FULL PAPER

Effect of titanyl sulfate concentration on growth of nanometer-scale rutile rod arrays on the surface of titanium substrate

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Nano-scale rod arrays of titania were prepared on commercially available pure titanium (cpTi) substrates by a chemical treatment at 80°C for 3 d and a subsequent aging treatment in ultra-pure water at 80°C for 1 d. Treating solutions (TSs) for chemical treatment contained titanyl sulfate (TiOSO₄), hydrogen peroxide (H₂O₂), and nitric acid (HNO₃). Fourier transform infrared spectroscopy analysis indicated that an amorphous titania gel layer containing Ti–O–O bonds formed on the chemically treated cpTi substrate in 0.10 mol·m⁻³ TS, which was then transformed into anatase rods during aging treatment. Thin-film X-ray diffraction and scanning-electron microscopy analyses showed that the 0.10 mol·m⁻³ TiOSO₄ TS provided randomly packed aggregates of oriented anatase and rutile rods, while 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs yielded highly ordered rutile rods of ca. 20 nm in diameter. The rutile rods grew perpendicular to the cpTi substrate and the rod array fully covered the surface of the cpTi substrate. It is proposed that the nucleation of rutile occurs on the amorphous titania gel layer, and the rate of nucleation and growth of rutile increase with increasing concentration of TS, accompanied by the consumption of amorphous titania gel. Rutile layers with high rod density and 3.0 μm thickness were successfully prepared on the surface of cpTi substrates.

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Key-words : Rutile, Anatase, Rod, Aging treatment, cpTi

[Received May 21, 2019; Accepted June 10, 2019]

1. Introduction

Titania nanorod arrays are good candidates for applications such as photocatalytic devices and biomedical implants because of desirable properties such as photochemical stability and high biocompatibility.^{1)–4)} It is well known that titania exists in three different crystal phases, namely anatase, rutile, and brookite. Ohno et al.⁵⁾ showed that rutile has more active photocatalytic oxidation than anatase due to the transferability of its electrons. Xiao et al.⁴⁾ and Wu et al.⁶⁾ have demonstrated the importance of rutile in inducing apatite deposition in vitro. Recently, we have shown a hydrothermal method with titanyl sulfate (TiOSO₄) precursor solution at 160°C to synthesize a titania polymorphic layer consisting of rutile and anatase on the surface of commercially available pure titanium (cpTi) plates with H₂O₂ pre-treatment, and we reported its ability to form apatite in vitro.^{4),7)} Unfortunately, pure rutile rods cannot easily be fabricated on cpTi substrates. Therefore, we undertook research to find reasonable synthesis conditions for the formation of pure rutile rods.

Wu et al.⁸⁾ have reported a chemical route (at 80°C) to prepare a titania layer by H₂O₂ treatment, whereas an amorphous titania gel layer or anatase with low crystallinity was obtained depending on the pH condition and a subsequent aging treatment with ultra-pure water. The subsequent aging treatment yielded pure anatase or titania polymorphs. It is necessary to employ the aging treatment to improve the crystallinity of titania prepared at low temperature.

In this paper, we report the successful preparation of pure rutile nanorod on the cpTi substrate by combining a chemical approach in treating solutions (TSs) at 80°C for 3 d with a subsequent aging treatment in ultra-pure water at 80°C for 1 d. Titanyl sulfate (TiOSO₄), hydrogen peroxide (H₂O₂), and nitric acid (HNO₃) were used as reactants in the TSs. The influence of the TiOSO₄ concentration in the TSs on the growth of rutile nanorods was examined. A possible growth mechanism of rutile rods is discussed.

2. Experimental procedures

Titanium discs, purchased from GC Corp. (Tokyo, Japan), were polished using SiC (#1000) abrasive sandpaper to achieve smooth cpTi substrates, and were then ultrasonically cleaned in ultra-pure water and acetone for

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5 min, in sequence. The cleaning cycle was repeated three times.

