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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Nanom-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 consisting of 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.

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

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1. Introduction

Titania nanorod arrays are good candidates for applications such as photocatalytic devices and biomedical implants because of desirable properties such as photocatalytic 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.⁴,⁶ 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.

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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
chemically treated in 0.10 mol·m\(^{-3}\) at 80°C for 1 d. The XRD patterns of cpTi substrates before and after the aging treatment in ultra-pure water after chemical treatment in various TSs at 80°C for 3 d, indicating that the surface structure was pure rutile phase. It can be seen that the intensity of the di ffraction peak corresponding to rutile (101) decreases in the chemically treated cpTi substrate in the 0.14 mol·m\(^{-3}\) TS compared with that in the 0.14 mol·m\(^{-3}\) TiOSO\(_4\) TS. After the aging treatment in Fig. 1(b), a strong di ffraction peak at 25° and a weak peak at 36° are observed on the cpTi substrate chemically treated with 0.10 mol·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 poly-morphs on the chemically treated cpTi substrate in 0.10 mol·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 mol·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 mol·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\(_2\)O. A notable difference can be seen for the FT-IR absorption spectra in Fig. 2(a) of chemically treated cpTi substrates in 0.10 mol·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\(_2\)O\(_2\) and the vibration of Ti–O–O bonds, 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\(^{-1}\), is 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 mol·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 mol·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 mol·m\(^{-3}\) TiOSO\(_4\) TS shows...
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\(^{-3}\) TiOSO\(_4\) TS [Fig. 2(c)] shows a similar FT-IR spectrum to that of 0.14 mol·m\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) TS appear slightly larger than that in 0.14 mol·m\(^{-3}\) TiOSO\(_4\) TS. The estimated density of the nanorod arrays, which is defined as the number of nanorods per unit area, is approximately 4.5 \(\times\) 10\(^2\), 1.0 \(\times\) 10\(^3\), and 1.3 \(\times\) 10\(^3\) \(\mu\)m\(^{-2}\) for chemically treated cpTi substrates in the 0.10, 0.14 and 0.18 mol·m\(^{-3}\) TiOSO\(_4\) TSs, respectively. Thus, chemically treated cpTi substrates in the 0.18 mol·m\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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 TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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 2θ/θ scan mode, the sample of 0.18 mol·m\(^{-3}\) TS gave
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 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

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 ($\times30$ k) of chemically treated cpTi substrates in 0.14 (a) and 0.18 (b) mol·m$^{-3}$ TSs after the aging treatment.

Fig. 5. TF-XRD patterns obtained in $2\theta$ 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 strong diffraction peak ascribed to the (002) plane of rutile and the high \( I_{(001)}/I_{(110)} \) 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\(^{-3}\) TiOSO\(_4\) TSs. On the other hand, chemical treatment with 0.10 mol·m\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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 H\(_2\)O\(_2\) 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 H\(_2\)O\(_2\)-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 H\(_2\)O\(_2\) 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\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) TSs can be explained by considering the pH and TiOSO\(_4\) 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 TiOCl\(_2\) 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 TiOSO\(_4\) solution in forming a titania layer on the surface of glass, and reported that a given pH value (\( \leq 1\) ) of TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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 TiOSO\(_4\) 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 H\(_2\)O\(_2\) 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 TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) TS thus results in titania rods composed of anatase and rutile. With increasing initial TiOSO\(_4\) concentration of TSs (0.14 mol·m\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) 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\(^{-3}\) TiOSO\(_4\) TS and 0.18 mol·m\(^{-3}\) TiOSO\(_4\) TS are the thickness of the porous layer and the density of the rutile rods. At a high TiOSO\(_4\) concentration in the TS (0.18 mol·m\(^{-3}\) TiOSO\(_4\) TS), the initiation of nucleation and the subsequent growth of rutile rods on the amorphous titania layer are accelerated. The
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 mol·m⁻³ TiOSO₄ TS. The strong diffraction intensity of rutile is observed on the cpTi substrates chemically treated in 0.14 mol·m⁻³ TS in Fig. 1(b), whereas rutile rods with high density were formed on the chemically treated cpTi substrates in 0.18 mol·m⁻³ TS. This suggests that the density of rutile rods depends on the concentration of TiOSO₄ in the TSs. The above findings indicate that improved density and orientation of rutile rods can be achieved by optimizing the TiOSO₄ concentration in the TSs.

As shown in Figs. 2(b) and 2(c), sulfate bands remained on the sample of 0.14 mol·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 mol·m⁻³ TS.

5. Conclusions

Titanium substrates were continuously immersed in various TSs including TiOSO₄, H₂O₂, and HNO₃ 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 mol·m⁻³ TiOSO₄ TS. On the other hand, 0.14 and 0.18 mol·m⁻³ TiOSO₄ 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.

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