

Fabrication of Crystalline-Oriented TiO₂ by Electrophoretic Deposition in a Strong Magnetic Field

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Crystalline-oriented titania thick films were fabricated from titania suspension by electrophoretic deposition (EPD) in a superconducting magnet. Single crystalline titania particles dispersed in an aqueous solvent were rotated due to their magnetic anisotropy in a strong magnetic field of 10 T, and then deposited on a substrate by electrophoresis in an electric field. It was found that changing the angle between the directions of the electric and magnetic fields during the EPD could control the crystalline orientation.

Key words: titania, crystalline orientation, electrophoretic deposition, strong magnetic field

1. INTRODUCTION

There has been increased interest in fabricating crystalline orientation controlled materials using the influence of an external magnetic field against the magnetic anisotropy of the materials. Many materials in asymmetric (non-cubic) crystalline structures have anisotropic magnetic susceptibilities, $\Delta\chi = \chi_{//} - \chi_{\perp}$, associated with their crystal structures, where $\chi_{//}$ and χ_{\perp} are the susceptibilities parallel and perpendicular to the magnetic principal axis, respectively. When a single crystal of these materials is placed in a magnetic field, the crystal is rotated and the crystallographic axis of high χ is aligned in the direction of the magnetic field. Schematic illustration of this particle's rotation is shown in Fig. 1. The driving force of the magnetic alignment is the energy of the crystal anisotropy and is given as[1]:

$$\Delta E = \Delta\chi V B^2 / 2\mu_0, \quad (1)$$

where V is the volume of the material, B is the applied magnetic field, and μ_0 is the permeability in a vacuum. This alignment occurs when the energy of anisotropy is higher than the energy of thermal motion, that is,

$$\Delta E > kT \quad (2)$$

where k is Boltzmann's constant.

Generally, the magnetic susceptibilities of feeble

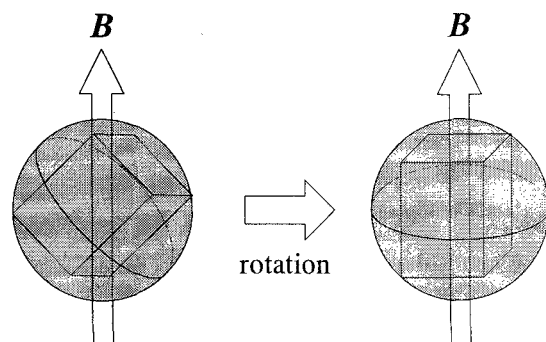


Fig.1 Schematic illustration of the orientation of a single crystalline particle with a non-cubic crystal structure in a magnetic field.

magnetic materials ($|\chi| = 10^{-3} \sim 10^{-6}$) are quite low in comparison with those of ferromagnetic materials ($|\chi| = 10^2 \sim 10^4$) and the ΔE of feeble magnetic materials is much lower than kT in a conventional magnetic field generated by a permanent magnet ($B = \sim 0.1$ T). Therefore, the influence of a magnetic field on feeble magnetic materials has not yet been taken into consideration. The recent development of superconducting magnet technologies has enabled one to introduce magnetic fields as high as ~ 10 T in academic laboratories. Under such strong magnetic fields, the magnetization force acting on feeble magnetic materials is not negligible.

Recently, it has been reported that crystalline-textured ceramics such as alumina[2], titania[3-5], zinc oxide[5,6] and SiC whisker-dispersed alumina[7] have been fabricated by slip casting under 10 T. In order to extend the use of a strong magnetic field for colloidal processing of ceramics, we have proposed the utilization of both magnetic and electric fields, i.e., electrophoretic deposition (EPD) in a strong magnetic field.[8-11] EPD is a colloidal process wherein ceramic bodies are directly shaped from a stable colloid suspension by a dc electric field.[12-14] A schematic illustration of the concept is shown in Fig. 2. Ceramic particles dispersed in a solvent are rotated due to their magnetic anisotropy and then deposited on a substrate. It is essential for each particle to be single crystalline and to be deflocculated

