Ceramics International 30 (2004) 1975–1978

CERAMICS
INTERNATIONAL

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Crystalline-oriented TiO_2 fabricated by the electrophoretic deposition in a strong magnetic field

T. Uchikoshi*, T.S. Suzuki, F. Tang, H. Okuyama, Y. Sakka

Materials Engineering Laboratory, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Received 27 November 2003; received in revised form 13 December 2003; accepted 23 December 2003

Abstract

Electrophoretic deposition of titania (anatase) suspension was conducted in a strong magnetic field of 10 T. The direction of the electric field $\boldsymbol{E}$ relative to the magnetic field $\boldsymbol{B}$ was altered ($\varphi_{B-E} = 0$, 30, 60 and 90°) to control the dominant crystal faces of the deposit surfaces. The crystalline orientation was investigated by the X-ray diffraction for the titania films of as-deposited, sintered at 650, 750 and 1200 °C as a function of the angle between the directions of $\boldsymbol{B}$ and $\boldsymbol{E}$ (φ_{B-E}). It was found that changing the angle φ_{B-E} during the EPD could control the crystalline orientation of the titania films.

Keywords: D. Titania; Crystalline orientation; Magnetic anisotropy; Electrophoretic deposition

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 $\chi_{\perp}$ 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. The driving force of the magnetic alignment is the energy of the crystal anisotropy and is given as [1]:

$$\Delta E = \frac{\Delta\chi V B^2}{2\mu_0} \tag{1}$$

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,

$$\Delta E > kT \tag{2}$$

where k is Boltzmann's constant.

Generally, the magnetic susceptibilities of feeble magnetic materials ($|\chi| = 10^{-3}$ to 10^{-6}) are quite low in comparison with those of ferromagnetic materials ($|\chi| = 10^2$ to 10^4) and the ΔE of feeble magnetic materials is much lower than kT in a conventional magnetic field generated by a permanent magnet ($B \sim 10^{-1}$ 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 provided academic laboratories with magnetic fields as high as ∼10 T. 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 the 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 in a dc electric field [12–14]. A schematic illustration of the concept is shown in Fig. 1. 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 be deflocculated for their rotation in a solvent [8]. We have reported that

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[*] Corresponding author. Fax: +81-29-859-2401.
E-mail address: uchikoshi.tetsuo@nims.go.jp (T. Uchikoshi).

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doi:10.1016/j.ceramint.2003.12.179

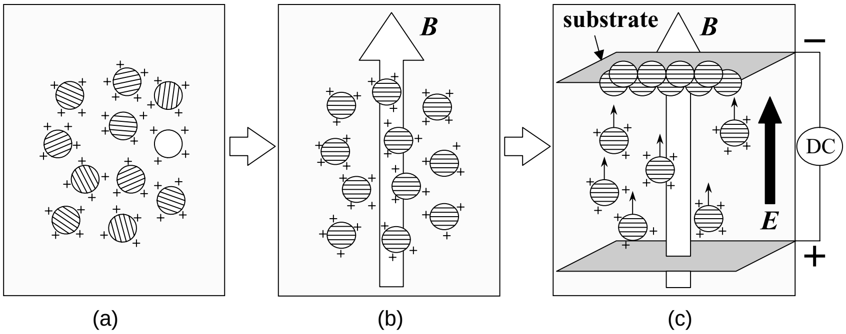

Fig. 1. Schematic diagram of the concept of the electrophoretic deposition in a high magnetic field; (a) deflocculated suspension, (b) orientation of the particles, (c) deposition of the particles.

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

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. 2. The powder was dispersed in distilled water at pH 4.5 by ultrasounds, and then a deflocculated titania suspension with a 5 vol.% solid content was prepared. Polyethylenimine (PEI) was added to improve the 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 mm × 20 mm and 20 mm spacing, held on a phenol resin support was placed 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. 3. The direction of the electric field $\boldsymbol{E}$ relative to the magnetic field $\boldsymbol{B}$ was altered ($\varphi_{B-E} = 0$, 30, 60 and 90°) to control the dominant crystal faces of the deposits. After the deposition, the deposits were taken out from the magnetic field and dried at room temperature. The dried deposits were exfoliated from the substrates. The thickness of the deposits were 2–3 mm. The sintering of the specimens was conducted in air out of the magnetic field at fixed temperatures for 2 h. The X-ray diffraction (XRD) analysis was carried out to investigate the crystalline orientation of the specimens.

