Surface structure and photocatalytic performance of an anodic oxide layer fabricated on titanium in a nitrate/ethylene glycol electrolyte with different treatment durations

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Abstract

Anodic oxidation of titanium substrate in an electrolyte comprising ammonium nitrate in ethylene glycol is an innovative technique for fabricating a visible-light-responsive photocatalytic titanium dioxide (TiO_2) layer. In this study, the effects of the duration of anodization on photocatalytic activity were investigated to improve its performance. Surface morphologies of the fabricated layer were comparatively flat for small durations of anodization, but small cracks were generated when anodizing for over 120 min. The thickness of the layer increased with treatment time up to 60 min, beyond which time no further increase in thickness was observed. The predominant structure of the oxide layer was TiO_2 with a rutile structure, and its amount increased with longer treatment duration. Nitrogen doping was observed in the layer regardless of the duration although its chemical state and photocatalytic activity varied depending on the duration. Under ultraviolet light irradiation, the change in activity was small, whereas the activity was drastically enhanced with longer treatment duration in the case of visible light irradiation. Based on these results, we concluded that the optimum duration of anodization is 60 min in the present setting because a TiO_2 layer showing good photocatalytic activity without any surface cracks could be formed.

Keywords: Anodic oxidation, Nitrate electrolyte, Visible-light response, Photocatalytic TiO_2 ,

Anodization duration

1. Introduction

Anodic treatment of titanium (Ti) has recently gained attention as a fabrication process for photocatalytic titanium dioxide (TiO₂) layer [1-6]. The technique is a simple process that involves connecting a target substrate to the anode in an electrolyte and applying voltage, resulting in the formation of a thin oxide layer on the target substrate. In the case of a Ti substrate, the oxide layer fabricated is generally TiO₂. A characteristic feature of this process is the incorporation of the constituent elements of the electrolyte [7-10]. A semiquantitative model constructed by Wood et al. explained that the electrolyte anions adsorbed on the topmost surface are incorporated with growth of the oxide layer [10]. The elements incorporated in the oxide layer affect the layer characteristics such as crystallinity and surface morphology [7, 11], and thus, this phenomenon often complicates the control of layer characteristics.

However, in the case of TiO₂ photocatalysis, this phenomenon is rather beneficial. In recent years, doping of specific elements into the TiO₂ layer has become a major technology for expanding its responsiveness to the visible light region [12-13]. Mizukoshi et al. fabricated a sulfur-doped TiO₂ layer on a Ti substrate using anodic treatment in sulfuric acid, and then revealed that the fabricated layer could bleach methylene-blue dye under visible light irradiation [14]. Our research group has synthesized a visible light responsive nitrogen-doped TiO₂ layer through anodic treatment [15-16]. The use of nitric acid as an electrolyte resulted in the formation nitrogen-doped TiO₂ layer with visible light photocatalytic activity, whereas the resultant layer was easily removed by wiping the

surface gently [15]. The problem of adhesion was drastically improved by changing the electrolyte solvent to ethylene glycol. We previously reported that the anodic layer fabricated in nitrate/ethylene glycol electrolyte acted as a photocatalyst both under UV-light and visible-light illumination and showed excellent antibacterial performance under both types of illumination [16]. We believe that the anodic treatment using a nitrate/ethylene glycol electrolyte is a promising method for fabricating antibacterial and environmental purification mediums applicable to industry.

In the previous study, only one set of treatment conditions was investigated [16]. Since the treatment conditions affect the layer characteristics and its photocatalytic activity, the parameters of the process should be optimized. Komiya et al. reported that the photocatalytic activity was drastically changed depending on the treatment time when anodizing the Ti substrate in an aqueous solution of a sulfuric salt [17]. Based on their findings, we chose the duration time as the investigating parameter. In the present study, therefore, we fabricated an anodic oxide layer on a Ti substrate in a nitrate/ethylene glycol electrolyte with different durations of anodization. Thereafter, its surface characteristics and photocatalytic performances were investigated in detail. Together with these results, we determined the optimum treatment duration for fabricating a high-performance nitrogen-doped TiO₂ layer that can be used in industry.

