Preparation of Anodized Titanium Plates with Photocatalytic Activity

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光触媒活性を有するチタン陽極酸化皮膜材の作製

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Introduction

Titanium oxide films formed by heating or anodic oxidation on the surface of metallic titanium plates interfere with visible light, and act as photocatalysts¹⁾. However, these oxide films lack durability because of their insufficient thickness which is less than 1 μm . Ito et al. previously developed a method of producing porous anodic oxide films that are more than 1 μm thick²⁾. This method consists of anodic oxidation of titanium plates under high voltage in a mixture of H_2SO_4 , H_3PO_4 , and H_2O_2 . Although these thick, gray films contain low valent titanium oxides and have sufficient durability³⁾, they are photocatalytically inactive. There is a possibility that the low valent titanium oxides cause the photocatalytic inactivity.

This study has sought to sustain photocatalytic activity with the thick, anodized films by removing the low valent titanium oxides.

Experimental

Commercially pure titanium (JIS H 4600, class 1) was used as a titanium substrate ($30 \times 50 \times 0.4 \text{ mm}$ [$W \times L \times T$]). For the first anodic oxidation, the voltage was raised from 0 to 200 V at a constant current density of DC 300 A/m² in a solution of 1.5-M H_2SO_4 , 0.3-M H_3PO_4 , and 0.3-M H_2O_2 , and then was kept at this voltage (which was a constant voltage). It took 10 minutes to raise the voltage to 200 V, and the total anodizing time was 30 minutes. The bath temperature was maintained at 303 K. The titanium substrate was employed as a cathode as well as an anode, and the distance between electrodes was 5 cm. The thickness of the anodic oxide film obtained was 5.5 μm . For the second anodic oxidation, the voltage was raised to 150

V at a constant current density of DC 300 A/m² for 2 minutes in a mixture of NH_4HF_2 and 0.3-M H_2O_2 , and was maintained at 150 V. Total anodizing time was varied in the range of 5 to 15 minutes. The cathode material and the distance between electrodes were identical to those in the first anodizing process.

Photocatalytic activity was evaluated in terms of the photooxidation decomposition reaction of CH_3CHO gas. A xenon lamp (Wacom HX-500) was used as a light source. The irradiation area and the strength of the light were set at 15 cm² and 28 W/m² (at 320–400 nm in wavelength), respectively. The volume of the reaction vessel was fixed at 640 mL. Acetaldehyde was quantitatively measured using a gas chromatograph (Shimadzu GC-9 A).

Results and Discussion

First anodizing

The diffraction peaks due solely to anatase and metallic titanium were seen in XRD patterns of the first anodized films. However, the films contain lower valent titanium oxides such as TiO and Ti_2O_3 , excepting TiO_2 ³⁾. A deep coloration (blue or black) of the films can be attributed to the lower valent titanium ions included in the films⁴⁾.

Second anodizing

The SEM photographs and XRD patterns of the samples obtained after re-anodization of the first anodized films were quite similar to those of the original samples. The depth profiles measured by a glow discharge-optical emission spectrometer (GDOES) showed the presence of P and S, which derive from PO_4^{3-} and SO_4^{2-} , respectively, in addition to Ti and O in both the first and second anodized films. Fluorine was also detected by XPS, and the F_{1s} peak intensity remained after etching the surface for 10 minutes with Ar^+ ions. After the 2nd anodic oxidation, the film color became whiter, and its L^* value (an indicator of lightness) increased from 54 to 57–69; the latter value depends on the electrolytic condi-

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Fig. 1 The variation of the CH_3CHO concentration with time and plots of $\ln(C^0/C)$ vs. time for titanium substrate, first and second anodized films.

■□ : titanium substrate
 ▲△ : first anodized film
 ●○ : second anodized film

tions. The thickness of the second anodized film decreased by about $1\ \mu\text{m}$ as compared to that of the first.

Photocatalytic activity

The photocatalytic activities are shown in **Fig. 1**. The second anodized film was prepared in a solution of $0.05\text{-M NH}_4\text{HF}_2$ and $0.3\text{-M H}_2\text{O}_2$ at a 303K bath for 5 minutes. The photocatalytic activity of the titanium substrate and the first anodized film are negligible, whereas the second anodized film is photocatalytically active under UV/vis light. Moreover, plotting $\ln(C^0/C)$ vs time (t) revealed a straight line, where C^0 and C are the concentration of acetaldehyde at $t=0$ and $t=t$, respectively. This result indicates that the photocatalytic reaction follows the first order rate equation⁵⁾. The apparent rate constant (k) was calculated from the slope of the straight line as 0.047 h^{-1} . **Table 1** summarizes k for the second anodized films produced under different conditions. The value of k increases with increasing lightness (L^*) for the second set of anodized films.

Generation of photocatalytic activity by the second anodic oxidation is clearly evident. Since the low valent titanium oxides exist in the first anodized films that are predominantly composed of anatase-type crystal as described above³⁾, the films have no photocatalytic activity. Some impurities in TiO_2 usually impede photocatalytic activity and decrease 0 quantum efficiency^{6),7)}. It is likely that TiO and Ti_2O_3 produced during the first anodic oxidation serve as the recombination centers of the photogenerated charge

Table 1 Apparent rate constant (k) and lightness (L^*) of second anodized films.

Bath temperature /K	$\text{NH}_4\text{HF}_2/\text{M}$	Anodic oxidation time /min	k/h^{-1}	L^*
293	0.01	5	≈ 0	56
	0.01	10	≈ 0	57
	0.01	15	≈ 0	59
	0.05	5	0.018	59
	0.05	10	0.023	60
	0.05	15	0.026	61
	0.1	5	0.027	61
303	0.01	5	0.025	57
	0.01	10	0.024	59
	0.01	15	0.027	60
	0.05	5	0.047	62
	0.05	10	0.054	69
	0.1	5	0.054	67
313	0.01	5	0.019	56
	0.01	10	0.022	60
	0.01	15	0.025	60
	0.05	5	0.051	64
	0.05	10	0.052	69

carriers to reduce the photocatalytic activity. Since most of these lower valent titanium oxides were removed during the second anodic oxidation, the resultant films consisting mainly of anatase TiO_2 exhibit photocatalytic activity. It follows that a positive correlation between the photocatalytic activity and the L^* value exists.

Conclusion

A porous anodic oxide film of about 5.5 mm in thickness was anodized on a titanium substrate at a voltage of 200 V in a mixture of H_2SO_4 , H_3PO_4 , and H_2O_2 (the first anodized film). The film was again anodized in a solution of NH_4HF_2 and H_2O_2 (the second anodized film). The first anodized film showed no photodecomposition reaction for CH_3CHO gas, although the film consisted predominantly of anatase (TiO_2). The second anodized film exhibited a higher degree of lightness with ample photocatalytic activity.

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