The typical TSs were prepared as follows: an appropriate amount of reagent-grade TiOSO_4 (Maikun Chemical Company, Shanghai, China) was added to a solution containing $15 \text{ mol} \cdot \text{m}^{-3}$ H_2O_2 . After stirring for about 10 min, the solution became clear. The pH value of the clear solution was then adjusted to 0.70 by using HNO_3 . The final molar content of TiOSO_4 (0.10 , 0.14 , $0.18 \text{ mol} \cdot \text{m}^{-3}$) and H_2O_2 ($15 \text{ mol} \cdot \text{m}^{-3}$) in the TSs was adjusted.

Polypropylene bottles (50 mL) were filled with 30 mL of the prepared TS, into which cleaned cpTi substrates were placed. The bottles were then placed in a constant-temperature oven at 80°C for 3 d. All chemically treated cpTi substrates were ultrasonically cleaned in ultra-pure water for 15 min. Finally, the samples were soaked in ultra-pure water at 80°C for 1 d, and then were dried at room temperature.

Thin-film X-ray diffraction (TF-XRD, X'Pert-ProMPD, PANalytical, Almelo, the Netherlands: $\text{Cu K}\alpha$, $\lambda = 0.15418 \text{ nm}$, 45 kV – 40 mA) was used to identify the crystalline phase, where all data were collected in the step-scan mode (step size: 0.02° in 2θ , counting time: 1 s per step) with a constant X-ray incident angle θ of 1.0° . The chemical structure of titania layers deposited on the sample surface was characterized by Fourier transform infrared (FT-IR) spectroscopy (Thermo Nicolet model Nexus 470, Thermo Fisher Scientific Inc., Chicago, IL, USA) with a deuterium triglycine sulfate detector, where spectral data were measured using the KBr disc method. Field-emission scanning-electron microscopy (FE-SEM; JSM-6701F, JEOL, Ltd., Tokyo, Japan) was used to characterize the surface morphology of the chemically treated titanium substrates with aging treatment. The substrates were coated with highly pure osmium for FE-SEM observation using a Neoc-STB Osmium Coater (Meiwa Fosis Co. Ltd., Tokyo, Japan).

3. Results

Figure 1 shows TF-XRD patterns of cpTi substrates after chemical treatment in various TSs at 80°C for 3 d, before and after the aging treatment in ultra-pure water at 80°C for 1 d. The XRD patterns of cpTi substrates chemically treated in $0.10 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS in Fig. 1(a) have diffraction peaks at 2θ angles of 35 , 38 , and 40° , which correspond well with the (100), (002), and (101) planes of α -titanium (ICDD-JCPDS PDF#44-1294). TSs of 0.14 and $0.18 \text{ mol} \cdot \text{m}^{-3}$ in Fig. 1(a) exhibit similar diffraction peaks at around 27 and 36° , which correspond well with the (110) and (101) planes of rutile titania. No other diffraction peaks except for rutile and titanium were detected from samples in 0.14 , and $0.18 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TSs, indicating that the surface structure was pure rutile phase. It can be seen that the intensity of the diffraction peak corresponding to rutile (101) decreases in the chemically treated cpTi substrate in the $0.18 \text{ mol} \cdot \text{m}^{-3}$ TS compared with that in the $0.14 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS. After the aging treatment in Fig. 1(b), a strong diffraction peak at

Fig. 1. TF-XRD patterns of chemically treated cpTi substrates in various TSs (0.10 , 0.14 and $0.18 \text{ mol} \cdot \text{m}^{-3}$) before (a) and after (b) the aging treatment in ultra-pure water at 80°C for 1 d.

25° and a weak peak at 36° are observed on the cpTi substrate chemically treated with $0.10 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS, which are attributed to the (101) plane of anatase and (101) plane of rutile, respectively. It was revealed that aging treatment induces the formation of titania polymorphs on the chemically treated cpTi substrate in $0.10 \text{ mol} \cdot \text{m}^{-3}$ TS. In contrast, the aging treatment gave no apparent change in TF-XRD patterns of the chemically treated cpTi substrates in 0.14 and $0.18 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TSs.

