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Effect of Accumulation of Ti^{4+} in 0.1 M H_2SO_4 Electrolyte on Growth and Crystallization of Anodic Titanium Oxide Films

Junheng Xing, Zhengbin Xia, Yanhong Zhang, Li Zhong*

School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China
*E-mail: cezhbxia@scut.edu.cn

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The influence of the accumulation of Ti^{4+} in the solution on formation and crystallization of anodic oxide films on titanium is investigated by performing the anodization of several pieces of titanium sheets at potentiostatic mode one after another without changing the electrolytic solution. The concentration of the dissolved Ti^{4+} in the solution is intermittently determined by graphite furnace atomic absorption spectroscopy (GFAAS). It is found that the dissolution rate of titanium anodized films is enhanced by the accumulation of Ti^{4+} in the solution. Moreover, with the increasing of Ti^{4+} in electrolyte, the "flower-like" crystalline grains on sample surface are enlarged and the crystallization and dehydration process of anodic oxide films are encouraged because of the enhancing of ionic migrations during titanium anodizing process.

Keywords: anodic oxide film; Ti^{4+}; crystallization; GFAAS; ionic migration

1. INTRODUCTION

Electrochemical anodization technology is an important method for the preparation of functional TiO_2 thin films [1-4]. The structure, morphology and properties of titanium oxide layers vary with anodizing parameters, like oxidation potentials [5, 6], oxidation time [7, 8], film growth modes [9] and film growth rates [10]. The electrolytic solution is also proved to play a key role on the formation and crystallization of anodic titanium oxides [11, 12]. Generally speaking, the titanium anodized films grown in strong acids (like $HClO_4$, HF and HNO_3) are more likely to have a porous and well crystallized structure, while in weak acids solution (like organic acids), the TiO_2 films tend to be thinner and more homogeneous. Moreover, as revealed by some authors, the growth and crystallization of titanium oxide films can be encouraged by increasing the electrolyte concentration or by enhancing the solution temperature [7, 11, 13].

The presence of impurity ions in the electrolyte can also influence the growth and crystallization of anodic titanium oxide films [14]. For instance, the presence of fluorine ions in the solution is reported to attack locally TiO_2 films, hence facilitate the formation of nanoporous and well crystallized titanium oxide films [15-17]. Besides these aggressive anions (like F^- and Cl^-), there also have other kinds of metal cations accumulated in the solution, which may influence the growth of Ti anodized films [18]. It is well-known that the anodic oxide films growth is usually accompanied by a dissolution process of titanium oxides, which means that plenty of Ti^{4+} will be accumulated in the solution during titanium anodization. By using inductively coupled plasma emission spectrometry (ICP), Shibata et al. revealed that after the initially film growth stage, the amount of Ti^{4+} dissolved in electrolyte increased significantly with time [19]. Hence, it is not difficult to imagine that such a great quantity of titanium cations will, to some extent, have an influence on the conductivity of electrolytic solution, and then on the growth and crystallization of anodic titanium oxide films. However, until now, few researchers have put their attention on this subject. In this paper, five pieces of highly pure titanium sheets are successively treated under potentiostatic condition for 1 h without changing the electrolytic solution, the concentration of titanium ions accumulated in the solution is determined, and the effect of the accumulation of Ti^{4+} in the electrolyte on the growth and crystallization of titanium anodized films is discussed.

2. EXPERIMENTAL

2.1. Anodization of pure Ti samples

In order to avoid the accumulation of impurity ions in the solution, highly pure titanium sheets (>99.99%) with a size of 10×10×1 mm were used as the working electrode. Before anodizing treatments, the titanium samples were first mechanically polished with 600, 1000, 1500 and finally with 3000 emery papers, and then chemically polished by etching in a solution of 1% HF and 3% HNO_3 for 3~4 s. After the surface polishing, all samples were ultrasonically cleaned with acetone for 20 min and later with deionized water for 20 min.

