Transactions of the Materials Research Society of Japan 29 [8] 3379-3382 (2004)

Deposition and Orientation of Titania Particles in an Electrical and Magnetic Field

Fengqiu Tang, Tetsuo Uchikoshi, Kiyoshi Ozawa, Tohru S. Suzuki and Yoshio Sakka
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
Fax: 81-29-8592401, e-mail: tang.fengqiu@nims.go.jp

Electrophoretic Deposition process was used to deposit titania particles on an electrode to form the thick films from an aqueous suspension, while a high magnetic field was used to align the particles at the same time. X-ray diffraction pattern and scanning electron microscope revealed that textured titania thick films were fabricated successfully, the grains in the c-axis direction were orientated along the high magnetic field even though the anisotropic susceptibility of titania is quite feeble. The heating temperature play important role on the alignment of the particles.
Keywords: Titania, Orientation, external field, anisotropic susceptibility

1. INTRODUCTION

The structural design of inorganic materials on a macro- or microscale has attracted considerable interest due to the potentially novel physicochemical properties arising from the designed materials. The employment of external fields, such as electric fields, magnetic fields, ultrasonic irradiation [1-3], etc., in ceramic processing may yield materials with well-defined microstructures. Electrophoretic deposition (EPD) is a straightforward method for the assembly of charge-carrying particles on an electrode from stable colloidal suspensions in a direct current (dc) field [4]. Compared with conventional slip casting, the thickness and morphologies of materials obtained via EPD can be controlled precisely by varying the electrochemical parameters and the shape of the electrodes. Recently, we have demonstrated the successful EPD of nanosized oxide particles from aqueous suspensions, in which bubble-free uniform microstructures have been readily obtained [5-7]. Another effort has been made in the utilization of an external magnetic field in the fabrication of textured ceramics by slip casting. Suzuki et al. demonstrated that well-ordered textured oxide ceramics, such as ZnO and Al_2O_3, could be fabricated by employing a strong magnetic field [8,9]. The magnetic anisotropy associated with the crystal structure is believed to play a key role in the rotation and alignment of particles in a stable suspension because crystalline materials with an anisotropic magnetic susceptibility tend to orient at a certain angle to minimize their system energy under a magnetic field.

Titanium oxides are of great interest due to their versatile applications in electrical, electrochemical, and photocatalytic fields [10]. The main polymorphic phases of titania, anatase and rutile with asymmetric unit cells are expected to show anisotropic susceptibilities. The energy of anisotropy associated with the crystals is estimated using

$$\Delta E=\Delta\chi VB^2/2\mu_0 \qquad (1)$$

where $\Delta\chi=\chi_{//}-\chi_{\perp}$ 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.

It is generally quite difficult to align diamagnetic ceramics such as Al_2O_3 or TiO_2 in a magnetic field because $\Delta\chi$ of this kind of materials is quite small. However, in a high magnetic field, the energy of the crystal magnetic anisotropy becomes comparable to or greater than the energy of thermal motion, the alignment of textured grains in the same direction is thus possible and of interest due to their potential new physicochemical properties. In this paper, we demonstrate the EPD fabrication of titania thick films by applying a high magnetic field. Two external forces, i.e., electrical and magnetic fields, contribute to the formation of deposits and the alignment of titania particles, respectively. A highly aligned texture of titania can be obtained upon heating the deposits.

2. EXPERIMENTAL

Spherical TiO_2 with an average particle diameter of 30 nm (NanoTek, Ltd., USA) was used as the starting material. The 5-vol% TiO_2 aqueous suspensions were

dispersed in distilled water with added polyethylenimine (PEI, Wako Pure Chemical Industry, Ltd., Japan) to modify the inherent surface charges of the ceramic particles at a certain pH value [7]. The suspensions were ultrasonicated for 10 min to break up the possible agglomeration of the TiO_2 particles, and then EPD processing of the well-dispersed suspensions was performed using a dc power source operating at a constant voltage at room temperature under a strong magnetic field of 10 T (Sumimoto Heavy Industry HF10-100VHT). A pair of electrodes, with an area of 20 × 20 mm^2 and a distance of 20 mm, was placed in the suspension. A palladium electrode was used as the cathode to adsorb the hydrogen evolved by the electrolysis of water in order to obtain bubble-free deposits [6,11]. The direction of the magnetic field was parallel to the direction of the particle flow. For comparison, the samples were also prepared by EPD without the magnetic field. All the green compacts were sintered in air at 1373-1473 K for 2 h outside the magnetic field.