Figure 2 shows FT-IR absorption spectra of titania layers deposited on chemically treated cpTi substrates in 0.10 , 0.14 and $0.18 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TSs before and after the aging treatment, showing the influence of the aging treatment on the molecular structure. The spectra of all resulting samples exhibited a strong absorption band at around 1630 – 1618 cm^{-1} assignable to the H–O–H bending of physisorbed H_2O . A notable difference can be seen for the FT-IR absorption spectra in Fig. 2(a) of chemically treated cpTi substrates in $0.10 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS before and after aging treatment. A strong absorption band at 488 cm^{-1} is attributed to the vibration of Ti–O bonds in amorphous titania gel. Furthermore, two weak absorption bands at 887 and 694 cm^{-1} can be assigned to the O–O stretching vibration for physisorbed H_2O_2 ⁹⁾ and the vibration of Ti–O–O bonds,^{10),11)} respectively. These bands were removed after the aging treatment. A broad absorption band at 700 – 500 cm^{-1} , together with a peak at 542 cm^{-1} , are assigned to the framework vibration of anatase lattice, which was detected after the aging treatment. The aging treatment eliminated Ti–O–O bonds and led to the formation of anatase on the chemically treated cpTi substrate in $0.10 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS as shown in Fig. 2(a). In contrast, there were no significant differences in FT-IR spectral profiles of the chemically treated cpTi substrates in $0.14 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS before and after the aging treatment as illustrated in Fig. 2(b). The spectrum of the chemically treated cpTi substrate in $0.14 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS shows

Fig. 2. FT-IR absorption spectra of titania layers deposited on chemically treated cpTi substrates in various TSs (a: 0.10, b: 0.14, c: 0.18 mol·m⁻³) before and after aging treatment at 80°C for 1 d.

a broad absorption band in 600–400 cm⁻¹ region with peaks at 461 and 526 cm⁻¹ assigned to Ti–O stretching vibration.^{12),13)} Here, three absorption bands appear at 1061, 1124 and 1198 cm⁻¹, together with an absorption band at 603 cm⁻¹, which are attributed to S–O stretching and O–S–O bending vibrations in sulfate anion. The chemically treated cpTi substrate in 0.18 mol·m⁻³ TiOSO₄

TS [Fig. 2(c)] shows a similar FT-IR spectrum to that of 0.14 mol·m⁻³ TiOSO₄ TS. The absorption bands corresponding to S–O stretching and O–S–O bending vibrations in sulfate anion are not detected after the aging treatment.

Figure 3 shows surface and cross-sectional SEM images of the chemically treated cpTi substrates after the aging treatment. The 0.10 mol·m⁻³ TiOSO₄ TS in Fig. 3(a) shows a characteristic surface morphology consisting of rods on the substrate. In addition, aggregates of oriented rods with an average width of around 30 nm are randomly packed on the whole surface of the cpTi substrates. On the other hand, the chemical treatment with the 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs in Fig. 3(b) and 3(c) gave highly oriented rutile rod arrays. These rods with average diameters of less than 20 nm were forced to grow perpendicular to the surface of cpTi substrates. The rods generated in 0.18 mol·m⁻³ TiOSO₄ TS appear slightly larger than that in 0.14 mol·m⁻³ TiOSO₄ TS. The estimated density of the nanorod arrays, which is defined as the number of nanorods per unit area, is approximately 4.5×10^2 , 1.0×10^3 , and $1.3 \times 10^3 \mu\text{m}^{-2}$ for chemically treated cpTi substrates in the 0.10, 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs, respectively. Thus, chemically treated cpTi substrates in the 0.18 mol·m⁻³ TiOSO₄ TS show the most dense nanorods.

