doi:10.1246/cl.2012.544

# Visible Light Responsive $TiO_2$ Photocatalyst Prepared by Anodization of Ti–6Al–4V Alloy

Yoshiteru Mizukoshi* and Naoya Masahashi
*Kansai Center for Industrial Materials Research (IMR), Tohoku University,*
*1-2 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531*

(Received January 27, 2012; CL-120068; E-mail: mizukosi@imr.tohoku.ac.jp)

Titanium alloy Ti–6Al–4V was galvanostatically anodized in an aqueous acetic acid electrolyte followed by annealing to form anatase-structured $TiO_2$. The formed pale yellowish oxide contained $Al^{3+}$, $V^{5+}$, and $V^{4+}$ in the topmost surface of the anodized oxide. The anodized $TiO_2$ photocatalytically decomposed acetaldehyde under visible light illumination (>400 nm).

About 40 years have passed since the first report of Honda and Fujishima on $TiO_2$ photocatalyst,[1] however, practical uses and applications of the photocatalyst have been limited contrary to expectation. Especially, the improvement in the visible light response of the photocatalytic activities is one of the issues to be settled. Doping[2,3] is well known to modify the band structures corresponding to light with longer wavelength than the band gap of pristine $TiO_2$. However, mass productivity and the durability in long-term usage have not been solved.

Recently, we reported the characteristics of $TiO_2$ photocatalyst prepared by anodic oxidation.[4] In the electrolyte of aqueous sulfuric acid solution, the photocatalytic activities of sulfur-doped $TiO_2$ under visible light illumination were improved probably due to narrowing the band gap. Anodic oxidation is well known as an easy method for surface modification of valve metal using simple equipment and is applicable for large and/or complicated-shaped substrates, which are advantageous for practical applications. In addition, the anodized $TiO_2$ is expected to have high durability because of high exfoliation strength. In the present study, we anodized Ti–6Al–4V (hereafter described as Ti64), which has commonly been used in Ti alloys having balanced workability and strength.

Ti64 plates ($9 \times 19 \times 1\,mm^3$) were used for an anode in the anodic oxidation. They were polished using a 40-nm colloidal silica suspension after mechanical and buff polishing followed by rinsing in ethanol using an ultrasonic cleaning bath. A constant current of $50\,mA\,cm^{-2}$ was applied to the plate in an acetic acid electrolyte (2 M), and a Pt mesh electrode ($25\,cm^2$) was used as the cathode. The anodic oxidation was controlled galvanostatically, and the oxidation was conducted for 0.5 h. Sparks on the anode were not observed during the anodization, which is different from that in an aqueous sulfuric acid electrolyte.[4] The anodized Ti64 was annealed at 723 K for 5 h in air (Figures S1 and S2[5]).

The diffuse reflection spectra are shown in Figure 1. The annealed anodic oxides on Ti64 absorb light with wavelength shorter than about 500 nm. According to CIELab* parameters ($L^* = 56.47$, $a^* = -4.28$, $b^* = 14.06$), the color of the annealed sample is green and yellow. And the band gap energy evaluated from the spectra is 2.28 eV, which is lower than those of annealed anodic oxide on Ti (3.21 eV) or the as-anodized oxide on Ti64 (3.13 eV). Differing from these anodized samples, metallic luster remained on the surface of annealed Ti64 plate (without anodization).

The photocatalytic activities of the anodized $TiO_2$ were evaluated by the decomposition of acetaldehyde under light illumination with wavelength longer than 400 or 422 nm. The decomposition of acetaldehyde was estimated by the amounts of evolved $CO_2$ measured by GC-TCD. Prior to the introduction of acetaldehyde, illumination by a high-pressure Hg lamp removed the remaining organic species originating from acetic acid until no $CO_2$ evolution. The photocatalytic activities under visible light illumination are shown in Figure 2. The annealed anodic oxide on Ti64 exhibits distinguished photocatalytic activity comparing with the as-anodized oxide on Ti64 and the annealed anodic oxide on Ti. In the case of the annealed Ti64 plate (free of anodic oxide), low photocatalytic activity was recognized under visible light illumination (>400 nm). Both anodization and annealing are necessary for improving the photocatalytic activities.

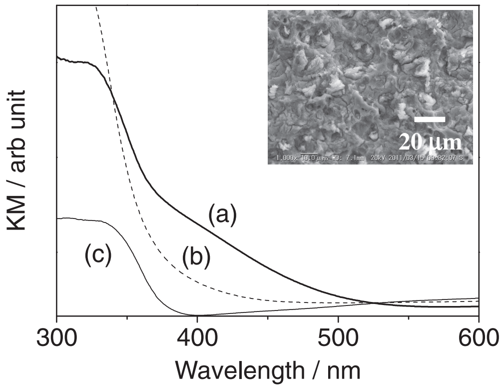

**Figure 1.** Diffuse reflection spectra of the annealed (a) and as-anodized (b) anodic oxide on Ti64, and annealed anodic oxide on Ti (c). The inset is SEM image of sample (a).