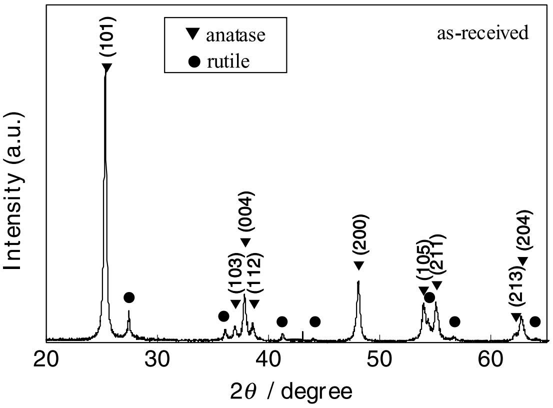

Fig. 2. XRD pattern of as-received titania powder.

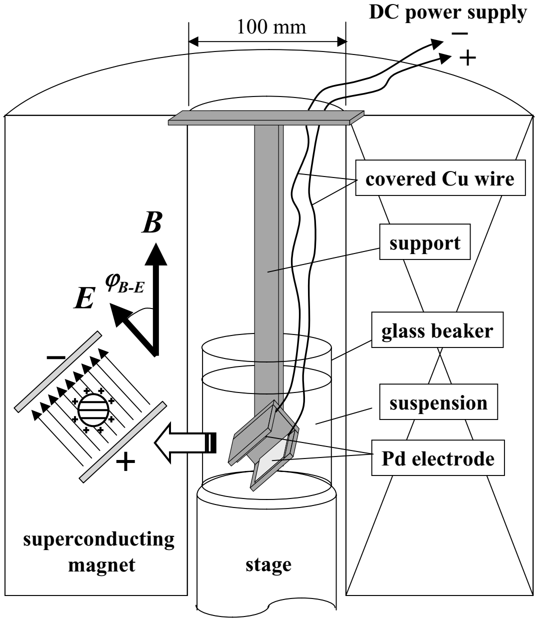

Fig. 3. Schematic illustration of the apparatus for EPD in a superconducting magnet.

3. Results and discussion

The variation in the XRD patterns of the titania films of as-deposited, sintered at 650, 750 and 1200 °C with the angle between the directions of ***B*** and ***E*** (φ_{B-E}) are shown in Figs. 4–7, respectively. To characterize the XRD peaks, the interplanar angles ϕ_{hkl} between the planes ($h\,k\,l$) and the basal plane ($0\,0\,l$) of a tetragonal unit cell were calculated for the anatase [16] and the rutile [17]. The standard XRD data of anatase and rutile with the ϕ_{hkl} are shown in Table 1. The ϕ_{hkl} are also shown at the XRD peaks of the ($h\,k\,l$) planes in Figs. 4–7.

From the XRD pattern in Fig. 4, the intensity of the diffraction peak of the (0 0 4) plane ($\phi_{004} = 0°$) is very strong in comparison with the standard XRD data in Table 1 when ***E*** is parallel to ***B*** ($\varphi_{B-E} = 0°$). In contrast, the diffraction peaks of the planes at high interplanar angles such as (1 0 1) ($\phi_{101} = 67.5°$), (2 0 0) ($\phi_{200} = 90°$) and (2 1 1) ($\phi_{211} = 79.51°$) are relatively weak. When φ_{B-E} is changed to 30°, the diffraction peak of the (0 0 4) plane becomes weak and the peak of (1 0 5) ($\phi_{105} = 25.8°$) becomes relatively strong. The peak of the (1 0 1) ($\phi_{101} = 67.5°$) plane also becomes stronger. When φ_{B-E} is changed to 60°, the diffraction peak of the (0 0 4) becomes much weaker and the peak of the (1 0 1) plane becomes the strongest one. Finally, when ***E*** is perpendicular to ***B*** ($\varphi_{B-E} = 90°$), the diffraction peak of (2 0 0) plane becomes much strong. The peak of (2 1 1) ($\phi_{211} = 79.5°$) plane is also relatively strong. The XRD data show that the dominant crystal faces of the deposit surfaces are changed by varying the angle of ***E*** versus ***B***. 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 while retaining their orientation relative to the magnetic field, and then deposit on a substrate. In the present study, the most well-oriented anatase film was obtained at

