研 究

Dense Nano-structured and Preferentially-oriented Anatase Synthesized by Pulsed High Current Heating

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SYNOPSIS

Dense nano-structured bulk anatase was synthesized with pulsed high current heating (PHC) method. Nano-powder anatase compact was successfully consolidated up to 90%TD (TD; theoretical density) with preferential orientation and no transformation to rutile, with suppressing the grain growth below about 300 nm. Nearly full densification over 95%TD was attained in the condition of coexisting both anatase and rutile phases. Remarkable preferential orientation was observed in the anatase consolidated at the temperature ranging from 700°C to 850°C. The preferential orientation depended on the angle (α) of crystallographic plane of anatase to the direction of current (and pressure). Degree of the orientation linearly increased with the increase of pressure and the angle in ranging from 45° to 90°, resulting in the appearance of strong preferential orientation in the (004) and (105) XRD peaks. While preferential orientation was not found in the crystallographic planes of anatase observed at the angle α less than 45°.

KEY WORDS

Nano-structured dense anatase, pulsed high current heating, preferential orientation, crystallite growth

1 Introduction

Environmental-conscious processing for synthesizing various functional materials has been required strongly in various fields. Ceramics and their related materials are now being applied to eco-materials, but some of them require high temperature and a long time treatment to fabricate them, in which a large amount of energy is consumed. In order to solve the requirements, rapid consolidation processing of powder materials based on pulsed high current (PHC) has been much interested in the fields of powder metallurgy and ceramics sintering¹⁻³⁾. In general, the PHC heating method has a great advantage for sintering refractory powder within several minutes at a fairly lower temperature than those in conventional method^{4,5)}. Recently, the PHC method has widely applied for nano-structured materials such as dielectric oxides and magnetic materials because grain growth can be suppressed by rapid heating⁶⁾.

In the present paper, however, our interest was faced not to high-temperature and structural materials but to anatase, which is one of typical eco-materials. As known

well, anatase is one of the practical oxides with various eco-catalytic abilities such as anti-bacterial and photocatalytic properties^{7,8)}. In these materials, to fabricate in a versatile shape and sometimes nano-porous solid structure is required to attain highly efficient functions. Bulk nano-structured anatase was generally synthesized by pressurizing nano-powder compact over 1 GPa below 500 °C [high-pressure and low temperature (HPLT) method] in order to avoid rapid grain growth in the final stage of sintering^{9,10)}. However, pressure-assisted transformation of metastable anatase to rutile prevents to synthesize fully densified single-phase anatase. While, it is greatly expected by high sinterability of PHC method that nano-powder anatase can be fully densified below its transformation temperature with suppressing the transformation to rutile phase.

In our previous paper¹¹⁾, we have already reported on the consolidation characteristics of nano-powder anatase by PHC heating method. In the present paper, characteristics of PHC processing to nano-powder and microstructural analysis of consolidated anatase are reported in more details.

2 Experimental procedures

Commercial available nano-powder (DN-1-0, Furukawa Metal Co. Ltd., average size 9 nm, specific area 290 m²/g) was used as the starting material. A pulsed high current heating equipment (Doctor sinter, SPS-1050, Sumitomo Coal Mining Co. Ltd.) was used for the consolidation of the nano-powder. Definite amount (about 5 g) of anatase nano-powder was filled into graphite die with 20 mm in diameter and consolidated below 1 Pa at a heating rate of 50 °C/min.. Temperature and holding time were varied from 600 °C to 1000 °C and from 0 min. to 30 min.. Pressurized condition was in the range from 10 MPa to 60 MPa. Specimen temperature was measured by inserting K-type thermocouple into the small hole with 10 mm length, in which was made in the center of the cylindrical hollow die with 12.5 mm in thickness. Consolidation of submicron powder (reagent grade, 300 nm) with PHC method was also performed for comparison.