2. Experimental methods

2.1. Anodic treatment of Ti substrate

The anodic treatment was performed in a 0.1 M nitrate solution prepared by dissolving NH_4NO_3 in industrial grade ethylene glycol (99%). Ti plates (99.5%, $10 \times 20 \times 1 \text{ mm}^3$) were chemically polished using a colloidal silica suspension until they achieve a mirror-like surface. The plates were thoroughly rinsed with ethanol in an ultrasonic cleaner. The Ti plate without surface masking was connected to a Pt plate as the cathode, after which galvanostatic direct current (DC) was applied at a constant value of $100 \text{ mA}\cdot\text{cm}^{-2}$. Here, the distance between the cathode and the anode was approximately 50 mm. The anodic treatment was performed in an ambient atmosphere; accordingly, the ethylene glycol solvent would contain trivial water from the atmosphere. The DC voltage varied accordingly. The temperature of the electrolyte was not controlled in this study because from our preliminary investigation, we obtained experimental evidence that the cooling of the electrolyte did not affect the performance. We prepared six anodized plates with different treatment times: 5, 15, 30, 60, 120, and 180 min. After the treatment, the sample was thoroughly rinsed in distilled water using ultrasonic agitation for ca. 600 s, and then heated at 723 K for 5 h in air.

2.2. Characterization of the surface

The surface morphologies of the specimens were observed by scanning electron microscopy (SEM; JCM-5000 Neo Scope, JEOL, Japan) using the secondary electron image mode, and the cross-sectional structures of the surfaces were observed using field-emission SEM (FE-SEM; JSM-6701F, JEOL, Japan). X-ray diffraction patterns (XRD; New D8 Advance, Brucker AXS,

Germany) were measured in the Bragg-Brentano geometry using Cu K α radiation. Chemical state and concentration of the incorporated nitrogen were analyzed using X-ray photoelectron spectroscopy (XPS; PHI 5000 Versa Probe, Ulvac-Phi, Japan). A monochromatized Al K α radiation ($h\nu = 1486.6$ eV) with the diameter of ca. 100 μm was used for photoelectron excitation. The photoelectron take-off angle (TOA) was set at 45°.

2.3. Evaluation of the photocatalytic activity

The photocatalytic activity was evaluated by the bleaching rate of a methylene blue (MB) dye under UV and visible lights illumination. As a preliminary treatment, the specimen surfaces were irradiated with comparatively high-intensity UV light (ca. 6 $\text{mW}\cdot\text{cm}^{-2}$) for 90 min to remove organic substances. Thereafter, the specimens were immersed in 10 $\text{mg}\cdot\text{L}^{-1}$ MB solution in a polypropylene vessel for 24 h to complete the adsorption of MB molecules onto the surface. The MB dye in the vessel was replaced to a new solution and then, UV and visible light from LED lamps with wavelengths of 370 nm or 420 nm, respectively, were illuminated onto the immersed specimen surface. A schematic illustration of the experimental setup is shown in Fig. 1. The radiation intensities were adjusted to 1 $\text{mW}\cdot\text{cm}^{-2}$. The photocatalytic activity was evaluated by measuring the absorbance of MB at 664 nm during irradiation every 20 min for 180 min using a UV-vis spectrometer (UV-2400PC, Shimadzu, Japan). The bleaching rate of MB was plotted against the duration of radiation, and the reaction rates for MB bleaching ($\text{min}^{-1}\cdot\text{mL}^{-1}$) were calculated from the

slope of its linear plot.

3. Results and discussions

3.1. Changes in surface morphology and layer thickness with prolonged treatment time

The topological microstructures of the surfaces anodized in nitrate/ethylene glycol electrolyte for different treatment durations are shown in Fig. 2. The surface morphology is comparatively flat for samples treated for 5 and 15 min. Small pores appeared on the surface after 30 min, but disappeared again upon increasing the treatment duration beyond 60 min. Further treatment beyond 120 min results in the generation of small cracks, which grow larger upon prolonging the duration to 180 min.

The change of the layer thickness with an increase in the treatment duration is shown in Fig. 3(b). Here, the thickness of the layer is estimated from the cross-sectional SEM image of the surface (Fig. 3(a)). We calculated the average value of several points. The thickness increases exponentially with an increase in the treatment duration up to 60 min, whereas the rate of increase becomes constant beyond 120 min. The thickness value at 120 min is about 20 μm .

To analyze the layer growth behavior further, we recorded the variations in the applied DC voltage during the anodization process (Fig. 4). At the beginning of the treatment, the DC voltage is abruptly raised to a maximum value, after which it decreases gradually up to about half of the maximum value. We confirmed that the electric conductivity of the electrolyte increased during the treatment, probably owing to the release of titanium ions from the substrate. Thus, it is concluded that the

decrease in the voltage was dominated by the change in electric conductivity. Furthermore, the trend in the voltage seems to be similar to the variation in the growth of thickness. This finding implies that layer thickness formed in nitrate/ethylene glycol electrolyte is related to the electrical conductivity. However, to clarify this hypothesis, further investigation is needed.