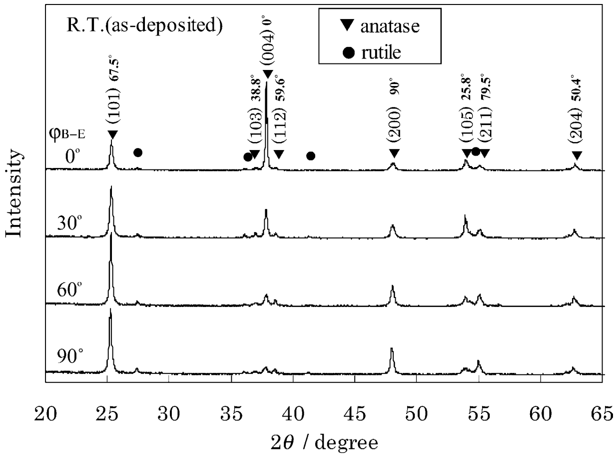

Fig. 4. XRD patterns of the surfaces of as-deposited titania films and their ***B***–***E*** angle (φ_{B-E}) dependence. The interplanar angles ϕ_{hkl} between the planes ($h\,k\,l$) and the basal plane ($0\,0\,l$) of a tetragonal unit cell of titania are also shown in this figure.

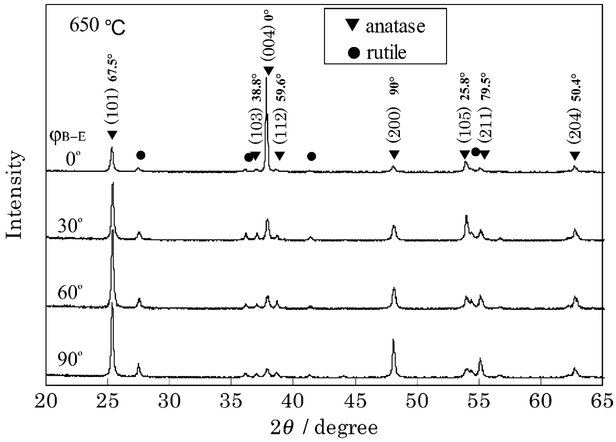

Fig. 5. XRD patterns of the titania films sintered at 650 °C for 2 h and their φ_{B-E} dependence. The ϕ_{hkl} of the ($h\,k\,l$) planes are also shown in the figure.

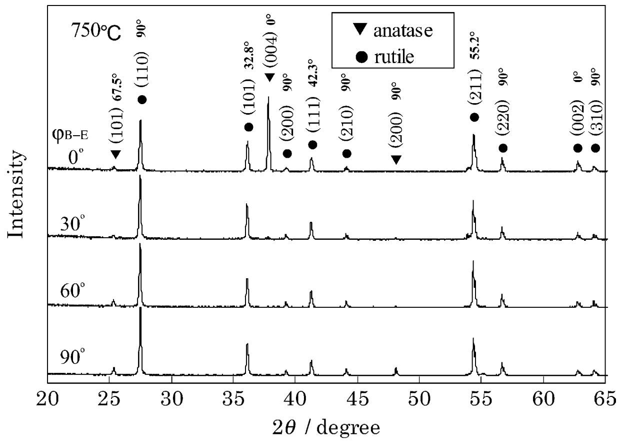

Fig. 6. XRD patterns of the titania films sintered at 750 °C for 2 h and their φ_{B-E} dependence. The ϕ_{hkl} of the ($h\,k\,l$) planes are also shown in the figure.