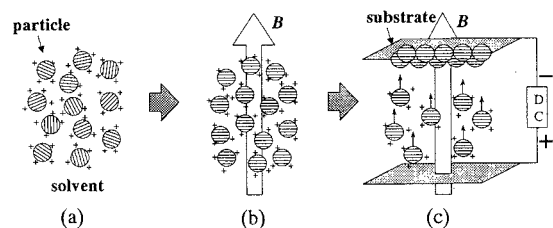


Fig.2 Schematic diagram of the concept of the electrophoretic deposition in a high magnetic field; (a) deflocculated suspension, (b) orientation, (c) deposition

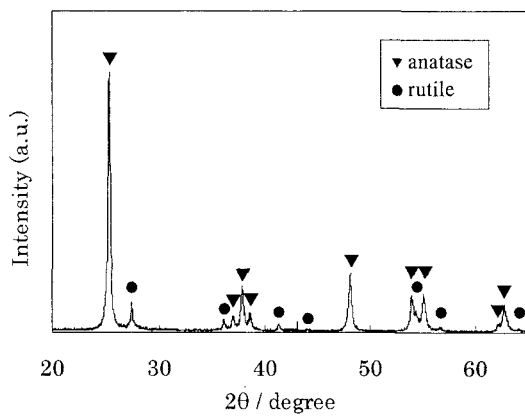


Fig. 3 XRD pattern of as-received titania powder.

for their rotation in a solvent.[8] We have reported that crystalline-textured alumina is fabricated by electrophoretic deposition (EPD) in a strong magnetic field.[8-11]

This paper reports the significant advantages of this facile and precise technique to synthesize crystalline-oriented titania thick films by controlling the directions between the magnetic and electric fields during EPD in a superconducting magnetic environment.

2. EXPERIMENTAL PROCEDURES

Spherical, single crystalline titania particles (Nanotek TiO_2 , 80% anatase, average particle size of 30 nm, high purity of 99.95%) were used in this study. The XRD pattern of the as-received powder is shown in Fig. 3. The powder was dispersed in distilled water at pH 4.5 by ultrasounds, and then a deflocculated titania suspension with a 2.5 vol% solid content was prepared. 0.7 wt of polyethylenimine (PEI) was added to improve the

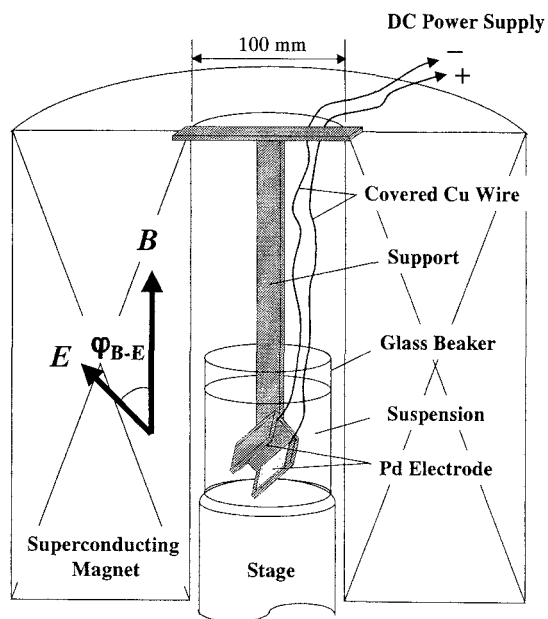


Fig. 4 Schematic illustration of the apparatus for EPD in a superconducting magnet.