Density of consolidated anatase powder was estimated by measuring its thickness of the consolidated circular disk. Phase identification of the consolidated anatase powder was performed by XRD method (Rigaku, Miniflex) using Cu K α radiation. Precise intensities of standard XRD peaks due to anatase phase were calculated using the program "Rietan"^{12,13}. In this calculation, the atomic positions of (0,0,0.2064) and (0,0,0) were used for oxygen and titanium atoms, and the values of $a=0.3785$ nm and $c=0.9514$ nm were used as the lattice constants, respectively¹⁴. These theoretically determined intensities were compared with the experimentally determined intensities for the purpose of examining preferential orientation in anatase phase. The preferential orientation was examined by selecting the peak due to (200) plane as the standard. Thus, the degree of preferential orientation was estimated by the ratio of $R[\text{exp}]$ to $R[\text{cal}]$, $R=R[\text{exp}]/R[\text{cal}]$, where $R[\text{exp}]$ and $R[\text{cal}]$ are expressed by $I(hkl)[\text{exp}]/I(200)[\text{exp}]$ and $I(hkl)[\text{cal}]/I(200)[\text{cal}]$, respectively. Further, $I(hkl)[\text{exp}]$ and $I(hkl)[\text{cal}]$ are the intensities of XRD peaks due to (hkl) plane determined experimentally and theoretically.

Growth of crystallite size in the consolidated body of anatase powder was estimated by assuming that the value determined from Scherrer's equation corresponds to the crystallite size. Microstructure of consolidated body of anatase powder was observed with a field emission-type secondary electron microscope (Hitachi, S-4500).

3 Results and Discussion

Temperature dependence of relative density for PHC and conventionally consolidated anatases is shown in

Fig. 1. Using PHC method, as shown in this figure, anatase nano-powder was consolidated up to 90%TD with almost no transformation of anatase phase, which will be shown later. Further, high densification around 95%TD was obtained when some amount of anatase transforms to rutile phase. In the PHC method, measured temperature of specimen is inclined to be a higher temperature than true value because thermocouple can not be in contact with the surface of specimen. In our previous work, the temperature of the sintered alumina was directly measured by using a special assembly of temperature measurement in PHC experiment^{15,16}. According to the result, the directly measured temperature differs from the conventionally measured temperature by about 100 °C or so when specimen temperature was around 800 °C. The temperature dependence corrected by 100 °C on the basis of the previous result was also shown in Fig. 1. If the correction is reasonable, densification behavior of anatase with PHC method is regarded as similar to that with conventional method up to 800 °C. Exceeding 800 °C, the effects of pulsed high current and pressurization appeared clearly in the densification. Later, correction of temperature will be discussed further by comparing with phase identification.

Pressurizing effect in the consolidation at 800 °C is also given in Fig. 1. With decreasing the pressure, relative density of consolidated body decreased linearly and the relative density was estimated to be about 53%TD at zero pressure. On the other hand, the relative density of anatase

Fig.1 Dependence of relative densities on consolidation temperature in the anatase bodies consolidated by PHC heating or conventional method.

consolidated at 800°C was about 58%TD in the conventional method, suggesting that the pressuring effect in PHC method appears over several MPa.

Densification behavior of submicron anatase powder was examined for the purpose of comparing that for nano-powder anatase. Remarkable difference was found in between the densification behaviors, as shown in Fig. 2. Relative density of nano-powder exceeded over 80%TD at the sintering time of 5min and reached a maximum around 90%TD, and then decreased slightly in the further sintering. While, the density of submicron powder was fairly lower than that for nano-powder and increased monotonously with increasing the sintering time. Thought for detailed reasons on the appearance of a maximum for nano-powder anatase are now unclear, the maximum is probably attributed to the phase change of anatase.

Fig. 3 shows the XRD patterns obtained from consolidated bodies of nano-anatase with PHC and conventional methods. These XRD patterns were obtained from the surfaces perpendicular to the directions of pulsed high current and pressure. Comparing with XRD patterns obtained at 900°C, transformation of anatase to rutile seems to begin somewhat rapidly in the body consolidated with PHC method. According to the previous result¹⁷⁾, the compressive stress as high as 60 MPa is enough effective for enhancing the rate of the transformation to rutile in the pressure-assisted

sintering of anatase. Therefore, it was explained that only a slight pressure effect was observed on the phase change to rutile in the consolidation with PHC method.