Anodizing of titanium samples was carried out in a two-electrode electrolytic cell by using an electrochemical workstation (Metrohm Autolab PGSTAT100, Switzerland), which was equipped with a Voltage Multiplier Module. A Pt plate, with the same size as the working electrode, was used as the counter electrode, and 0.1 M H_2SO_4 (800 ml in volume), prepared by analytical reagent and high purity water, was used as the electrolyte. Five sheets of titanium, marked as “Sample 1”, “Sample 2”… and “Sample 5”, respectively, were successively treated one by one under potentiostatic mode for 1 h with the voltage of 30 V. The solution was not changed from the beginning to the end of the experiments, and the electrolytic cell was cooled by circulating water, so that the titanium oxide films could grow at a constant temperature (25 ^oC). After anodizing treatments, the specimens were immediately took out from the solution, rinsed with deionized water and dried by air blowing, and then conserved in a vacuum drying oven before further characterization.

2.2. Solution analysis

After 1 h film formation for each titanium specimen, 2 ml solution sample was removed from the cell, and the concentration of titanium ions dissolved in the electrolyte was determined by GFAAS. A SHIMADZU AA-6800 atomic absorption spectrophotometer (Japan), with an ASC-6100 autosampler, a pyrolytic coated graphite tube and a Ti hollow cathode lamp was used for the measurements. Calibration standard solutions of 300 ppb (μg/L) were prepared by diluting the stock solution with 1% HNO_3.

2.3. Characterization

The Raman spectra were recorded by a LabRAM Aramis (HORIBA Jobin Yvon, France) instrument, which was performed with the incidence power of 10.4 mW and the excitation wavelength of 532 nm. Spectroscopic ellipsometer (SE, HORIBA Jobin Yvon Auto SE, France), which was performed at an incidence angle of 70° with the wavelength range of 439-842 nm, was used to determine the thickness of titanium oxide films. A single layer model (Ti substrate and TiO_2 film) was used in the modelling procedure. Scanning electron microscopy (SEM, LEO 1530 Vp, Germany) with electron beam of 5 kV was used to observe the surface topography of titanium oxide films. X-ray photoelectron spectroscopy (XPS) was perfomed on a Kratos Axis Ultra DLD spectrometer (UK), using an Al Kα (1486.6 eV) X-ray source operated at 15 kV and 150 W. The spectral positions were corrected by normalizing the C 1s spectrum at 284.6 eV, and a Shirley background was used for the peak fitting.

3. RESULTS AND DISCUSSION

3.1. Concentration of Ti^{4+} in solution

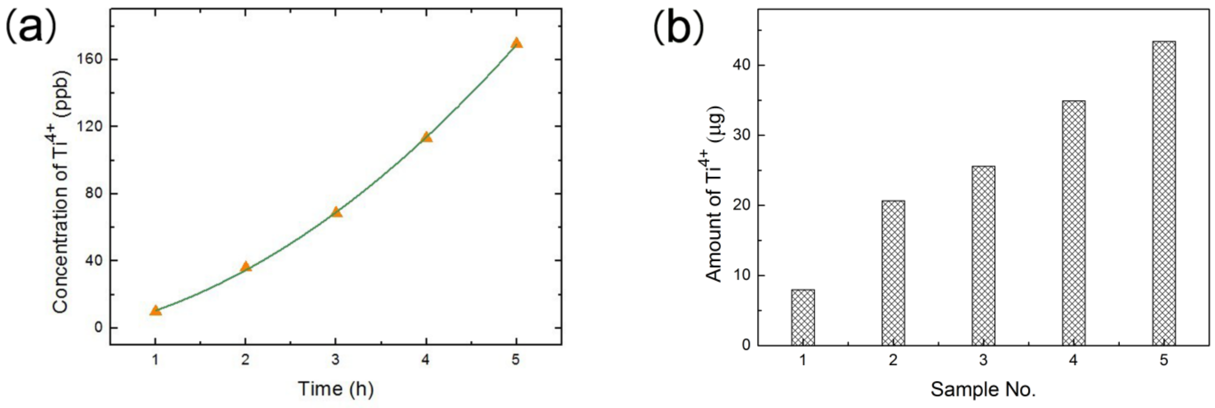

Figure 1. (a) Concentration evolution of dissolved Ti^{4+} in solution during anodization of five titanium samples, and (b) the amount of Ti^{4+} dissolved in solution during the 1 hour film formation for each sample.

