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Effect of pre-nitridation treatment on the formation of anatase TiO_2 films by anodization

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Abstract

High performance-anatase TiO_2 films were successfully formed on metallic titanium by anodization in an acidic electrolyte composed of H_2SO_4, H_3PO_4 and H_2O_2 subsequent to pre-nitridation treatment. The pre-nitridation treatment was carried out by pre-annealing metallic titanium under a nitrogen atmosphere of 0.1 MPa. The anodized films showed photocatalytic activity in photooxidization of the iodide anion into the tri-iodide anion. The nitridation treatment had a significant effect not only on the formation of anatase TiO_2 films but also on the photocatalytic activity of the anodized films.

Keywords: A. Films; D. Nitrides; D. TiO_2; E. Functional applications

1. Introduction

TiO_2 photocatalysts have received much attention in various applications, such as purification of air and water [1–4], splitting of water into hydrogen [5,6], bactericidal action [7–9], and dye-sensitized solar cell [10,11]. Anatase type TiO_2 has a higher activity than rutile type [12,13], because its conduction band is at a higher energy. In one application, a suspension of TiO_2 fine particles is used to purify aqueous solutions containing organic chemicals. The particles must then be separated from the solution following purification. This problem could be avoided by using a TiO_2 coating. In general, TiO_2 films easily detach from the substrate because of the weak adhesive strength of binder chemicals. Furthermore, when using an organic binder for coating procedures, TiO_2 photocatalysts act to decompose the binder chemicals, thus limiting the coating binders that can be used to inorganic chemicals, such as silica.

To solve the above problems encountered in conventional coating procedures, some researchers have investigated the use of anodization in fabrication of TiO_2 films on metallic titanium. Anodization has been shown to be useful as a surface treatment of valve metals, such as aluminium, titanium and others. This technique is commonly utilized to increase corrosion resistance through the formation of protective thin oxide films in various electrolytes under a DC power supply. In conventional anodization using phosphoric acid as an electrolyte, amorphous TiO_2 films are usually obtained. Nakahira et al. reported that an anatase TiO_2 film was prepared by anodization in 0.25 M phosphoric acid at an extremely high applied voltage (250–350 V) [14], but an XRD pattern of the film showed a broad peak indicating the films was almost amorphous. Kuraki et al. prepared an anatase TiO_2 film by anodization at an applied voltage at 150–200 V in an acidic electrolyte composed of 1.5 M H_2SO_4, 0.3 M H_3PO_4 and 0.3 M H_2O_2, but the films hardly showed any photocatalytic activity due to the existence of a low valence oxide phase, such as TiO and Ti_2O_3, which disabled the activity [15]. However, they were able to demonstrate that anodized films with photocatalytic activity could be prepared by re-anodization in a mixture of NH_4HF_2 and H_2O_2, which effectively removed the low valence oxide phase created as a byproduct in the anodization process.

In this paper, to develop a new preparation method for obtaining the high performance-anatase TiO_2 films by anodization, we examined a simple and inexpensive nitridation treatment involving annealing of metallic titanium under a nitrogen atmosphere of 0.1 MPa. High performance-anatase TiO_2 films were successfully formed by the combination

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treatment of pre-nitridation and anodization. The anodized films showed photocatalytic activity in photooxidization of the iodide anion into the tri-iodide anion. The pre-nitridation treatment had a significant effect on the photocatalytic activity of anodized films.

2. Experimental

2.1. Preparation of anatase TiO_2 films by anodization process

A commercially pure Ti plate of purity greater than 99.5% (Nippon Steel Corporation, Japan) was ultrasonically degreased with n-hexane for 15 min. The Ti plates were annealed under a nitrogen atmosphere of 0.1 MPa at 750 °C, 850 °C, or 950 °C for 6 h with a furnace (GR-6156-15-S, Koyo Thermo System Co. Ltd., Japan). The Ti plates were anodized using a DC power supply (PAS320-3, Kikusui Electronics Corporation, Japan) and a function generator (HB-105, Hokuto Denko Corporation, Japan) to control the applied voltage. The applied voltage was gradually increased at a scan rate of 94 mV/s until reaching a fixed voltage in the range from 150 V to 200 V, and was held for 10 min at this fixed voltage. Fig. 1 showed a schematic diagram of the preparation method. The electrolyte was composed of 1.5 M H_2SO_4, 0.3 M H_3PO_4, and 0.3 M H_2O_2 [15]. To obtain high performance-anatase TiO_2 films, we investigated the effect of changes in the nitridation temperature and the applied voltage.