As shown in these results, preferential orientation was remarkably observed in the XRD peaks due to (004) and

Fig.2 Dependence of relative densities on consolidated temperature in the nano- and submicron-powder anatases consolidated by PHC heating, respectively.

Fig.3 X-ray diffraction patterns obtained from anatase bodies consolidated at various temperatures. (a) conventional method, (b) PHC heating method

(105) planes of the bodies consolidated at 700 °C and 800 °C. To show the preferential orientation in the anatase body consolidated with PHC method, the relative intensities of (004) peaks to (101) peaks were compared with those for conventionally consolidated anatases. As given in Fig. 4, the intensity of (004) peak showed several times to those for conventionally consolidated anatases. Further, quite remarkably preferential orientation was observed in the anatase with some amount of rutile, which consolidated at 850 °C. The remarkable orientation disappeared with approaching the transformation temperature of anatase to rutile. This is quite natural because atomic arrangement of anatase structure becomes unstable in this temperature. For the purpose of examining the preferential orientation in details, relation between the relative intensity of each peak due to anatase and the angle (z) of crystallographic plane of the corresponding peak to the direction of electric current was examined. As explained before, relative intensity of each anatase XRD peak was normalized by using the corresponding relative intensity calculated theoretically. Dependence of the normalized relative intensity on the angle z was shown in Fig. 5. The normalized relative intensity was almost unchanged at the angle z less than 45° and then linearly increased with the angle z . The slope of the linear relation becomes steeper with the increase of experimental temperature and pressure in the consolidation.

Preferential orientation was not observed at the

consolidation temperature below 600 °C, so pressure and high current were not effective for the occurrence of the preferential orientation below 600 °C. Thus, it is indicated that heating of anatase nano-powder over 700 °C is important for the occurrence of the preferential orientation. As

Fig. 4 Dependence of relative intensity $[100 \cdot I(004)/I(101)]$ of (004) XRD peak to maximum XRD (101) peak $[I(101)]$ against consolidation temperature in the anatase bodies consolidated nano- and submicron-powders by PHC heating, respectively.

Fig. 5 Relation between ratio of relative intensity in XRD peaks and the angle of the crystallographic plane of respective XRD peak to the direction of electric current (z -axis). (a) dependence on pressure, (b) effect of consolidation temperature

suggested from the densification behavior, deformation of nano-powders and probably atomic transfer within particle will be allowed in the temperature range from 700 °C to 800 °C. Further, as shown in Fig. 5 (b), similar degree of preferential orientation was obtained in both anatase bodies consolidated at 850 °C under 30 MPa and at 800 °C under 60 MPa. Accordingly, the effect of pressure difference of 30 MPa on the enhancement of preferential orientation corresponds to that of temperature difference of 50 °C.

SEM photographs of anatase bodies consolidated at various temperatures are shown in Fig. 6. It was found that anatase particles were scarcely coalesced below 700 °C and the coalescence of particles proceeded over 800 °C. Size of coalesced particles was less than several hundreds nanometer even after attaining fairly full densification over 90%TD. As shown in Fig. 6, the size of coalesced particle can be regarded as the grain size, so that fairly densified anatase body consisting of grains with the order of hundreds

Raw powder ($\times 100K$)

600 °C ($\times 50K$)

700 °C ($\times 50K$)

800 °C ($\times 50K$)

850 °C ($\times 50K$)

900 °C ($\times 50K$)

Fig.6 SEM photographs of anatase nano-powders consolidated at several temperatures. SEM photograph of raw nano powder is shown together.

nanometer can be produced by PHC method.

