Formation of Photocatalytically Active TiO₂ Layers on Ti–Nb Alloys by Two-Step Thermal Oxidation

Shota Sado, Takatoshi Ueda, Yosuke Tokuda, Naoki Sato, Kyosuke Ueda and Takayuki Narushima*

Department of Materials Processing, Tohoku University, Sendai 980-8579, Japan

A two-step thermal oxidation process was applied to Ti–xNb binary alloys ($x = 0, 1, 10, 15$, and $30 \text{ at\%}$) to prepare anatase-containing TiO₂ layers, and their photocatalytic activities were evaluated by measuring the water contact angle and decomposition of methylene blue (MB) under UV irradiation. The condition of the first-step treatment was fixed as heating in Ar–1%CO atmosphere at 1073 K for 3.6 ks, and the subsequent second-step treatment was conducted in air at 673–1073 K for 10.8 ks. The reaction layer formed after the two-step thermal oxidation consisted of TiO₂. The anatase fraction of the TiO₂ layers increased with decreasing second-step temperature and increasing Nb content of the Ti–Nb alloys. In addition, Nb and carbon were introduced into the TiO₂ layers. A water contact angle of around 5° was observed on the TiO₂ layers formed at the second-step temperatures of 673–973 K. The rate constant of MB decomposition showed a maximum for an anatase fraction of 0.6–0.8 at which the recombination of exited electrons and holes are suppressed. The TiO₂ layer formed on the Ti–10 at%Nb alloy exhibited a higher rate constant of MB decomposition compared with Ti–30 at%Nb, in which the TiNb₂O₇ phase formed. These results indicate that Nb is an effective alloying element for producing a photocatalytically active TiO₂ layer on Ti by the two-step thermal oxidation process. Nevertheless, the presence of an anatase-rich TiO₂ layer and an appropriate Nb content in TiO₂ are required for achieving high photocatalytic activities.

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1. Introduction

Ti and its alloys are used as implant materials in orthopedic and dental fields.¹⁾ Although they can be directly connected to a living bone at an optical microscopic level (osseointegration),^{2,3)} a relatively long period is required by these implants to integrate with the bone tissue and the fixation depends on the state of the bone. Therefore, surface treatment of Ti and its alloys is required to further improve their bone compatibility.⁴⁾ Recently, an improvement in bone compatibility by forming a TiO₂ layer on the Ti surface through UV irradiation has been reported,^{5–7)} which is considered to be due to the cleaning of surface by decomposition of hydrocarbon contaminants through the photocatalytic activity of the TiO₂ layer.⁶⁾ In addition, the organic decomposition ability is related to antibacterial property. Thus, photocatalytically active TiO₂ coatings help improve the bone-forming ability as well as antibacterial activity of Ti implants.

High-temperature oxidation of Ti can produce a TiO₂ layer with high crystallinity and excellent adhesion to Ti; however, the formed TiO₂ layer generally consists of only the rutile phase. It is known that anatase exhibits excellent photocatalytic activity as compared to rutile.⁸⁾ Therefore, we developed a two-step thermal oxidation process for the formation of anatase-rich TiO₂ on Ti substrates.^{9–11)} In this process, the Ti substrates are treated first in a CO-containing atmosphere (first step) and subsequently in air (second step). An anatase-rich TiO₂ layer is formed on commercially pure (CP) Ti and Ti alloys using this process,^{9–12)} indicating that the carbon dissolution in TiO₂ and/or the similarity between anatase and NaCl-type Ti(C,O) crystal structures stabilized the anatase phase.⁹⁾ The anatase-rich TiO₂ layer exhibited photocatalytic activity.^{9,12)}

In a previous study, a TiO₂ layer formed on the surface of a Ti–25 mass%Nb alloy (Ti–14.6 at%Nb) exhibited excellent

photocatalytic activity.⁹⁾ However, the effect of Nb content of the Ti–Nb alloy on the phase constitution and photocatalytic activity of the TiO₂ layer formed by the two-step thermal oxidation process has not been revealed. Nb is an alloying element widely used for biomedical Ti alloys, such as TNTZ (Ti–29 mass%Nb–13 mass%Ta–4.6 mass%Zr) alloy,¹³⁾ and the information on TiO₂ layers formed on Ti–Nb alloys is expected to provide basic data for applying TiO₂ coatings on the Ti implants for biomedical applications.