2.2. Characterization of the anodized films

X-ray diffraction (XRD) patterns of the anodized films after pre-nitridation treatment and those of anodized films were obtained with an X-ray diffractometer (M18X-CE, Bruker AXS, Japan, Cu Kα radiation, operated at 40 kV and 100 mA). The degree of anatase TiO_2 film formation was evaluated by monitoring the integral XRD intensity of (1 0 1) reflection. The morphologies of anodized films were observed using a scanning electron microscope (S-2380, Hitachi High-Technologies Corporation, Japan) and a field-emission scanning electron microscope (JSM6700F, JEOL, Japan).

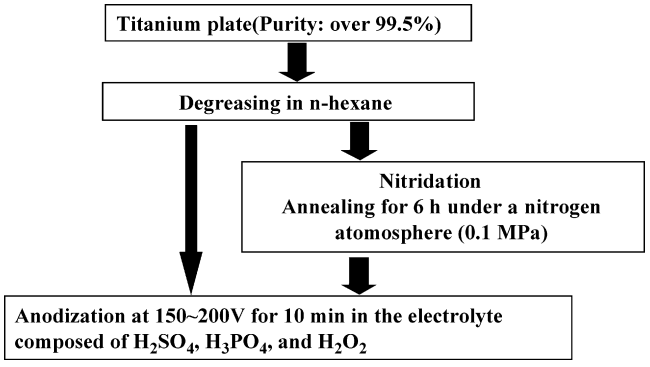

Fig. 1. Schematic diagram of the experimental procedures.

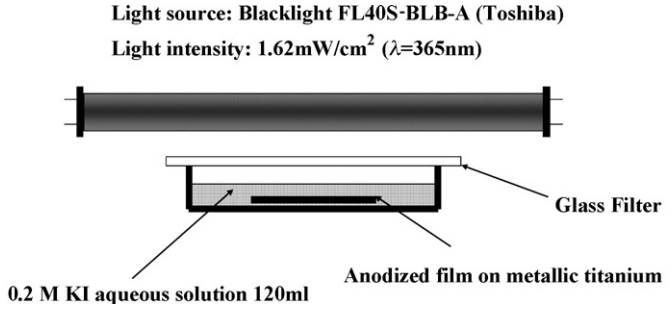

Fig. 2. Schematic diagram of experimental procedures evaluated photocatalytic activity of the anodized films.

2.3. Photocatalytic activities of the anodized films

The photocatalytic activity was evaluated by monitoring amount of the tri-iodide anion resulting from photooxidation of the iodide anion in a 0.2 M potassium iodide aqueous solution [16–18]. The reaction vessel, containing 120 ml of 0.2 M potassium iodide aqueous solution and the anodized sample (surface area = 25 cm^2), was irradiated from the upper side. A fluorescent lamp emitting in the near-UV region (Blacklight FL40S·BLB-A, Toshiba Lighting & Technology Corporation, Japan) was used in this study; an excitation light intensity of 1.62 mW/cm^2 was obtained at the surface of the specimens, as shown in Fig. 2. Under UV irradiation, pairs of electrons and positive holes can be generated at the surface of TiO_2 films (Eq. (1)). The positive holes react with the adsorbed iodide anion on the surface of the titanium oxide films to form iodine (Eq. (2)). When iodide anions remain in excess, iodine also reacts with iodide anions to form the tri-iodide anion (Eq. (3)), which has an absorption maximum of 288 nm. By monitoring the absorbance of the aqueous solution at 288 nm with a UV–vis spectrometer (UVmini1240, Shimadzu, Japan), the photocatalytic activities of the anodized films were determined.