Particle size of nano-powder corresponds to grain size itself in the initial stage of consolidation. In other words, crystallite size is equivalent to grain size because nano-particles do not coalesce in the initial stage of consolidation. With the evolution of densification, however, the grains in the consolidated body change to the aggregates of crystallites by the coalescence of nano-particles. It is suggested that the chemically active character of the aggregates is maintained by suppressing the growth of crystallite size similar to grain size. Thus, crystallite size as well as grain size is important for chemical activity in nano-structured bulk materials. In the present study, the crystallite size (δ) of anatase was estimated from the broadening (FWHM; B) of XRD peak using the Scherrer's formula ($\delta = K\lambda/B\cos\theta$, $K=0.9$). Dependence of crystallite size on the relative density was shown in Fig. 7. The crystallite size of the anatase consolidated with PHC heating method gently increased from 9 nm (in the starting powder) up to 43 nm, with increasing the relative density. While the size of conventionally consolidated anatase rapidly increased over 50 nm irrespective of the relative density less than 80%TD. Thus, anatase nano-powder compact can be consolidated with the PHC heating method, with suppressing the growth of crystallite as well as attaining nearly full densification.

Up to the present time, fabrication of nano-structured titanium oxides were made by various methods including HPLT and PHC heating (or SPS) methods. For example, according to Liao et al., dense TiO_2 over 90%TD, was obtained from nano powder of 27 nm by HPLT method⁹. In this method, however, the pressure as high as 1.5 GPa is required to obtain the nano-structured TiO_2 . Besides, it is unavoidable to coexist rutile phase on account of phase change from anatase to rutile due to high pressure. Synthesis of dense nano-structured TiO_2 was also made by spark plasma sintering (that is, PHC) method. Angerer et al. consolidated nano powder of anatase with 40 nm at 1000 °C for 1 min by SPS method and obtained dense nano-structured TiO_2 with the average grain size of about 130 nm¹⁸. It has been also reported by Lee et al. that fully densified TiO_2 was successfully obtained from nano-powder of 20 nm by consolidating at 700 °C for 1hr using SPS method¹⁹. In these results, however, the consolidated bodies consist of rutile phase and occurrence of preferential orientation was not observed in these bodies. Though some experimental conditions such as consolidation temperature and holding time differ from those in the present study, the important factor for the remarkable preferential orientation and high

Fig. 7 Dependence of crystallite size on relative density of the anatase bodies consolidated by PHC heating or conventional method, respectively.

densification without changing to rutile phase may be attributable to the smaller particle size of 9 nm. Especially, interaction of mass transfer in the surface of nano-powder with pulsed high current may have important roles on the remarkable preferential orientation. Field-added (or current induced) diffusion and enhancement of crystal growth are easily considered as the plausible reasons for the remarkable preferential orientation. Field-aided diffusion of oxygen in a defect-induced structure can be expected in the consolidation of anatase nano powder by PHC heating because the consolidation is proceeded in a reducing condition. However, the reason why the field-added diffusion can be enhanced in the direction perpendicular to (001) planes remains unclear. Therefore, it is necessary to investigate further for obtaining clear evidence on the remarkable preferential orientation in PHC-consolidated anatase.

4 Summary

- (1) Rapid consolidation of nano-powder anatase was performed with the pulsed high current heating method. Dense nano-structured bulk anatase with about 90%TD was successfully produced by consolidating at 850 °C for 20 min under the pressure of 30 MPa, though a small amount of rutile was detected. Further, nearly full densification over 95%TD was obtained in the condition of coexisting anatase and a fairly amount of rutile.

- (2) Preferential orientation was observed in the anatases consolidated at the temperature ranging from 700 °C to 850 °C. Remarkable preferential orientation was observed in the (004) and (105) crystallographic planes. Examining dependence of the preferential orientation on the angles (α) of crystallographic plane to the direction of current and pressure, the crystallographic planes with the angle higher than 45 degree were oriented preferentially and the preferential orientation becomes more remarkable with the increase of the angle (α).
- (3) From SEM observation, grain size was suppressed below about 300 nm even in the anatase with nearly full density. Crystallite growth was also suppressed up to 43 nm in the same anatase.
- (4) Conclusively, it is reported that the pulsed high current heating method is capable of producing dense nano-structured and preferentially-oriented bulk anatase within 20 min at the temperature below the transformation point to rutile, with suppressing grain and crystallite sizes up to 300 nm and 43 nm.