X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) were employed to examine the planes parallel and perpendicular to the substrate, which was designated as top and side, respectively. Grain size was calculated using the linear intercept method on the surface perpendicular to the magnetic field.

3. RESULTS AND DISCUSSION

The titania nanoparticles used in this study were in the anatase phase. The XRD pattern revealed that TiO_2 converts from the anatase to the rutile phase completely above 1073 K. The XRD patterns of the top and the side surfaces of the TiO_2 thick films deposited by EPD and heated at 1473 K without the magnetic field showed similar profiles. The degree of crystalline orientation (P) can be estimated from the intensities of the XRD data using the equation [12]:

$$P = \frac{I_{002}}{I_{002} + I_{110}} \qquad (2)$$

where I_{002} and I_{110} are the intensities from the (002) and (110) reflections on the surface perpendicular to the magnetic field, respectively. The textured degree of samples prepared without the magnetic field was only ca. 9.6 %, which is in consistent with that calculated from the standard XRD pattern of rutile. The results implied that the orientation of polycrystalline titania without the magnetic field is randomly distributed.

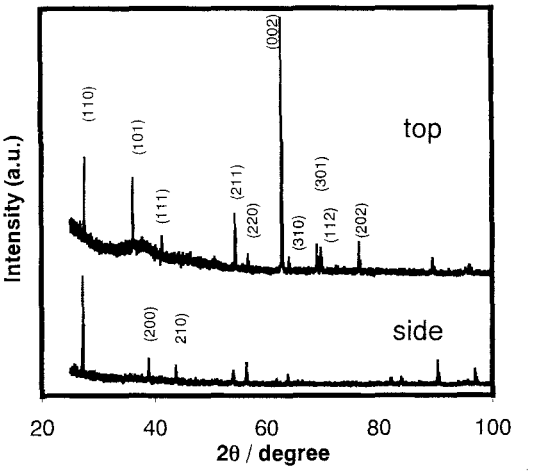


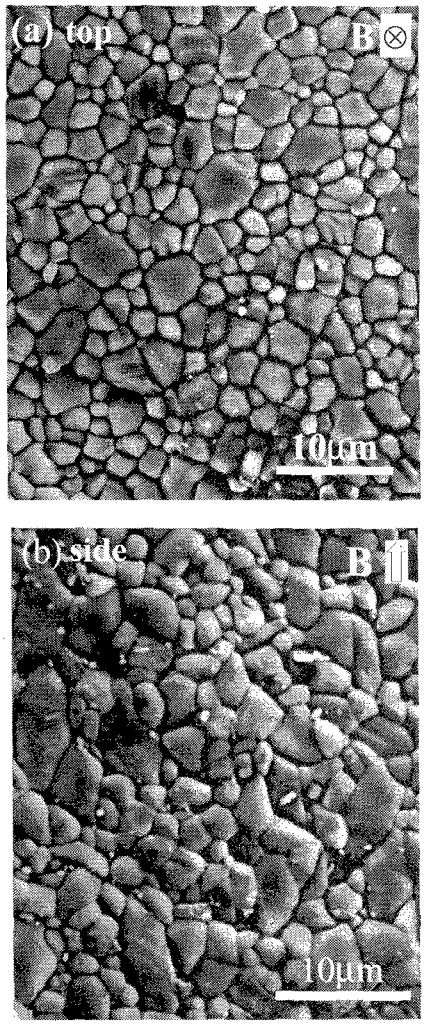
Figure 1 XRD patterns of the top and side surfaces of the TiO_2 deposited by EPD in a magnetic field of 10 T and sintered at 1473 K

Figure 1 shows the XRD patterns of the TiO_2 deposited in 10 T at pH 4, followed by heating at 1473 K. Compared with the samples prepared without the magnetic field, the intensity of the (002) on the surface perpendicular to the magnetic field (top surface) was very pronounced and the other planes, such as (101), (112) and (202) with interplanar angles less than 45° also became strong, whereas planes of (110), (200), (210), (220) with interplanar angles of 90° and (211), (301) with interplanar angles of 63.06° and 65.86°, respectively, were considerably suppressed. On the other hand, the intensities of (110), (200), (210) and (220) on the surface parallel to the magnetic field (side surface) became enhanced, whereas the intensity of (002) with an interplanar angle of 0° disappeared. The XRD data clearly indicated that the crystalline orientation with the c axis aligned along the magnetic field was attained by EPD in a high magnetic field. This alignment is attributable to the anisotropic susceptibility of the titania particles [12].

