Applied Surface Science 296 (2014) 163–168

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Structural changes of anodic layer on titanium in sulfate solution as a function of anodization duration in constant current mode

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ARTICLE INFO

Article history:
Received 24 September 2013
Received in revised form
28 December 2013
Accepted 11 January 2014
Available online 21 January 2014

Keywords:
Anodization
Titanium
Photocatalyst
Visible light response

ABSTRACT

The present study investigated the effect of anodization time, in constant current mode, on the anodic oxide layer formed on titanium (Ti). Anodization of the Ti substrate was carried out in a 0.1 M $(NH_4)_2SO_4$ aqueous solution with reaction times of various durations, after which the characteristics and photocatalytic activity were investigated in detail. The TiO_2 layer fabricated in a short duration exhibited comparatively flat surface morphology and an anatase-type crystal structure. This layer acted as a photocatalyst only under ultraviolet light (UV) illumination. Upon prolonging the anodization, the layer structure changed drastically. The surface morphology became rough, and the crystal structure changed to rutile-type TiO_2. Furthermore, the layer showed photocatalytic activity both under UV and visible light illumination. Further anodization increased the amount of methylene blue (MB) adsorbed on the surface, but did not cause additional change to the structure of the anodic layer. The surface morphology and crystal structure of the anodic layer were predominantly controlled by the anodization time; thus, the anodization time is an important parameter for controlling the characteristics of the anodic layer.

1. Introduction

Anodization has recently attracted attention as a fabrication process of a photocatalytic titanium dioxide (TiO_2) layer, as an alternative to conventional techniques such as sol–gel method [1,2,25], spattering [3], thermal chemical vapor deposition [4], and thermal oxidation [5]. This technique is a simple process, which involves connecting the Ti substrate to an anode in electrolyte solution, and then applying a current. Other advantages include strong adhesion between the oxide layer and the substrate [23,24], and facile control of the surface morphology [8,19,26,29]. As demonstrated by Ohtsu et al., the anion composition in the electrolyte can change the characteristics of the anodic oxide layer, such as adhesion strength, surface morphology, and crystal structure. Furthermore, the anions of the electrolyte become incorporated in the layer [9]. This has further implications for the layer characteristics; although normal TiO_2 demonstrates photocatalytic activity only under UV light illumination, due to its energy band gap of 3.2 eV for anatase-type structure and 3.0 eV for rutile-type structure, incorporating elements such as sulfur or nitrogen extend its photocatalytic activity into the visible region by narrowing the band gap [27,30,31]. This allows visible-light-responsive TiO_2 photocatalysts to be fabricated using anodization. For example, Mizukoshi et al. reported that a sulfur-incorporated rutile-type TiO_2 layer fabricated by anodization in a highly concentrated sulfuric acid solution can degrade methylene blue (MB) under visible light illumination [10]. However, the photocatalytic activity of such a layer under visible light is notably lower than that under UV light illumination [11–14]. Enhancement of the visible-light-responsive activity is therefore of interest.

Photocatalytic activity is affected by several factors, such as surface morphology and crystal structure, because it is related to the number of catalytic sites and the recombination of photo generated electron-hole pairs [15–17,22]. Mizukoshi et al. observed that anodic TiO_2 layers fabricated in 1.2 M sulfuric acid solution exhibited changes in crystal structure and surface morphology depending on the anodization time; controlling these changes improved the photocatalytic activity [18]. The authors suggested that the anodization duration is an important factor for controlling the crystal structure and surface morphology and for thus enhancing the visible light response. However, their experimental conditions render such a conclusion slightly ambiguous. First, the anodization was not carried out under completely galvanostatic conditions because the applied voltage was restricted below 220 V. Galvanostatic conditions, without voltage restriction, are required in order to precisely understand the effect of anodization duration. Furthermore, Mizukoshi et al. tested only a single electrolyte concentration: 1.2 M sulfuric acid [18]. A variety of electrolyte concentrations must be tested, because the results may differ at lower concentrations.

In this study, therefore, TiO_2 layers were fabricated by anodizing Ti plate galvanostatically in 0.1 M ammonium sulfate solution

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http://dx.doi.org/10.1016/j.apsusc.2014.01.066

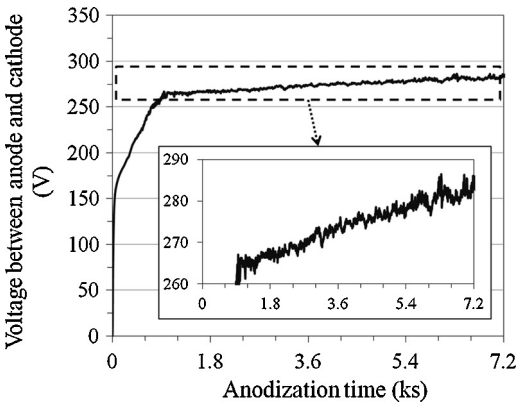

Fig. 1. Time transient analysis of the voltage between the cathode and the anode during the anodization.

at various anodization durations. The characteristics and photocatalytic activity of the layers were investigated in detail. The results elucidate the effect of the anodization duration on the TiO_2 layer fabricated in different electrolyte concentrations compared to the work of Mizukoshi et al.