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (1)$$

$$2I^- + 2h^+ \rightarrow I_2 \quad (2)$$

$$I_2 + I^- \rightarrow I_3^- \quad (3)$$

3. Result and discussion

Fig. 3 shows the integral XRD intensity of each reflection of the TiN phase as a function of annealing temperature under a nitrogen atmosphere of 0.1 MPa. It is obvious that the integral XRD intensities of the TiN phase depend on the nitridation temperature at over 750 °C. We consider that the TiN film forms on Ti substrate as a result of thermal diffusion of nitrogen into Ti substrate. It is difficult to determine the film thickness of the TiN phase due to coexistence of a low valence nitride phase, such as $TiN_{0.3}$ and $TiN_{0.5}$ [19]. However, it is clear that TiN films can be fabricated by easy and inexpensive procedures, such as annealing of a Ti plate under a nitrogen atmosphere.

Fig. 4 shows the XRD integral intensities of the anatase TiO_2 phase (1 0 1) as a function of applied voltage. Ti plates obtained

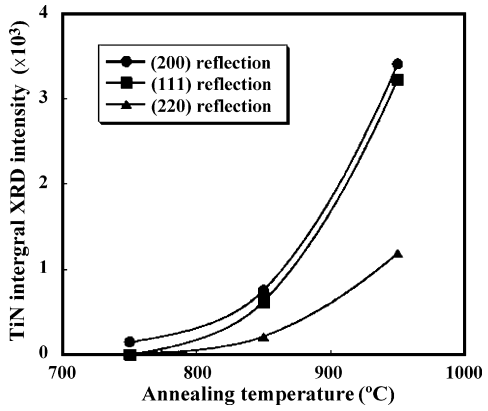

Fig. 3. TiN integral XRD intensity as a function of annealing temperature under a nitrogen atmosphere.

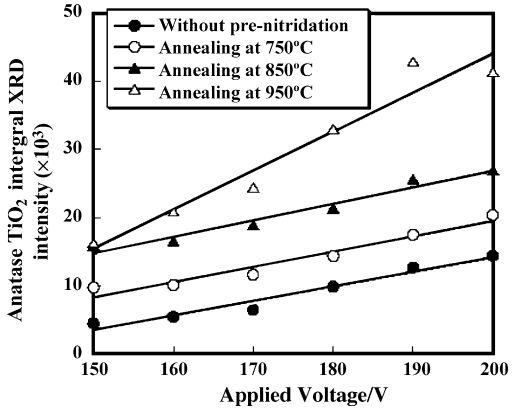

Fig. 4. XRD integral intensities of the anatase TiO_2 phase (1 0 1) as a function of the applied voltage. Electrolyte is composed of 1.5 M H_2SO_4, 0.3 M H_3PO_4 and 0.3 M H_2O_2.

after the nitridation treatment are anodized at various voltages for 10 min in the acidic electrolyte, composed of 1.5 M H_2SO_4, 0.3 M H_3PO_4, and 0.3 M H_2O_2. As shown in Fig. 4, it is obvious that the degree of anatase TiO_2 film formation is dependent not only on the applied voltage but also on the nitridation temperature. From these results, it can be seen that the pre-nitridation treatment has a significant effect on the formation of the anatase TiO_2 films. In conventional anodization processes, anatase TiO_2 films hardly form at all on metallic titanium because the passive amorphous films formed in these processes act as a barrier to prevent further anodization. Montero et al. reported that the titanium nitride films may increase the reactivity with oxygen [20]. Azumi et al. reported an oxide layer could be grown readily on a TiN coating, as compared with an anodic oxide film on metallic titanium [21]. Metallic titanium is highly corrosion resistant because the bare Ti surface is oxidized easily and a compact oxide film is subsequently formed. Even if the oxide film is broken, a protective oxide film, called a passive film, is immediately renewed on the Ti substrate due to high repassivation capability of Ti [21]. The TiN surface is also covered with an oxide layer, which is thought to be associated with its corrosion resistance. However, we consider that the TiN film does not provide a good barrier against anodization, due to its lack of repassivation capability [21]. If we consider the crystal structures, metallic titanium has a hexagonal closed packed structure whereas TiN has a cubic structure. Oxygen atoms can easily migrate into the TiN crystal due to the difference in crystal structure [20]. Thus we consider that the nitridation treatment has a significant effect on the formation of anatase TiO_2 films because of the different reactivity of TiN resulting from its crystal structure.