In this study, TiO₂ layers were formed on Ti–xNb alloys ($x = 0, 1, 10, 15$, and $30 \text{ at\%}$) by a two-step thermal oxidation process, and the photocatalytic activity of TiO₂ layer under UV irradiation was investigated by measuring the water contact angle and decomposition of methylene blue (MB).

2. Experimental

2.1 Alloy preparation

Ingots of Ti–xNb alloys ($x = 1, 10, 15$, and $30 \text{ at\%}$) with a size of $70 \times 40 \times 25 \text{ mm}$ were prepared using a non-consumable W electrode Ar arc melting furnace (ACM-05-A, DIAVAC Ltd., Yachiyo, Japan). A CP Ti plate with 4 mm thickness (JIS Gr. 2) and a Nb plate with 1 mm thickness (99.9%) were used as raw materials for the melting after pickling them in a solution with the composition HF:HNO₃:H₂O = 2:13:85 (vol%). The ingots were subjected to hot forging at 1373 K and a subsequent second hot forging at 1273 K to shape them into bars with a diameter of 12 mm. Coin-shaped alloys with 1 mm thickness were cut from the bars. The Nb content of the alloys was quantitatively analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent8800, Agilent Technologies, CA, USA). The Nb content of the alloys and the alloy designations are summarized in Table 1. For the alloy without added Nb, a coin-shaped CP Ti with a diameter of 12 mm and thickness of 1 mm, which was cut from the CP Ti bar (JIS Gr. 2, UEX

*Corresponding author, E-mail: narut@material.tohoku.ac.jp

Table 1 Chemical composition and designations of Ti–Nb alloys used in this study.

Designation	0Nb	1Nb	10Nb	15Nb	30Nb
Nb (at%)	-	1.1	10.5	16.4	31.7

Fig. 1 Schematic diagram depicting the heating pattern of the two-step thermal oxidation process.

Co., Ltd., Tokyo, Japan), was used. Hereafter, the Ti–*x*Nb alloys (*x* = 0, 1, 10, 15, and 30 at%) are referred to as 0Nb, 1Nb, 10Nb, 15Nb, and 30Nb, respectively. The specimens were mirror polished and ultrasonically cleaned in ethanol and ultrapure water for 0.3 ks each.

The coin-shaped Ti–*x*Nb alloys were subjected to two-step thermal oxidation, which is schematically shown in Fig. 1. The first-step treatment in Ar–1%CO gas atmosphere was conducted at 1073 K for 3.6 ks. The second-step treatment in air was conducted at temperatures ranging from 673 K to 1073 K for 10.8 ks. The phase of the reaction layers formed on the Ti–*x*Nb alloy surface was analyzed by α -2 θ X-ray diffraction (XRD, RU-200B, Rigaku Co., Tokyo, Japan) with an incident angle of 0.3° and Cu K α radiation, and Raman spectroscopy (NRS-5100AMS, JASCO Co., Tokyo, Japan) with a laser wavelength of 532 nm. The cross section of the reaction layers was observed using a scanning electron microscope (SEM, JSM-7800F, JEOL Ltd., Tokyo, Japan). The reaction layer was analyzed by radio-frequency glow discharge optical emission spectroscopy (GD-OES, GD-Profilier 2, Horiba, Ltd., Kyoto, Japan), X-ray photoelectron spectroscopy (XPS, Theta Probe, Thermo Fisher Scientific K.K., Tokyo, Japan), and transmission electron microscopy (TEM, JEM-2100, JEOL Ltd., Tokyo, Japan).

2.2 Evaluation of photocatalytic activity

The water contact angles on the reaction layers of the Ti–*x*Nb alloys were measured under UV irradiation using a contact angle gauge (DM-501, Kyowa Interface Science Co., Ltd., Niiza, Japan). A UV lamp (127B-BL, Raytronics Co., Fujimino, Japan) with a peak wavelength of 351 nm was used for UV irradiation. The irradiance of the UV light source was set as 1.0 mW·cm^{−2} at the surface of the specimen, which was measured using a UV radiometer (UVR-300, Topcon Technohouse Co., Tokyo, Japan) with a wavelength range of 310–400 nm in the light-receiving section. Before the water contact angle measurements, the specimens were ultrasonically cleaned in ultrapure water and ethanol for 0.6 ks each. The water contact angle was measured at five different points on the reaction layers after various UV irradiation periods of up to 7.2 ks. The average of five values was used as the water contact angle for each irradiation time.