As shown in the cross-sectional images, the upper edge of the specimens is identified as the titania layer, while the interface between titania layers and cpTi substrate is found in the middle part of each figure. Titania layers can be confirmed in the 0.10, 0.14, and 0.18 mol·m⁻³ TiOSO₄ TSs. Upon careful observation of the titania layers, it is noted that many nano-sized loose pores exist at the bottom of the layers obtained in the 0.10 and 0.14 mol·m⁻³ TiOSO₄ TSs [Figs. 3(a') and 3(b')], while the layer of chemically treated cpTi substrate in the 0.18 mol·m⁻³ TS [Fig. 3(c')] is dense. The estimated thickness of the dense and porous layers on the chemically treated cpTi substrate in the 0.10, 0.14 and 0.18 mol·m⁻³ conditions is also presented. The thickness of the porous layer decreases and that of the dense layer slightly increases as the concentration of TiOSO₄ is increased to 0.14 mol·m⁻³ or more.

Figure 4 shows high magnification cross-sectional images of chemically treated cpTi substrates in 0.14 and 0.18 mol·m⁻³ TSs after the aging treatment. It can be clearly seen that chemically treated cpTi in 0.14 mol·m⁻³ TS gave a multilayer structure. Nanorods are found on the top surface of the sample, and a dense layer existed in the middle of Fig. 4(a). In addition, there are nano-sized loose pores at the bottom layer obtained in the 0.14 mol·m⁻³ TiOSO₄ TSs. However, 0.18 mol·m⁻³ TS yielded a bilayer consisting of a thin nanorod layer and a dense layer. As can be seen from Fig. 4(b), rods on the sample of 0.18 mol·m⁻³ TS packed tightly with each other and the gap between rods on the sample of 0.18 mol·m⁻³ TS is obviously smaller than that of 0.14 mol·m⁻³ TS.

XRD patterns obtained in two different scan modes for the sample for 0.18 mol·m⁻³ TS are shown in **Fig. 5**. In 2 θ / θ scan mode, the sample of 0.18 mol·m⁻³ TS gave

Fig. 3. FE-SEM images of surface (a, b and c) and cross-sectional (a', b' and c') images of chemically treated cpTi substrates in various TSs (a and a': 0.10, b and b': 0.14, c and c': 0.18 mol·m⁻³) after the aging treatment at 80°C for 1 d.

Fig. 4. High magnification cross-sectional images ($\times 30\text{k}$) of chemically treated cpTi substrates in 0.14 (a) and 0.18 (b) mol·m⁻³ TSs after the aging treatment.

strong peaks corresponding to diffraction from (100), (002), (101), (102), and (110) planes of α -Ti and weak peaks corresponding to diffraction from (110), (101), (111), and (211) planes of rutile. A strong peak at 63.0° can be assigned to diffraction from (002) plane of rutile and (110) plane of α -Ti. In 2θ scan mode, the depth of the titania layer that can be detected by XRD measurement increased with the increase of the incident angle. The intensity of diffraction peaks of rutile was enhanced with the increase in the incident angle from 1 to 3°. The relative intensity of diffraction peaks corresponding to the (101) and (110) plane ($I_{(101)}/I_{(110)}$) is calculated on the basis of

Fig. 5. TF-XRD patterns obtained in 2θ scan mode (incident angles of 1 and 3°) for chemically treated cpTi substrate in 0.18 mol·m⁻³ TS after aging treatment. For comparison, the XRD pattern obtained in $2\theta/\theta$ scan mode is also shown.

the XRD pattern in $2\theta/\theta$ scan mode. The value of $I_{(101)}/I_{(110)}$ for the sample of 0.18 mol·m⁻³ TSs is ca. 7.1. The $I_{(101)}/I_{(110)}$ value is higher than the value of 2.2 in our

previous reports.⁴⁾ The strong diffraction peak ascribed to the (002) plane of rutile and the high $I_{(101)}/I_{(110)}$ value indicate that rutile crystals have a preferred orientation along *c*-axis.