2. Experimental procedures

A pure titanium plate (99%) with dimensions of $20 \times 10 \times 1\ mm^3$ was used as a substrate. The substrate was polished with a colloidal suspension of 40 nm silica particles, and then, ultrasonically washed in ethanol. The electrolyte used for anodization was 0.1 M ammonium sulfate solution ($(NH_4)_2SO_4$), whose pH was about 5.4. Ti and Pt wires of 1 mm in diameter were welded to the Ti substrate and a Pt plate ($20 \times 10 \times 1\ mm^3$), and then, were connected to the anode and cathode, respectively. The substrate and the Pt plate were completely soaked in the electrolyte, and anodization was carried out galvanostatically using direct current of $50\ mA\ cm^{-2}$ for 600 s, 1.8 ks, 3.6 ks, or 7.2 ks. During the treatment, the temperature of the electrolyte solution was kept at 298 K using a water bath. After anodization, the substrates were ultrasonically washed in distilled water for 600 s, and annealed at 723 K in air for 18 ks.

The surface morphology of the substrates was observed by scanning electron microscopy (SEM; JCM-5000 Neo Scope, JEOL, Japan) in secondary electron image mode with an acceleration voltage of 10 kV, and scanning probe microscopy (SPM; SPM-9700, Shimadzu, Japan) in dynamic mode. The crystal structure was obtained by X-ray diffraction (XRD; New D8 Advance, Bruker AXS, Germany) with Bragg-Brentano geometry using CuKα radiation. Quantitative analysis of the sulfur incorporated in the TiO_2 layer was conducted by X-ray fluorescence spectrometry (XRF; S8 Tiger, Bruker AXS, Germany) using Rh X-ray source.

Surface adsorption behavior and photocatalytic activity were estimated by soaking the substrate in MB solution, filled in a polystyrene vessel. Prior to soaking the substrate, the oxide layer on one side was removed by polishing while paying attention not to cause damage to the other side. The substrate was put at the bottom of the polystyrene vessel with the polished side down. These measures were conducted to reduce the errors caused by the MB adsorption on the surface in contact with the vessel. At the beginning of the measurement, the substrate was illuminated with UV light at an intensity of $2\ mW\ cm^{-2}$ for 5.4 ks, in order to eliminate surface contamination. The substrate was then soaked in a 10 μM MB solution of $100\ cm^3$, and the solution including the substrate was statically placed in the dark. During the soaking, the change of the absorbance (664 nm) of the solution corresponding to the MB was measured using a UV–vis spectrometer every 3.6 ks for a total duration of 14.4 ks, after which we calculated the amount of MB adsorption from this data. Subsequently, the substrate was soaked in fresh MB solution with a concentration of 10 μM and the vessels were illuminated using LED lights. The photocatalytic activity was evaluated by degradation of MB under light illumination. Here, the light illumination was carried out using LED lamps with wavelengths of 370 nm, 420 nm, and 450 nm. The intensity of the radiation was adjusted to $1\ mW\ cm^{-2}$. The change of the MB concentration was measured from the absorbance corresponding to the MB every 1.2 ks for a total duration of 10.8 ks. Then, the concentration was linearly plotted against the illumination period, and the rate of MB degradation ($nmol\ cm^{-3}\ s^{-1}$) was calculated from this plot.

3. Results

3.1. Effect of anodization time on morphology of the anodic layer

Fig. 1 shows the time transient of the applied voltage between the cathode and the anode during the anodization. The voltage increased in three stages. At the beginning of the anodization, the voltage increased abruptly up to about 160 V within 60 s. Thereafter, the rate of increase was moderate until about 900 s, whereupon its value reached about 260 V. When the voltage reached about 250 V, we could observe the luminescence on the surface of the substrate. In the voltage region where luminescence was observed, the turbulence of the voltage was found in the voltage profile, indicating that the luminescence observed was probably due to electric spark. Finally, the rate of increase significantly slowed, and the absolute increase of voltage was quite small during this third stage. The voltage at 7.2 ks was about 280 V.

Fig. 2 shows the appearance of the anodized substrates at each anodization time. The Ti substrate without anodization appears gray with metallic luster (Fig. 2(a)). However, the substrate became tarnished by anodization for 600 s (Fig. 2(b)), indicating that a new layer is formed on the surface. Furthermore, at 1.8 ks (Fig. 2(c)), corresponding to the early third stage, some areas of the substrate appeared white, indicating that the new oxide layer began to form. The entire substrate appears white after 3.6 ks (Fig. 2(d)). These

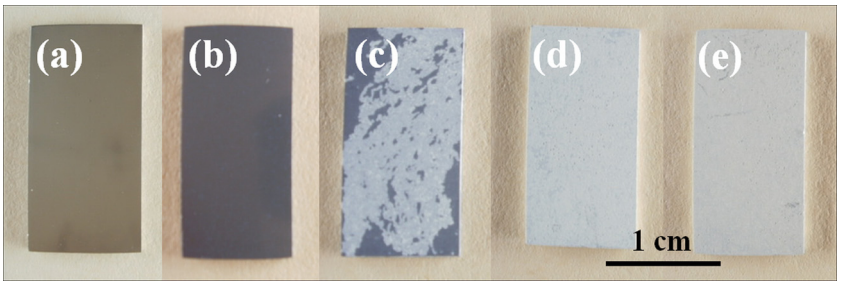

Fig. 2. Photographs of the substrate (a) without anodization, and anodized in 0.1 M $(NH_4)_2SO_4$ aqueous solution for (b) 600 s, (c) 1.8 ks, (d) 3.6 ks, and (e) 7.2 ks.