The surface areas measured by using a laser microscope with a wavelength of 408 nm are summarized in Table 1. Projected surface for measurement was about $340\,\mu m^2$. Surface area of sample (3) exhibiting superior photocatalytic activities was smaller than those of samples (1) and (2), suggesting that the surface area is not a predominant factor for the photocatalytic activities.

Figure 3 is the XRD patterns measured with Cu K$\alpha$ radiation (0.15406 nm), at a scan rate of $1°\,min^{-1}$, and a rotating detector. The sample was set in a thin-film geometry arrangement at 0.5° glancing angle. The diffraction peaks due to $TiO_2$ were not detected in the as-anodized Ti64 (Figure 3c), which explains low photocatalytic activities.[6] In the annealed and anodized Ti64 (Figure 3d), the predominant phase of anatase $TiO_2$ was recognized. When Ti64 plate was annealed (Figure 3b), no peaks due to anatase $TiO_2$ were observed. In contrast to the anodic oxide prepared in sulfuric acid electrolyte,[4] peaks from rutile phase were not detected. This suggests that the Ti64 surface is not exposed to high temperature, which is supported by an absence of sparking during the anodization. Peaks from vanadium oxide and aluminum oxide were not observed, which indicates that these oxides were not formed or below the detection limit of X-ray diffraction analyses.

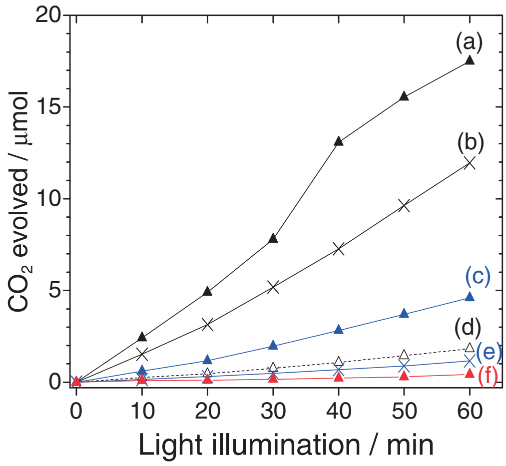

**Figure 2.** $CO_2$ evolution from the decomposition of acetaldehyde under visible light illumination. Triangle and cross symbols correspond to those under light illumination with the wavelengths >400 and >422 nm, respectively. (a) and (b) are annealed anodic oxides on Ti64, and (c) and (e) are those on Ti. (d) is as-anodized oxide on Ti64 and (f) is annealed Ti64 plate.

**Table 1.** Surface areas measured by laser microscopy

| Sample | Surface area/μm$^2$ |
|---|---|
| (1) Annealed anodic oxide on Ti | 4570 |
| (2) As-anodized oxide on Ti64 | 3306 |
| (3) Annealed anodic oxide on Ti64 | 2610 |
| (4) Annealed Ti64 | 734 |

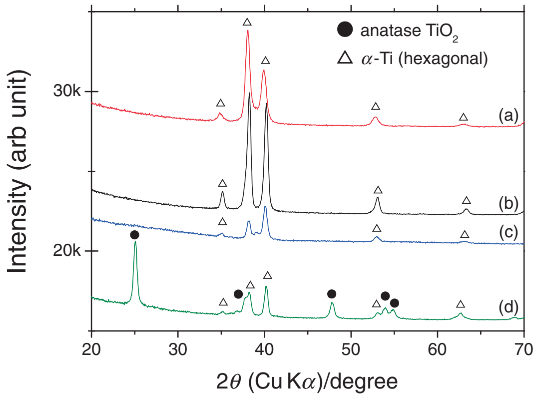

**Figure 3.** XRD patterns of Ti64 plate (a) before and (b) after annealing and Ti64 anodized in 2 M acetic acid (c) before and (d) after annealing.