Fig. 5 shows the top-view and cross-section SEM images of the anodized films prepared without the pre-nitridation

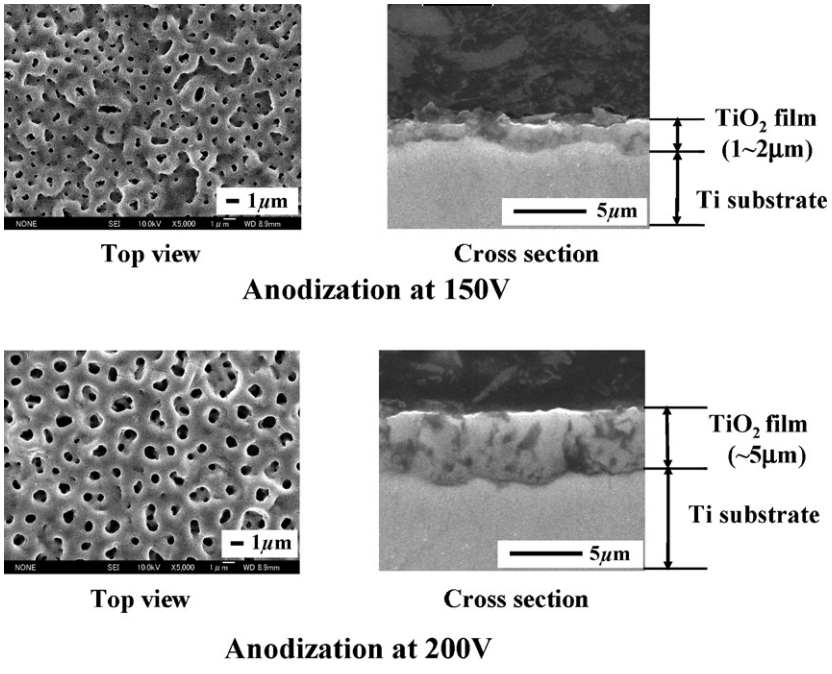

Fig. 5. SEM images of anodized films without pre-nitridation treatment.

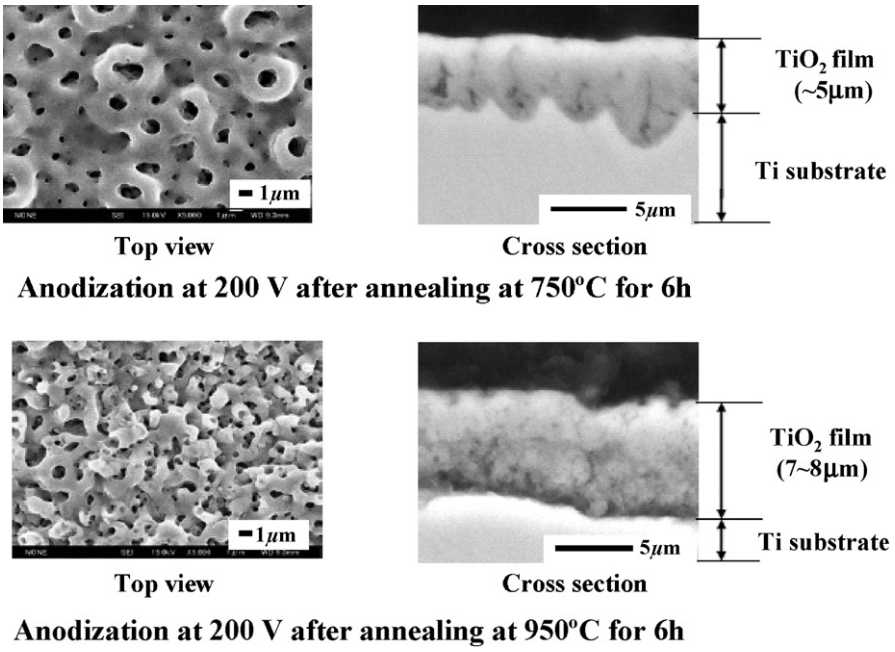

Fig. 6. SEM images of anodized films with pre-nitridation treatment.