From the above analysis, it was found that highly oriented rutile rod arrays are successfully prepared on cpTi substrates by chemical treatment with the 0.14, and 0.18 mol·m⁻³ TiOSO₄ TSs. On the other hand, chemical treatment with 0.10 mol·m⁻³ TiOSO₄ TSs gives an amorphous titania gel on cpTi substrates and the transformation of the amorphous titania gel into anatase is induced by the aging treatment, accompanied by the elimination of Ti–O–O bonds.

4. Discussion

After being chemically treated in 0.10 mol·m⁻³ TiOSO₄ TS and subsequently aged in ultra-pure water, the cpTi substrates had titania rods mainly in the anatase form on their surface according to Figs. 1(b) and 3(a). Previous reports^{4),7)} indicated that H₂O₂ pre-treatment of cpTi substrates gives an amorphous titania gel layer, which is necessary in order to obtain nano-crystalline titania layers. Wu et al.^{14),15)} reported that nano-crystalline anatase layers grow on the surface of H₂O₂-oxidized cpTi substrates after aging treatment, because aging treatment accelerates the transformation of an amorphous titania gel into anatase. Our results at 0.10 mol·m⁻³ TS are very similar to the results of Wu et al.^{14),15)} That is, the contribution of H₂O₂ cannot be ignored for the formation of amorphous titania gel and anatase by a chemical approach in TS. It is reasonable to suggest that amorphous titania gel layers with Ti–O–O bonds are preferentially formed on the surface of the cpTi substrates, and then transformed into anatase nanorods during the aging treatment. The cross-sectional SEM investigation [Fig. 3(a')] indicated that both porous and dense layers exist on the chemically treated cpTi substrates in 0.10 mol·m⁻³ TiOSO₄ TSs after the aging treatment. It is highly probable that the amorphous titania gel results in the porous layer.

The fact that rutile rods were deposited on the surface of the chemically treated cpTi in 0.14 and 0.18 mol·m⁻³ TiOSO₄ TSs can be explained by considering the pH and TiOSO₄ concentration of the TSs. Wu et al.¹⁶⁾ demonstrated that a low pH value of a titanium solution favors the formation of titania in the rutile phase. Furthermore, Inada et al.^{17),18)} have reported that rutile could be produced in low pH value of TiOCl₂ starting solution at a low temperature (50°C) or a relatively high temperature (100°C). Yamabi et al.¹⁹⁾ discussed the influence of the pH value of the TiOSO₄ solution in forming a titania layer on the surface of glass, and reported that a given pH value (<1) of TiOSO₄ solution results in the preferential deposition of rutile phase from Ti complexes. Therefore, Ti ions in the present TSs (pH value = 0.7) favor the production of Ti-complex species, which will dehydrate to form rutile. As shown in the TF-XRD patterns [Fig. 1(b)] and cross-sectional SEM images [Fig. 3(b')] of the substrates in 0.14 mol·m⁻³ TiOSO₄ TS, we clearly found that rutile rods

grew on the porous layers. In addition, by comparing the XRD and SEM analysis results of substrates in 0.14 and 0.18 mol·m⁻³ TiOSO₄ TS, 0.18 mol·m⁻³ TS favored the formation of rutile nanorods with high rod density, and the thickness of the porous layer was remarkably decreased with the increase in TiOSO₄ concentration. We also found that the thickness of the dense layer was slightly increased in 0.18 mol·m⁻³ TS. This means that the porous layer favors the growing of rutile rods. Taking the above into consideration, the detailed mechanism for rutile rod fabrication in our case can be explained as follows:

- (1) The chemical interaction of cpTi substrates with H₂O₂ yields an amorphous titania gel layer on cpTi substrates.
- (2) Complicated Ti-complex species derived from the TS contribute to rutile nucleation on the amorphous titania gel layers. The rate of rutile nucleation depends on the concentration of TiOSO₄ in TSs.
- (3) The nucleation and growth of rutile proceed at the expense of the amorphous titania gel layer, probably due to the transformation of amorphous titania into rutile, and their growth orientation is perpendicular to the cpTi substrate.

