 98%.

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