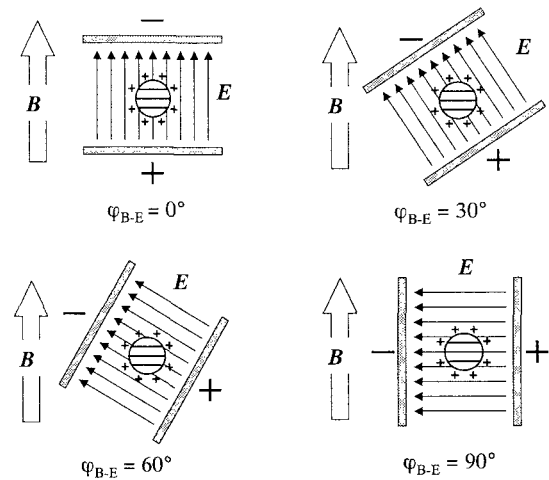


Fig. 5 Schematic illustration of the angle variation between B and E during deposition.

stability of the suspension. The suspension was placed in a superconducting magnet (Japan Magnet Technology JMTD-10T100 with a room temperature bore of 100 mm) and then a strong 10 T magnetic field was applied to the suspension to rotate each particle. A pair of electrodes, with an area of $20 \times 20 \text{ mm}^2$ and 20 mm spacing, held on a phenol resin support was put in the suspension and then an electric current was applied. The center of the magnetic field was at the center of the two electrodes. The magnetic field was maintained in the suspension during the EPD at a constant voltage of 30 V. A palladium sheet was used as the cathodic substrate to absorb hydrogen produced by electrolysis of the solvent.[15] A schematic illustration of the apparatus is shown in Fig. 4. The direction of the electric field relative to the magnetic field was altered (0° , 30° , 60° and 90°) to control the dominant crystal faces as shown in Fig. 5. The thermal treatment of the deposits was conducted at 650°C for 2 h in air out of the magnetic field. The X-ray diffraction (XRD) analysis was carried out to investigate the crystalline orientation.

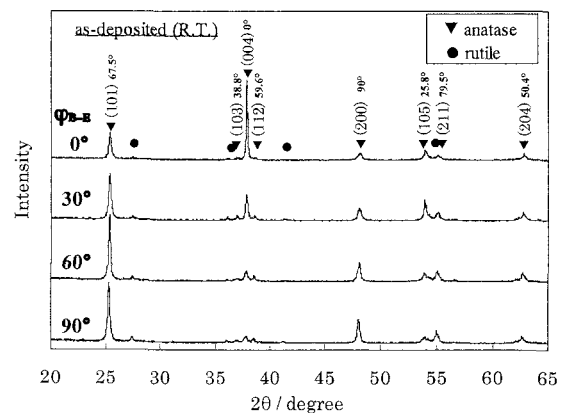


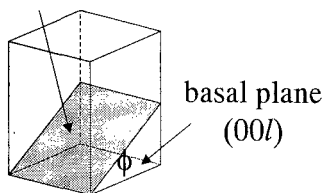
Fig. 6 XRD patterns of the surfaces of as-deposited titania films and their B - E angle (ϕ_{B-E}) dependence. The interplanar angles ϕ_{hkl} between the planes (hkl) and the basal plane (001) of the tetragonal unit cell of anatase are also shown in this figure.