The organic decomposition ability of the reaction layer on the Ti–*x*Nb alloys under UV irradiation was evaluated by the decomposition test of MB (Fujifilm Wako Pure Chemical Co., Osaka, Japan) based on JIS R1703-2: 2007. Before UV irradiation, the specimen was placed in a 0.02 mM MB solution and stored under dark for 86.4 ks to reach an absorption equilibrium for MB on the reaction layer. After this treatment, the specimen was immersed in 2.5 mL of 0.01 mM MB solution and irradiated with UV light with an irradiance of 1.0 mW·cm^{−2}. The change in MB concentration on the TiO₂ layer under UV irradiation was evaluated using a UV–vis spectrophotometer (V-650, JASCO Co., Tokyo, Japan) at 663 nm. The concentration of MB was measured every 1.2 ks of UV irradiation up to 10.8 ks. The detailed procedures of evaluating photocatalytic activities have been reported elsewhere.⁹⁾

3. Results

3.1 Reaction layers

The α -2 θ XRD patterns of the reaction layers on the Ti–*x*Nb alloys after the first-step and second-step treatments are shown in Fig. 2. The presence of Ti(C,O) was confirmed after the first-step treatment, and the TiO₂ phase was found to be the main phase of the reaction layer after the second-step treatment. A single phase of anatase was detected at the second-step temperature of 673 K, while the rutile phase was formed at 873 K and became dominant at 1073 K. The powder diffraction pattern of the anatase phase (PDF#21-1272) is presented in Fig. 2(b). No peak shift is detected for the anatase phase formed on the alloys. In addition to TiO₂, a minor TiNb₂O₇ phase was detected in the case of 30Nb at 1073 K. The presence of TiNb₂O₇ phase was also confirmed by Raman spectroscopy and TEM analysis. When the Ti–*x*Nb alloys were subjected to air oxidation at 673–873 K for 10.8 ks, i.e., without the first-step treatment, only rutile phase was detected as an oxidation product.

Figure 3 shows the phase fraction of TiO₂ as a function of Nb content in the alloys and the second-step temperature. The anatase fraction (f_A) was calculated using eq. (1).¹⁴⁾

$$f_A = I_A / (I_A + 1.26I_R) \quad (1)$$

Here, I_A and I_R are the strongest peak intensities for anatase and rutile, respectively, in the XRD patterns of the reaction layers. The anatase fraction increased with decreasing second-step temperature and increasing Nb content of the alloys.

The depth profiles of oxygen, carbon, and Nb of the reaction layers of 10Nb after the second-step treatment at 673, 873, and 1073 K, which were measured by GD-OES, are shown in Fig. 4. The region with the high intensity of oxygen is considered to correspond to the TiO₂ layer. SEM observation demonstrated that the thickness of the TiO₂

Fig. 2 α -2 θ XRD patterns of the reaction layers on Ti- x Nb alloys after (a) first-step treatment and (b–d) second-step treatment. The second-step temperatures of (b), (c), and (d) are 673, 873, and 1073 K, respectively.

Fig. 3 Phase fraction of TiO_2 layers formed on Ti- x Nb alloys after second-step treatment.

layers on 10Nb at 673 and 873 K was 1 μm and that at 1073 K was 2.5 μm . A high oxygen intensity in the GD-OES profile was detected up to sputtering times of around 200 s for 673 and 873 K and around 600 s for 1073 K, respectively; this is consistent with the thickness of the TiO_2 layers, as determined by SEM observation. Compared with the intensity of the TiO_2 region in the GD-OES profile, it is suggested that the carbon content decreased and the Nb content increased with increasing second-step temperature. The chemical state of carbon in the TiO_2 layers was not investigated in this study; however, in our previous study,⁹⁾ both carbon dissolution and the existence of amorphous carbon/disordered graphite in the anatase layer were suggested after two-step thermal oxidation.

3.2 Photocatalytic activity

Figure 5 shows the initial and final water contact angles after UV irradiation on the TiO_2 layers for 7.2 ks as a function of the second-step temperature. In the second-step temper-

ature range of 673–973 K, the final water contact angle decreased to around 5°. On the other hand, at the second-step temperature of 1073 K, the final water contact angle depended on the Nb content of the alloys: a final water contact angle of around 5° was obtained for 10Nb and 15Nb, while that of 1Nb and 30Nb were 20° and 10°, respectively. No decrease in the final water contact angle was detected for 0Nb.