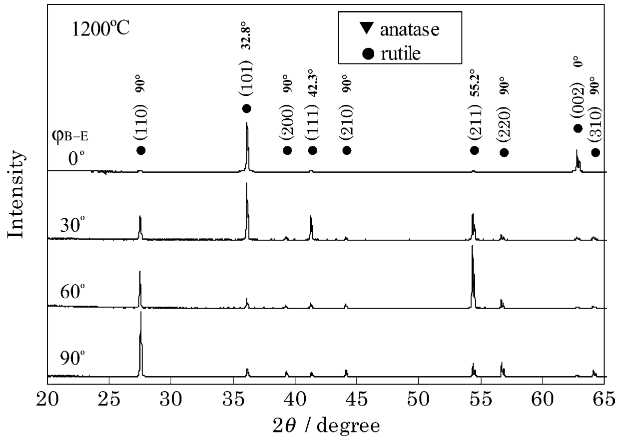

Fig. 7. XRD patterns of the titania films sintered at 1200 °C for 2 h and their φ_{B-E} dependence. The ϕ_{hkl} of the ($h\,k\,l$) planes are also shown in the figure.

Table 1
The standard XRD data of anatase and rutile with the interplanar angles ϕ_{hkl} between the planes ($h\,k\,l$) and the basal plane ($0\,0\,l$)

d (Å)	2θ (Cu Kα) (°)	I/I_0	($h\,k\,l$)	ϕ_{hkl} (°)
#21-1272 TiO_2 (anatase)				
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
#21-1276 TiO_2 (rutile)				
3.247	27.445	100	(1 1 0)	90
2.487	36.083	50	(1 0 1)	32.79
2.297	39.185	8	(2 0 0)	90
2.188	41.223	25	(1 1 1)	42.34
2.054	44.049	10	(2 1 0)	90
1.6874	54.319	60	(2 1 1)	55.23
1.6237	56.638	20	(2 2 0)	90
1.4797	62.737	10	(0 0 2)	0
1.4528	64.036	10	(3 1 0)	90
1.4243	65.475	2	(2 2 1)	61.24

$\varphi_{B-E} = 0°$, and the orientation at $\varphi_{B-E} = 30$, 60 and 90° was inferior to that of at $\varphi_{B-E} = 0°$. When $\boldsymbol{E} \times \boldsymbol{B} \neq 0$, 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. The orientation of the anatase films was somewhat improved after the thermal treatment at 650 °C as shown in Fig. 5. Similar characteristics of the improvement of the crystalline orientation by the following sintering have been reported elsewhere [5,10].

The phase transformation of the titania from anatase to rutile occurs at the temperature between 650 and 750 °C as shown in Fig. 6. It seems that the crystalline orientation has died out after the phase transformation since no orientation is observed for the rutile peaks in Fig. 6. However, it is quite interesting that the strong crystalline orientation has come back to the rutile phase after the sintering at 1200 °C as shown in Fig. 7. For example, the intensity of the diffraction peak of the (0 0 2) ($\phi_{002} = 0°$) plane is the strongest when $\varphi_{B-E} = 0°$, and the intensity of the diffraction peak of the (1 1 0) ($\phi_{110} = 90°$) plane is the strongest when $\varphi_{B-E} = 90°$. The reason for this phenomenon is considered as follows. The phase transformation of titania from the anatase to the rutile requires no big movement of atoms since both of the two phases have tetragonal crystalline structures. Therefore, most of the arrangement of the atoms in anatase was taken over to those of in rutile after the phase transformation, and crystalline oriented rutile was formed. Farther investigation is necessary to reveal the phenomenon.

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 specific crystal face appeared, thin films for functional applications.

4. Conclusions

The crystalline-orientated titania ceramics were prepared by EPD in a strong magnetic field. By varying the angle of $\boldsymbol{E}$ versus $\boldsymbol{B}$, the dominant crystal faces at the surface can be controlled. Crystalline orientation was retained after the phase transformation from the anatase to the rutile.

Acknowledgements

The authors wish to thank Dr. Partho Sarkar of the Alberta Research Council for his valuable comments. This research was partially supported by the Budget for Nuclear Research of the Ministry of Education, Culture, Sports, Science and Technology.

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