When the samples were sintered at temperature from 1373 K to 1473 K, the textured degree of the specimen increased from 64% to 75%, indicating that sintering at high temperature is favorable for an increment in the crystallite alignment degree, as is the case with α-Al_2O_3 [8].

Figure 2 shows the microstructure of the top and side surfaces of the specimen prepared at pH 4 in a high

magnetic field of 10 T and then sintered at 1373 K (Fig.2a,b) and 1473 K (Fig.2c,d). The equiaxed grains are observed to arrange randomly on the top surface of the specimen, which is perpendicular to the magnetic field, while slightly elongated grains are aligned on the side surface, which is parallel to the magnetic field when sintered at 1373 K (Fig. 2b). The elongated grains are more apparent on the side surface when sintered at 1473 K (Fig.2d), which provides direct evidence that the particles of titania ceramics with a weak magnetic susceptibility are aligned in the direction of the magnetic field. For comparison, SEM images of the specimen surface prepared without the magnetic field are shown in Fig. 3. The microstructures on both the top and side surfaces were similar, and the grain was equiaxed when prepared without the magnetic field; the grains were randomly distributed and no orientation occurred along a certain direction. Interestingly, the average grain size was 2.2 μm (1373 K) and 9.4 μm



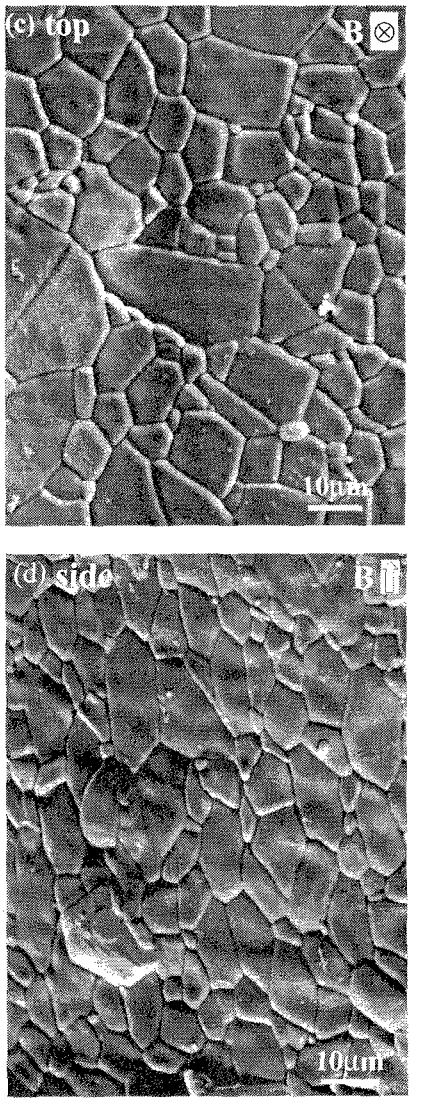


Figure 2 SEM images of TiO_2 samples prepared in a 10 T magnetic field. (a) top (b) side surfaces sintered at 1373 K and (c) top (d) side surface sintered at 1473 K, respectively

(1473 K) prepared in a high magnetic field, respectively, whereas the grain size values were only about 1.1 μm and 3.9 μm under the same conditions without the magnetic field. The grain growth rate of samples prepared in a high magnetic field is much faster than that without magnetic field application.

It should be of great interest to understand the effect of heating temperature on the degree of texture of the samples. From the SEM image at low temperature (Fig. 2b, 1373 K), we can found that the majority of the orientated grains were those with larger grain size, whereas the smaller grains did not show apparent alignment. This fact suggests that the oriented grains' growth along the c-axis may be preferable in this case.