In the 0.10 mol·m⁻³ TiOSO₄ TS, it is not possible to generate adequate rutile nucleus on the amorphous titania gel layer; hence, the amorphous titania gel layer remains, and is transformed into anatase nanorods during the aging treatment. Using 0.10 mol·m⁻³ TiOSO₄ TS thus results in titania rods composed of anatase and rutile. With increasing initial TiOSO₄ concentration of TSs (0.14 mol·m⁻³ TiOSO₄ TS), the rate of rutile nucleation increases. The nucleation and growth of rutile are accompanied by the consumption of the amorphous titania gel layers due to their transformation into rutile. Therefore, a thinner amorphous layer is observed on the cpTi substrates chemically treated in 0.14, and 0.18 mol·m⁻³ TiOSO₄ TS. Numerous rutile crystals grow in the same direction (perpendicular to the cpTi substrates) to form well-ordered rutile rods. The growth mechanism of highly ordered rutile nanorods can be summarized in Fig. 6. Significant differences between rutile layers obtained in 0.14 mol·m⁻³ TiOSO₄ TS and 0.18 mol·m⁻³ TiOSO₄ TS are the thickness of the porous layer and the density of the rutile rods. At a high TiOSO₄ concentration in the TS (0.18 mol·m⁻³ TiOSO₄ TS), the initiation of nucleation and the subsequent growth of rutile rods on the amorphous titania layer are accelerated. The

Fig. 6. Schematic illustration of the growth mechanism of highly ordered rutile nanorods.

porous layer is quickly exhausted because of the growth of more rutile rods. Thus, dense rutile layers with high rod density are observed on the chemically treated cpTi substrate in $0.18 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS. The strong diffraction intensity of rutile is observed on the cpTi substrates chemically treated in $0.14 \text{ mol} \cdot \text{m}^{-3}$ TS in Fig. 1(b), whereas rutile rods with high density were formed on the chemically treated cpTi substrates in $0.18 \text{ mol} \cdot \text{m}^{-3}$ TS. This suggests that the density of rutile rods depends on the concentration of TiOSO_4 in the TSs. The above findings indicate that improved density and orientation of rutile rods can be achieved by optimizing the TiOSO_4 concentration in the TSs.

As shown in Figs. 2(b) and 2(c), sulfate bands remained on the sample of $0.14 \text{ mol} \cdot \text{m}^{-3}$ TS after the aging treatment. One possible reason is that water molecule could not penetrate into the bottom porous layer due to the hindrance of the upper dense layer during the aging treatment. As a result, the sulfate ions remain trapped in the gap of the porous layer of the sample of $0.14 \text{ mol} \cdot \text{m}^{-3}$ TS.

5. Conclusions

Titanium substrates were continuously immersed in various TSs including TiOSO_4 , H_2O_2 , and HNO_3 at 80°C for 3 d and subsequently soaked in ultra-pure water at 80°C for 1 d, on which nanometer-scale titania rods were prepared. Anatase and rutile rods were deposited on the cpTi substrate in $0.10 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TS. On the other hand, 0.14 and $0.18 \text{ mol} \cdot \text{m}^{-3}$ TiOSO_4 TSs led to the deposition of highly ordered rutile rod arrays through the nucleation and growth of rutile on the amorphous titania gel layer, accompanied by consumption of the amorphous titania gel.

Acknowledgment The authors are grateful to Dr. Noriyuki Nagaoka at Okayama University for his assistance with the FE-SEM cross-sectional observation of prepared titania layers. The authors would like to thank Editage (www.editage.jp) for English language editing.

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