3.2. Changes of the layer crystallinity with prolonged treatment time

The XRD patterns of the anodized Ti surfaces are shown in Fig. 5. Here, the anodized surfaces measured were heated at 723 K in air. In the all patterns, a broad peak at 27.4° and a sharp peak at 25.4° are observed. The former peak is attributed to TiO_2 with a rutile structure, and the latter to TiO_2 with an anatase structure. Peaks because of Ti with a hexagonal closed packed (HCP) structure are also observed, which originates from the substrate. On the surface anodized for 5 min, the intensities of the anatase and rutile peaks are almost similar. The rutile intensity increases with an increase in the treatment duration, but that of the anatase is almost constant. At 60 min, the predominant phase of the oxide changes to the rutile phase.

The analytical results from XRD revealed that the increase in the treatment duration contributed to the formation of rutile-type TiO_2 . Nevertheless, the mechanism of this phenomenon is still unclear.

As mentioned above, the specimens measured were heated at 723 K in air. This temperature is enough for forming the anatase phase, but is much lower than that required for crystallizing to the rutile phase. Several researchers reported that an anodic oxide layer is crystallized without a

post-heating treatment owing to the high internal compressive stress during this growth process, caused by high electric-field-induced electrostriction [8, 18-19]. This effect is known as field crystallization. We deduced that the appearance of the rutile phase is related to the field crystallization effect. To confirm this, we measured the XRD pattern of the anodized Ti surface without a post-heating treatment (Fig. 6). A very broad, indistinct peak is observed around the position corresponding to rutile-type TiO_2 . Based on these results, we inferred that the formation mechanism of the rutile phase is as follows: extremely small crystals of rutile-type TiO_2 are formed in the surface layer during anodic treatment because of field crystallization, and thereafter, the crystals grow comparatively large because of the post-heating treatment. As a result, a distinctive peak corresponding to the rutile phase appeared in the XRD pattern. Extension of the treatment duration results in the increase of the amount of small, crystalline rutile-type TiO_2 . Consequently, the peak intensity of the rutile phase increases with an increase in the treatment time.

3.3. Chemical state of nitrogen in the surface layer

Nitrogen incorporated in the oxide layer is related to the visible-light response of photocatalytic TiO_2 , and thus, its chemical state and concentration were examined using XPS. The data were collected after etching the layer surface (ca. 100 nm) using an Ar ion gun (3 kV). The N 1s XPS spectra for the surface anodized for 5, 30, and 60 min are shown in Fig. 7. All the spectra comprised two chemical state: nitrogen atom incorporated at an interstitial site (ca. 399.9 eV) and atomically

substituted nitrogen (ca. 396. 7 eV) [20]. Valentin et al. reported that both interstitial and substitutional nitrogen induce a few localized states, which contribute to the visible-light activity [21]. The ratio of these two nitrogen states varied depending on the treatment duration. Furthermore, the atomic ratio of nitrogen in the TiO₂ layer, calculated from the spectral intensities of the Ti 2p, O 1s, and N 1s XPS peaks, were 1.7, 1.2, and 0.7 at% at 5 min, 30 min, and 60 min, respectively. Many researchers accept that a nitrogen ratio of approximately 1 at% is an appropriate concentration to extend the photoactive region toward the visible-light region.

The diffusion reflection spectrum (DRS) for the surface anodized for 60 min is shown in Fig. 8. Here, the DRS spectra obtained from a dip-coated TiO₂ layer fabricated using a commercially available reagent (ST-K211, Ishihara Sangyo Kaisha, Japan) is also shown for comparison. It should be noted that the DRS obtained from a thin layer often includes a comparatively high background, owing to a specular reflection from a substrate material. In the present study, all the DRS were thus normalized to show the absorbance from a band gap obviously. Compared to the dip-coated layer, the spectral curve for the anodic layer was shifted to the higher wavelength side, showing the reduction of band gap caused by nitrogen doping.

3.4. Photocatalytic activity under ultraviolet and visible light irradiation

To evaluate the photocatalytic activity on the anodic layers with different treatment durations,

reaction rates for MB bleaching at a wavelength of 370 nm or 420 nm were measured (Fig. 9). Prior to the bleaching test, we confirmed that MB dye was not bleached under the 370-nm and 420-nm light irradiations without a photocatalyst. The anodic layers fabricated showed photocatalytic activity under the 370-nm light irradiation, regardless of the treatment duration. The activity is slightly low on the 15 min surface, whereas the surfaces prepared using treatment times from 30 to 180 min are almost constant. In contrast, in the case of the 420-nm light, which corresponds to visible light, the activity is quite low on the surface at less than 30 min treatment time, which is about 15% of the ultraviolet case. Beyond 60 min, the activity drastically enhanced, and is almost equal to that under ultraviolet light.