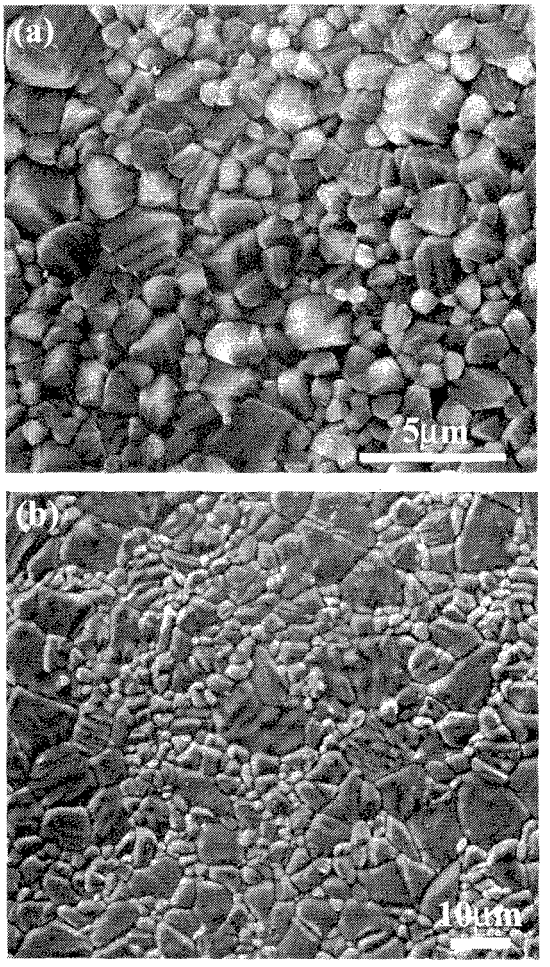


Figure 3 SEM images of the surface of TiO_2 samples prepared without the magnetic field and sintered at (a) 1373 K and (b) 1473 K, respectively

According to Eq.(1), the energy of anisotropy of the crystals is proportional to the volume size of each particle; therefore, large particles more easily align in the direction of a high magnetic field than do small particles. According to the sintering theory of grain growth [13], the driving force and the rate of grain growth are inversely proportional to the grain size, accordingly, the larger aligned grains with small boundary curvature tended to increase by merging with neighboring smaller grains at elevated temperature, whereas the small grains shrunk and finally disappeared, as revealed by SEM images at 1473 K (Fig. 2b→d).

The samples with apparently different grain sizes prepared with or without the magnetic field may also be elucidated from the grain growth habit of the textured ceramics. The competition of the grain growth for randomly arranged titania particles upon heating is comparable, whereas the growth of the well-oriented grains may be much faster by merging with neighboring grains in this case, thus yielding a microstructure with larger grain sizes.

4. CONCLUSIONS

In summary, highly textured TiO_2 ceramics were prepared through EPD processing in a high magnetic field. The c-axis of the TiO_2 particles is parallel to the direction of the magnetic field. The degree of crystalline texture increased with sintering temperature, suggesting that high magnetic field and followed by heating are effective ways to align low anisotropic susceptibility of titania ceramics.

REFERENCES

1 R.C. Hayward, D.A. Saville, I. A. Aksay, *Nature* **404**, 56-59 (2000).
2 T. Kimura, H. Ago, M. Tobita, S. Ohshima, M. Kyotani and M. Yumura, *Adv. Mater.* **14**, 1380-1383 (2002).
3 L. Thien-Nga, K. Hernadi, E. Ljubovic, S. Garaj, L. Forro, *Nano Lett.* **2**, 1349-1352 (2002).
4 P. Sarkar and P.S. Nicholson, *J. Am. Ceram. Soc.*, **79**, 1987-2002 (1996).
5 F.Q. Tang, Y. Sakka, T. Uchikoshi, *Mater. Res. Bull.*, **38**, 207-212 (2003).
6 T. Uchikoshi, K. Ozawa, B.D. Hatton, Y. Sakka, *J. Mater. Res.*, **16**, 321-23 (2001).
7 F.Q. Tang, T. Uchikoshi, Y. Sakka, *J. Am. Ceram. Soc.*, **85**, 2161-65 (2002).
8 T.S. Suzuki, Y. Sakka, and K. kitazawa, *Adv. Eng. Mat.*, **3**, 490-492 (2001).
9 T.S. Suzuki, Y. Sakka, *Chem. Lett.*, **31**, 1204-05 (2002).
10 R. Dillert, A.E. Cassano, R. Goslich, D. Bahnemann. *Catal. Today,* **54**, 267-282 (1999).
11 F.Q. Tang, T. Uchikoshi, K. Ozawa, Y. Sakka, *Mater. Res. Bull.*, **37**, 653-660 (2002).
12 T.S. Suzuki, Y. Sakka, *Jpn. J. Appl. Phys.*, **41**, L1272-74 (2002).
13 W.D. Kingery, Introduction to Ceramics, John Wiley & Sons, Inc., P361, 1976.

(Received October 8, 2003; Accepted March 12, 2004)