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References

- 1) R.S.Doboe, G.D.West and M.H.Lewis: "Spark plasma sintering of ceramics", *Bulletin of EcerS*, **1**(2003)19-24.
- 2) M.Omori: "Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS)", *Mater. Sci. Eng.*, **A287**(2000)183-188.
- 3) M.Tokita: "Trends in advanced SPS spark plasma sintering system and technology", *J. Soc. Powder Technol.*, **30**(1993)790-804.
- 4) Y.Zhou, K.Hirao, M.Toriyama and H.Tanaka: "Very rapid densification of nanometer silicon carbide powder by pulse electric current sintering", *J. Am. Ceram. Soc.*, **83**(2000)654-656.
- 5) K.A.Khor, K.H.Cheng, L.G.Yu and F.Boey: "Thermal conductivity and dielectric constant of spark plasma sintered aluminum nitride", *Mater. Sci. and Eng.*, **A147**(2003)300-305.
- 6) Y.Makino: "Synthesis of nano-structured materials with pulsed high current heating", *J. High Temperature Soc.*, **31**(2005) 202-208.
- 7) I.Sopyan, M.Watanabe, S.Murasawa, K.Hashimoto and A.Fujishima: "An efficient TiO₂ thin-film photocatalyst; photocatalytic properties in gas-phase acetaldehyde degradation", *J. Photochem. Photobiol.*, **A98**(1996)79-86.
- 8) N.Negishi, K.Takeuchi and T.Ibusuki: "Surface structure of the TiO₂ thin film photocatalyst", *J. Mater. Sci.*, **33**(1998)5789-5794.
- 9) S.-C.Liao, K.D.Pae and W.E.Mayo: "High pressure and low temperature sintering of bulk nanocrystalline TiO₂", *Mater. Sci. Eng.*, **A204**(1995)152-159.
- 10) S.-C.Liao, Y.-J.Chen and W.E.Mayo: "Transformation-assisted consolidation of bulk nanocrystalline TiO₂", *Nano-Struct. Mater.*, **11**(1999)553-557.
- 11) Y.Makino, T.Mori, H.Eguchi, H.Saito, B.Kyoh and S.Miyake: "Preferentially oriented anatase nanopowder densified by pulsed high current heating", *J. Mater. Sci. Letts.*, **22**(2003)403-405.
- 12) F.Izumi: "Rietveld analysis of x-ray and neutron diffraction patterns", *J. Mineralogr. Jpn.*, **17**(1985) 37-50.
- 13) F.Izumi: "A software package for Rietveld analysis of x-ray and neutron diffraction patterns", *J. Crystallogr. Jpn.*, **27**(1985)27-31.
- 14) T.Hahn: *International Table of Crystallography*, Vol.C, Kluwer, Boston, (1992).
- 15) Y.Makino: "Characteristics of sintering process based on pulsed high current", *New Ceramics*, **10**(1997)39-42.
- 16) Y.Makino, M.Kamai, T.Ohmae and S.Miyake: "Evaluation of current path and effect on sintering in pulsed high current process", *Proc. of Intl. Symp. on Microwave, Plasma and Thermochemical Processing of Advanced Materials*, Feb.3-4, Osaka, Japan, (1997) 77-81.
- 17) D.C.Hague and M.J.Mayo: "The effect of crystallization and a phase transformation on the grain growth of nanocrystalline titania", *Nano-Struct. Mater.*, **3**(1993) 61-69.
- 18) P.Angerer, L.G.Yu, K.A.Khor and G.K.Krumpel: "Spark-plasma-sintering (SPS) of nanostructured and submicron titanium oxide powders", *Mater. Sci. Eng.*, **A381**(2004)16-19.
- 19) Y.I.Lee, J.-H.Lee, S.-H.Hong and D.F.Y.Kim: "Preparation of nanostructured TiO₂ ceramics by spark-plasma-sintering", *Mater. Res. Bull.*, **38**(2003)925-930.