The trends in dependence of activity variation on the duration are different for the ultraviolet and visible light cases (Fig. 9). This result indicates that the layer characteristics dominating the activities are different from each other. Chen et al. investigated the correlation of the film thickness on the photocatalytic activity of TiO₂ film under an ultraviolet light irradiation [22]. They showed that the increase in the thickness of the film results in an increase in the photocatalytic activity below 10 μm . They demonstrated that the activity of the 10- μm thick TiO₂ layer was approximately 2.3 times higher than that of the 2.5- μm thick layer. Similar to previous literature, in this study, transition of the activity increase seems to correlate with the thickness increase. The activity of the layer with treatment duration below 15 min was comparatively low because the thickness is lower than 10 μm . The activity was almost constant when surfaces were treated for more than 30 min because the layer

thickness exceeded 10 μm .

On the other hand, the behavior under visible light cannot be explained from the view of thickness. The visible light response is dominated by the band-gap structure of the TiO_2 layer, and hence, is related to the crystal structure or nitrogen doping. The XRD peak intensity at 27.4° corresponding to rutile-type TiO_2 , obtained from the layers with different treatment durations, are plotted against the visible-light photocatalytic activity (Fig. 10). There is good correlation between the intensity and the visible-light activity. Understandably, the band gap of TiO_2 with the rutile structure is 3.0 eV, which is narrower than the gap for the anatase structure of 3.2 eV. Accordingly, it can be said that the rutile structure has an advantage with respect to the visible-light responsiveness. This is one possible mechanism explaining the change in visible-light responsiveness. Moreover, the XPS result showed that the chemical state and concentration of nitrogen incorporation vary depending on the treatment duration. By increasing the treatment time, nitrogen incorporation is varied from the substitutional site to a generic interstitial, and concomitantly, the atomic concentration is slightly decreased. This behavior may be another possible mechanism for the change in visible-light responsiveness. We will not discuss the effect of these changes on visible-light photocatalytic activity here because support of a theoretical calculation and/or result of a local structure analysis such as XAFS are required for the accurate discussion. We plan to investigate the effect of nitrogen doping further, which will be reported in the near future.

4. Conclusion

To fabricate high performance visible-light responsive photocatalytic TiO₂ layer through anodic oxidation in nitrate/ethylene glycol electrolyte, the effect of the treatment duration on the layer characteristics and the photocatalytic activity were investigated. The surface morphologies were comparatively flat regardless of the duration, but small cracks appeared upon treatment beyond 120 min. The thickness of the layer increased with an increase in the treatment duration, but the growth saturated in the range beyond 60 min. The surface layer consisted of TiO₂ with rutile and anatase structures, and the amount of the rutile phase increased with an increase in the treatment duration. The nitrogen doping in the layer was confirmed regardless of the duration, whereas its chemical state and concentration are varied depending on the duration. A change in the photocatalytic activity depending on the treatment duration was also found. Under ultraviolet light irradiation, the activity is slightly low below 15 min, whereas the activity is almost constant beyond 30 min. In the case of visible light, the activity for a treatment time below 30 min was quite low, but was drastically enhanced when the treatment duration exceeded 60 min. In conclusion, we determined the optimum anodization duration to be 60 min in the present setting because a TiO₂ layer showing good photocatalytic activity without surface cracks could be formed.

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Figure captions

Fig. 1. A schematic illustration of methylene-blue bleaching experiment.

Fig. 2. SEM images of Ti substrates anodized in nitrate/ethylene glycol electrolyte for different durations: (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min, (e) 120, and (f) 180 min.

Fig. 3. (a) Cross-sectional surface image of a Ti substrate anodized for 60 min, and (b) the change in the layer thickness with increase in treatment duration.

Fig. 4. Variations of the applied DC voltage during anodic treatment.

Fig. 5. XRD patterns obtained from the surface anodized for different durations, then heated at 723 K for 5 h in air.

Fig. 6. XRD pattern obtained for a Ti substrate anodized for 60 min without a post-heating treatment.

Fig. 7. XPS spectra of the N 1s region obtained from the surface anodized for 5, 30, and 60 min.

Fig. 8. Reflection diffusion spectra of the TiO₂ layers prepared by anodic oxidation in the nitrate/ethylene glycol electrolyte and dip-coating process.

Fig. 9. Bleaching rate of MB under 370 nm or 420 nm LED light irradiation. The TiO₂ layers were

fabricated by anodizing in the nitrate/ethylene glycol electrolyte with the durations ranging from 5 to 180 min.

Fig. 10. Correlation between the XRD peak intensity of rutile-type TiO_2 and the photocatalytic activity under visible light.

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