3. RESULTS AND DISCUSSION

Fig. 6 shows the variation in the XRD patterns of as-deposited titania films with the angle between the directions of B and E (φ_{B-E}). This result shows that the dominant crystal faces of the deposit surfaces are changed by varying the angle of E versus B . To characterize the XRD peaks, the interplanar angles ϕ_{hkl} between the planes (hkl) and the basal plane ($00l$) were calculated for a tetragonal unit cell of anatase ($a=3.7852$ nm, $c=9.5139$ nm).[16] Schematic illustration of an anatase unit cell and the standard XRD data of anatase with the ϕ_{hkl} are shown in Fig. 7. When E is parallel to B ($\varphi_{B-E}=0^\circ$), the intensity of the diffraction peak of the (004) plane ($\phi_{hkl}=0^\circ$) is very strong in comparison with the standard data shown in Fig.7. In contrast, the diffraction peaks of the planes at high interplanar angles such as (101)($\phi_{101}=67.5^\circ$), (200)($\phi_{200}=90^\circ$) and (211)($\phi_{211}=79.51^\circ$) are relatively weak. When φ_{B-E} is changed to 30° , the diffraction peak of the (004) plane becomes weak and the peak of (105)($\phi_{105}=25.8^\circ$) becomes relatively strong. The peak of the (101)($\phi_{101}=67.5^\circ$) plane also becomes stronger. When φ_{B-E} is changed to 60° , the diffraction peak of the (004) becomes much weaker and the peak of the (101) plane becomes the strongest one. Finally when E is perpendicular to B ($\varphi_{B-E}=90^\circ$), the diffraction peak of (200)($\phi_{200}=90^\circ$) plane becomes much strong. The peak of (211)($\phi_{211}=79.5^\circ$) plane is also relatively strong.

This result is explained as follows. The magnetic field fixes the orientation of each particle; the c -axis of anatase is aligned parallel to B in a solvent in this case. When an electrical field is then applied to the oriented particles, they move along with the electric field retaining their orientation against the magnetic field, and

(hkl) plane



Anatase (ICDD# 21-1272)

d (Å)	2θ (CuK α) (deg)	I/I_0	(hkl)	ϕ (deg)
3.52	25.28	100	1 0 1	67.5
2.431	36.944	10	1 0 3	38.83
2.378	37.799	20	0 0 4	0
2.332	38.573	10	1 1 2	59.64
1.892	48.047	35	2 0 0	90
1.6999	53.887	20	1 0 5	25.77
1.6665	55.058	20	2 1 1	79.51
1.493	62.116	4	2 1 3	60.94
1.4806	62.695	14	2 0 4	50.36
1.3641	68.757	6	1 1 6	29.64

Fig. 7 Schematic illustration of an anatase unit cell and the standard powder XRD data of anatase

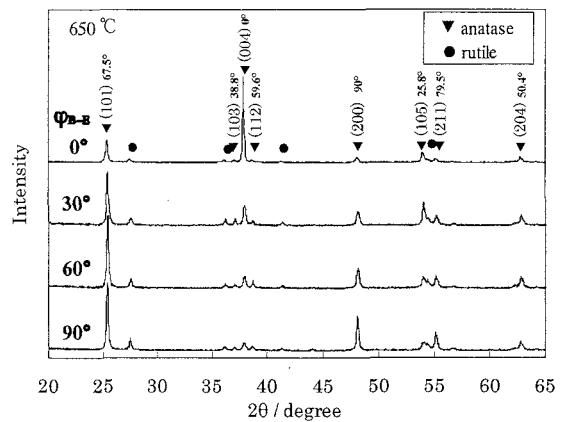


Fig. 8 XRD patterns of the surfaces of titania films after thermal treatment at 650°C for 2 h and their B - E angle (φ_{B-E}) dependence.

then deposit on a substrate. Fig. 8 shows the variation in the XRD patterns after the thermal treatment at 650°C . The orientation of the anatase films was a little improved.

In the present study, the most well-oriented anatase film was obtained at $\varphi_{B-E}=0^\circ$, and the orientation at $\varphi_{B-E}=30^\circ$, 60° and 90° was inferior to that of at $\varphi_{B-E}=0^\circ$. This reason is considered as follows. When $E \times B \neq 0$, the particles should be affected by the Lorentz force. It is probable that the Lorentz force causes a stirring effect of the suspension and disturbs the orientation of each particle during deposition.

Electrophoretic deposition in a strong magnetic field is a promising method to fabricate crystalline oriented titania. This method can be applied for other ceramic materials to fabricate crystalline oriented, or specified crystal face, thin films for functional applications.

4. CONCLUSIONS

The crystalline-orientation titania ceramics are prepared by EPD in a strong magnetic field. By varying the angle of E versus B , the dominant crystal faces at the surface can be controlled.

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