The concentration of the dissolved Ti^{4+} in the electrolyte after 1 h potentiostatic treatment of each sample is presented in Fig. 1a. It is clearly that the titanium ions concentration increases with time, but not in a linear fashion. The amount of Ti^{4+} dissolved in the solution during 1 h film formation for each sample is shown in Fig. 1b. As seen in the picture, the mass of the dissolved ions increases with the replacement of the sample. After 1 h anodization of Sample 1, only about 7.96 μg titanium ions is dissolved in the solution, while after 1 h film formation of Sample 5, about 43.41 μg titanium ions is generated. This implies that the film dissolution rate during titanium anodization is enhanced by the increasing of Ti^{4+} concentration in the solution.

3.2. Film properties

Fig. 2 displays the Raman spectra of five anodized titanium samples, from which four Raman bands at about 144 cm^{-1}, 399 cm^{-1}, 516 cm^{-1} and 639 cm^{-1}, corresponding to anatase type of TiO_2, can be clearly seen for all samples. Moreover, it can be also found that the intensity of the Raman peaks increases progressively with the sample number. In other words, the crystallization of anodic titanium oxide films can be encouraged by the increasing of Ti^{4+} in the electrolytic solution.

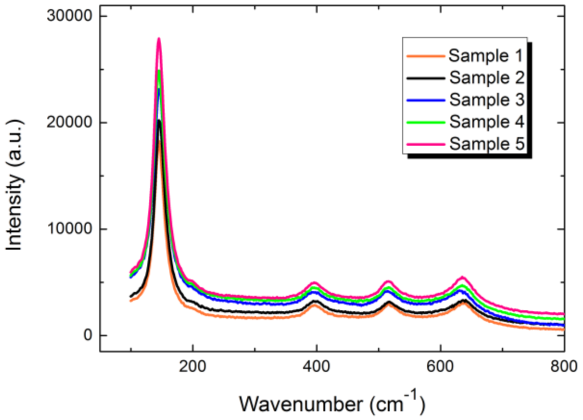

Figure 2. Raman spectra recorded from the titanium oxide films of five anodized samples.

In order to well understand the influence of the accumulation of Ti^{4+} in the solution on the crystallinity of anodic titanium oxides, the intensity of the strongest Raman peak at 144 cm^{-1} and the thickness of titanium anodized films are presented in Fig. 3, from which it is found that the intensity of Raman band (at 144 cm^{-1}) increases and the film thickness decreases gradually with the replacement of the sample. As revealed in section 3.1, the film dissolution rate is enhanced by the accumulation of titanium ions in the solution. Thus, it is not difficult to image that the film thickness will decrease as the concentration of Ti^{4+} in the solution increasing. Moreover, the Raman peak height is reported almost proportional to the thickness of titanium oxide films, and higher crystallinity oxide films can also lead to a higher Raman intensity [20]. Hence, it can be obviously concluded from Fig. 3 that the crystallinity of the formed titanium oxide films increases significantly with the increasing of Ti^{4+} concentration in the solution.

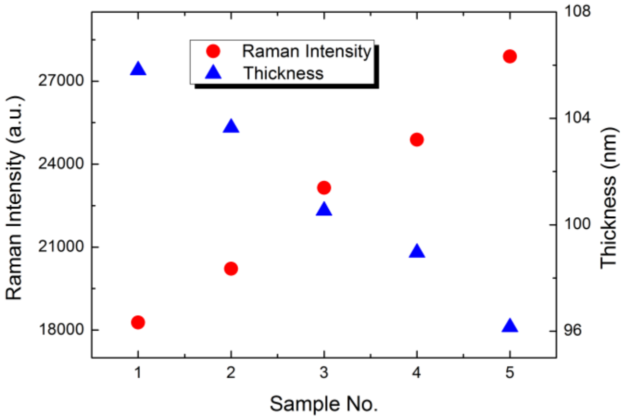

Figure 3. Intensity of Raman peak at 144 cm^{-1} and thickness of titanium oxide films for five anodized samples.