The changes in the normalized concentration of MB with UV irradiation time for 0Nb, 10Nb, and 30Nb are shown in Fig. 6. The vertical axis shows the logarithm of C/C_0 , where C is the MB concentration during UV irradiation and C_0 is the initial MB concentration before UV irradiation. A decrease in MB concentration was detected for all the alloys subjected to the second-step treatment in the temperature range of 673–973 K and the organic decomposition ability of the TiO_2 layer was confirmed. Among the alloys subjected to the second-step treatment at 973 K, only 10Nb showed a decrease in MB concentration. On the other hand, none of the alloys showed a decrease in MB concentration when the alloys were subjected to the second-step treatment at 1073 K.

4. Discussion

4.1 Effect of Nb content on TiO_2 layers

Hanaor and Sorrell¹⁵⁾ reviewed the effect of doping elements in TiO_2 on the irreversible transformation from anatase to rutile and showed that the elements having large ionic radii and valence in TiO_2 inhibit the transformation. Nb is classified as an inhibitor of transformation. The addition of Nb to the alloy, that is, the introduction of Nb to the TiO_2 layer increased the anatase fraction under the same second-step temperature, as shown in Fig. 3. Figure 7 shows the XPS spectra of the TiO_2 layer formed on 10Nb at the second-step temperature of 873 K. The presence of Nb^{5+} and Nb^{4+} ions in the TiO_2 layer was confirmed. It was reported that Nb addition to Ti decreased its oxidation rates at high temperatures.^{16–18)} The reduction in oxygen vacancy concentration in TiO_2 through eq. (2) is considered the mechanism through which the oxidation resistance of Ti is improved.¹⁹⁾

Fig. 4 GD-OES spectra of the reaction layers of 10Nb alloy after second-step treatment at (a) 673, (b) 873, and (c) 1073 K.

Fig. 5 Initial and final water contact angles on TiO₂ layers formed on (a) 0Nb, (b) 1Nb, (c) 10Nb, (d) 15Nb, and (e) 30Nb alloys after UV irradiation for 7.2 ks as a function of the second-step temperature.

Theoretical studies have been reported on the chemical state of Nb,^{20,21)} however, it has not been clarified whether Nb can dissolve into TiO₂ or not. Presently, it is likely that Nb dissolves into TiO₂ because of the inhibition of the anatase-to-rutile transformation (Fig. 3) and the appearance of Nb signals in the XPS spectrum (Fig. 7).

4.2 Effect of Nb content on photocatalytic activity

The rate equation of MB decomposition is represented by eq. (3).^{9,22)}

$$\ln(C/C_0) = -k \cdot t \quad (3)$$

where k is a rate constant of MB decomposition. The gradient of the lines shown in Fig. 6 exhibits the k value. Figure 8 shows the k values as a function of anatase fraction in TiO₂. The k value shows a maximum in the range of $f_A = 0.6$ – 0.8 , independent of the Nb content of the alloys. In Fig. 8, the rate constants of MB decomposition on the anatase-type TiO₂ layer ($f_A = 1$), fabricated by the pulsed laser ablation method,²³⁾ are shown for comparison, where the irradiation conditions, such as the UV light source irradiance of 1.6 mW·cm^{−2} and the initial MB concentration of 0.031 mM,

Fig. 6 Decomposition of methylene blue on TiO₂ layers of Ti-*x*Nb alloys after second-step treatment at (a) 673, (b) 773, (c) 873, (d) 973, and (e) 1073 K.

Fig. 7 Nb 3d XPS spectra of the reaction layer of 10Nb alloy after second-step treatment at 873 K.

were close to those used in this study. The reported k values and those found herein are in agreement; however, the effect of anatase fraction on the k value was not shown in Ref. 23. Jung and Park²⁴⁾ studied the decomposition of trichloroethylene using the photocatalytic activity of TiO₂ synthesized by the sol-gel method and reported that TiO₂ with an anatase fraction of 0.9 exhibited a superior decomposition rate than that with a single-phase anatase. Bickley *et al.*²⁵⁾ proposed a photocatalytic mechanism of Degussa P25, which has an anatase fraction of 0.8, wherein the electron-hole separation between rutile and anatase resulted in the suppression of the recombination of the excited electrons and holes. It is suggested that this mechanism is applicable to the anatase-rich TiO₂ layer prepared by the two-step thermal oxidation of Ti-*x*Nb alloys.