In XPS analyses, a signal appeared in the $Al_{2p}$ region, attributable to $Al^{3+}$ (BE = 73.8 eV). V was also detected as mainly $V^{5+}$ on the topmost surface of the sample, which was contrary to the previous reports that V species were not detected near the surface of the anodized Ti64.[7,8] TOA (take off angle) dependence of $V_{2p}$ spectra is shown in Figure 4. The $V_{2p}$ peak is located in a lower binding energy position in TOA = 15° (the topmost surface) than TOA = 90° (the oxide inside), and it could be deconvoluted into two peaks corresponding to $V^{4+}$ and $V^{5+}$, which suggests that some V atoms substitute for Ti atoms forming Ti–O–V structures.[9]

The band gap energy of $Al_2O_3$ is 9.2 eV and the absorption band lies in the vacuum UV region (at 135 nm),[10] as a result $Al_2O_3$ has no photocatalytic activity under UV light illumination. The photocatalytic activities of V-doped $TiO_2$ have been extensively reported.[9,11] It is generally accepted that $V^{5+}$ ($V_2O_5$) is not preferable because it becomes the recombination centers of the photoexited electrons and holes.[12] On the other hand, the charge transfer between 3d electrons of $V^{4+}$ and $TiO_2$ conduction band links to the appearance of absorbance in the visible region.[13] The authors considered that the present anodized Ti64 exhibits excellent photocatalytic activities under visible light illumination with the contribution of $V^{4+}$ rather than the interference of $V^{5+}$.

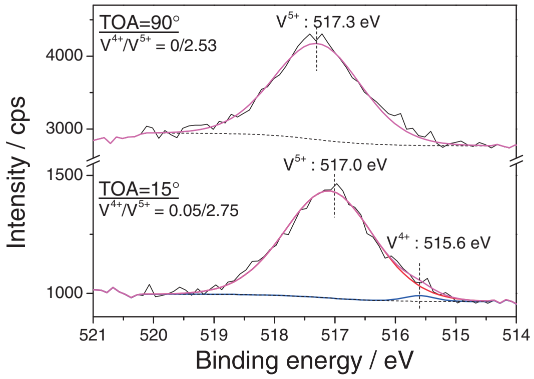

**Figure 4.** $V_{2p}$ XPS spectra of annealed anodic oxide on Ti64. TOA = 15° is deconvoluted into two Gaussian-type peaks.

Visible light response was confirmed in the anodic oxide on Ti64. The anodized $TiO_2$ is expected to be useful because of its simple procedure of preparation, higher durability, and superior mass-productivity compared to conventional $TiO_2$ coating techniques such as chemical vapor deposition.

The authors wish to acknowledge Ms. Y. Matsuda and Mr. S. Sugiyama from IMR, Tohoku Univ. for sample preparations and characterizations, Ms. K. Ohmura from IMR, Tohoku Univ. for XPS analyses, Mr. T. Abumiya from Titanium Meister for Ti64 supply.

## References and Notes

1 A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37.
2 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, *293*, 269.
3 M. Anpo, M. Takeuchi, *J. Catal.* **2003**, *216*, 505.
4 a) N. Masahashi, Y. Mizukoshi, S. Semboshi, N. Ohtsu, *Appl. Catal., B* **2009**, *90*, 255. b) Y. Mizukoshi, N. Ohtsu, S. Semboshi, N. Masahashi, *Appl. Catal., B* **2009**, *91*, 152.
5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
6 a) M. Inagaki, Y. Nakazawa, M. Hirano, Y. Kobayashi, M. Toyoda, *Int. J. Inorg. Mater.* **2001**, *3*, 809. b) A. G. Agrios, P. Pichat, *J. Photochem. Photobiol., A* **2006**, *180*, 130. c) G. Benkö, B. Skårman, R. Wallenberg, A. Hagfeldt, V. Sundström, A. P. Yartsev, *J. Phys. Chem. B* **2003**, *107*, 1370.
7 M. Ask, J. Lausmaa, B. Kasemo, *Appl. Surf. Sci.* **1989**, *35*, 283.
8 L. P. Bicelli, G. Razzini, C. Malitesta, L. Sabbatini, *Int. J. Hydrogen Energy* **1987**, *12*, 219.
9 H. Li, G. Zhao, Z. Chen, G. Han, B. Song, *J. Colloid Interface Sci.* **2010**, *344*, 247.
10 V. N. Abramov, M. G. Karin, F. I. Kuznetsov, K. K. Sidorkin, *Sov. Phys.-Solid State* **1979**, *21*, 47.
11 T. Kamegawa, J. Sonoda, K. Sugimura, K. Mori, H. Yamashita, *J. Alloys Compd.* **2009**, *486*, 685.
12 S. T. Martin, C. L. Morrison, M. R. Hoffmann, *J. Phys. Chem.* **1994**, *98*, 13695.
13 a) K. Iketani, R.-D. Sun, M. Toki, K. Hirota, O. Yamaguchi, *Mater. Sci. Eng., B* **2004**, *108*, 187. b) S. Klosek, D. Raftery, *J. Phys. Chem. B* **2001**, *105*, 2815.