treatment. From the cross-section SEM image, the film thickness of TiO_2 film at an applied voltage of 150 V is determined to be 1–2 μm, whereas the thickness obtained at an applied voltage of 200 V is 5 μm. It is obvious that the thickness of the anodized film depends upon the applied voltage. The increasing degree of anatase TiO_2 film formation that occurs with increasing applied voltage (Fig. 4) is considered to result from an increase in the thickness of the anodic oxide film with applied voltage. In addition, the diameter of the pore size also depends upon the applied voltage. The TiO_2 layers on titanium substrate have a number of pores as a result of the electric discharge spark.

Fig. 6 shows SEM images of the anodized films prepared with the pre-nitridation treatment. From the cross-section SEM image, a film thickness of the TiO_2 film with pre-nitridation temperature of 750 °C and 950 °C is 5 μm and 7–8 μm, respectively. Since the film thickness of TiO_2 film without pre-nitridation is 5 μm (Fig. 5), we consider that the film thickness of the anodized film hardly depends upon the pre-nitridation temperature. The increasing degree of anatase TiO_2 film formation that occurs with increasing pre-nitridation temperature (Fig. 4) is considered to be due to an increase in density of the formed anatase TiO_2 film, resulting from the pre-nitridation effect on the formation of anatase TiO_2 films. From the top-view SEM images, it can be seen clearly that the surface areas increase with the nitridation temperature. Fig. 7 shows the photocatalytic activity of anodized films fabricated by various anodization conditions in an acidic electrolyte after pre-annealing metallic titanium at 950 °C for 6 h under a nitrogen atmosphere. It is clear that the anodized films have photocatalytic activity, the extent of which depends significantly on the nitridation temperature. The obtained photocatalytic activities are consistent with the formation of anatase TiO_2 films.

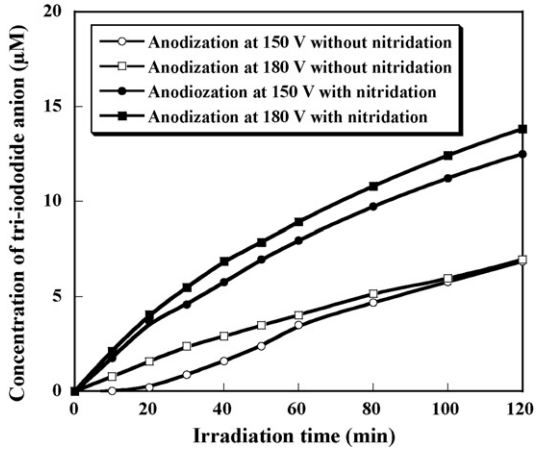

Fig. 7. Photocatalytic activity of the anodized films. Pre-nitridation is carried out by annealing metallic titanium under a nitrogen atmosphere at 950 °C for 6 h.

4. Conclusion

The effect of pre-nitridation treatment on the formation of anatase TiO_2 films by anodization in an acidic electrolyte (1.5 M H_2SO_4, 0.3 M H_3PO_4, and 0.3 M H_2O_2) was investigated. The amount of deposited anatase TiO_2 phase was found to depend on the applied voltage and pre-nitridation temperature, that is annealing temperature under a nitrogen atmosphere. The anodized films showed photocatalytic activity, the extent of which depended significantly on the nitridation treatment. It was revealed that pre-nitridation treatment had an accelerating effect on the formation the high performance-anatase TiO_2 films by anodization.

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