Fig. 8 Change in rate constant of decomposition of methylene blue (MB) under UV irradiation as a function of anatase fraction of TiO₂ layers.

A comparison of the k values of 0Nb and 10Nb with an anatase fraction of around 0.5 reveals that 10Nb exhibits higher k values than 0Nb does. The Nb⁵⁺ ions introduced into TiO₂ could trap the excited electrons (eq. (5)), thereby suppressing the recombination of the excited electrons and holes.²⁶⁾

On the other hand, the k values of 30Nb are less than those of 10Nb and 0Nb. The effect of Nb addition to TiO₂ on its photocatalytic activity has been studied.^{27,28)} It was reported that Nb addition improves the photocatalytic activity of TiO₂ up to a certain concentration; however, further addition of Nb

Fig. 9 Relationship between final water contact angle and rate constant of methylene blue (MB) decomposition.

deteriorates the photocatalytic activity, which agrees with the present results. Our study suggests that the TiNb₂O₇ formed in TiO₂ possibly acts as a site of recombination of the excited electrons and holes in the case of 30Nb.

As shown in Fig. 5, 10Nb and 15Nb after the second-step treatment at 1073 K exhibited a low final water contact angle of around 5° despite the formation of single-phase rutile or rutile-rich TiO₂ on them. The mechanism responsible for the low final water contact angle of TiO₂ under UV irradiation is still under discussion.²⁹⁾ Therefore, presently, it is difficult to clarify the reason for the low water contact angle of around 5° of rutile-rich TiO₂ with added Nb under UV irradiation. It is reported that the addition of Nb oxide to TiO₂ increases the surface acidity of TiO₂,³⁰⁾ which might contribute to the low water contact angle of the rutile-rich TiO₂ layer by inducing an interaction between the outer water molecules and the surface hydroxyl groups.³¹⁾

Figure 9 shows the relationship between the final water contact angle and the rate constant of MB decomposition (k values). A low final water contact angle of around 5° does not necessarily lead to high k values. These results suggest that the presence of an anatase-rich TiO₂ layer and an appropriate Nb content in TiO₂ are required for achieving high photocatalytic activities. The hydrophilicity of TiO₂ is reportedly related to the ability of organic decomposition and change in surface structure of TiO₂ during UV irradiation.²⁹⁾ The relationship shown in Fig. 9 suggests that the change in TiO₂ surface structure cannot be ignored for expression of hydrophilicity, which would not contribute to the expression of organic decomposition ability.

5. Conclusion

TiO₂ layers were formed on Ti– x Nb alloys ($x = 0, 1, 10, 15$, and 30 at%) using a two-step thermal oxidation process, in which the alloys are treated in Ar–1%CO gas atmosphere in the first step and in air in the second step. The water contact angle and the decomposition rate of MB on the reaction layer mainly consisting of TiO₂ were measured under UV irradiation, and the following results were obtained.

- (1) The TiO₂ layer consisted of rutile and/or anatase phase. Nb and carbon were present in the TiO₂ layer. The anatase fraction in the TiO₂ layer increased with decreasing second-step temperature and increasing Nb content of the alloys.
- (2) The water contact angle on the TiO₂ layers formed on Ti–10 at%Nb and Ti–15 at%Nb alloys decreased to around 5°.
- (3) The rate constant of MB decomposition showed a maximum for an anatase fraction of 0.6–0.8, which might be caused by charge separation between rutile and anatase.
- (4) The TiO₂ layer formed on the Ti–10 at%Nb alloy exhibited a high rate constant of MB decomposition than that on the Ti–30 at%Nb alloy. The TiNb₂O₇ phase formed in the TiO₂ layer on the Ti–30 at%Nb alloy is considered to act as a recombination site for the excited electrons and holes.
- (5) Nb is an effective alloying element for producing a photocatalytically active TiO₂ layer on Ti by the two-step thermal oxidation process. Nevertheless, the presence of an anatase-rich TiO₂ layer and an appropriate Nb content in TiO₂ are required for achieving high photocatalytic activities.

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