For the potentiostatically grown films, with the oxidation voltage of 30 V, there are many “flower-like” TiO_2 crystalline grains randomly distributed on the surface (Fig. 4). Similar to the Raman results, the surface features of the five anodized samples also show some differences.

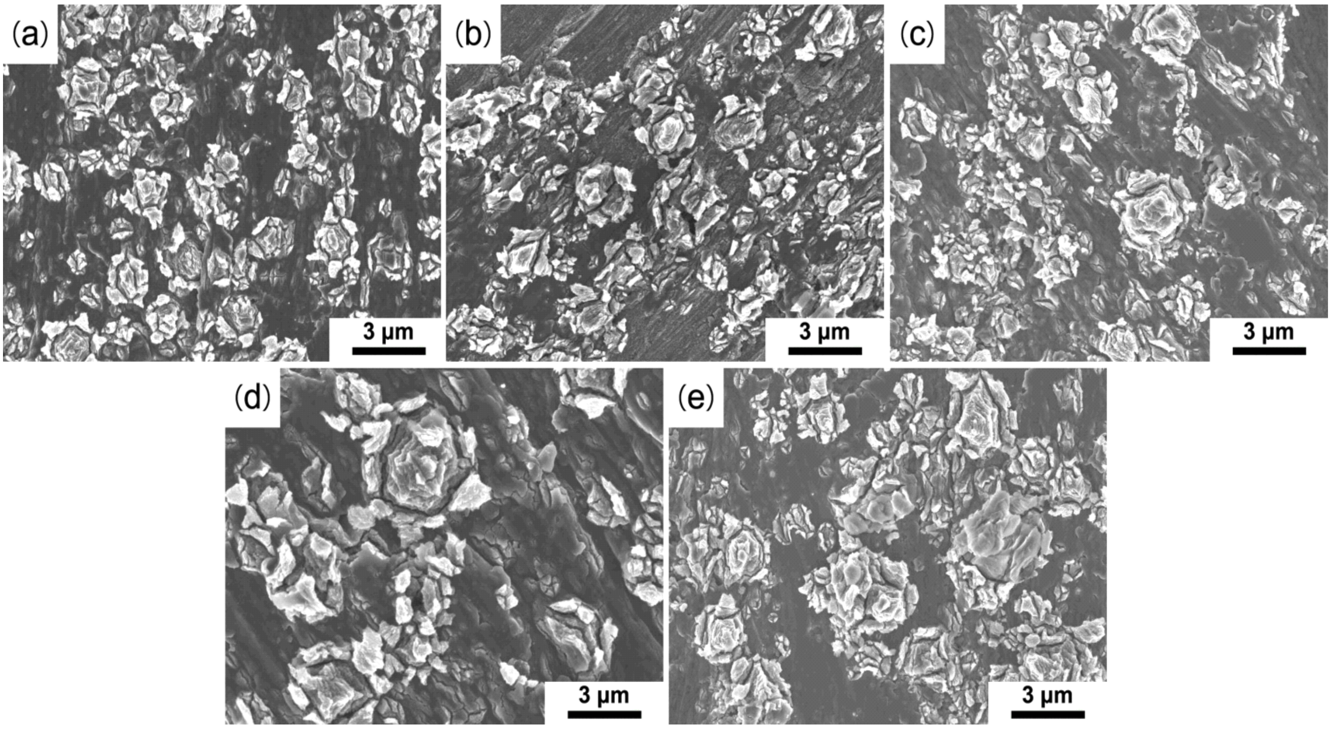

Figure 4. SEM images of anodic oxide films surface of (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4 and (e) Sample 5.

For Sample 1, which is anodic oxidized without the dissolved titanium ions in the solution, the formed "flower-like" crystals are relatively small, with a homogeneous size of about 2 μm (Fig. 4a). While as the concentration of Ti^{4+} in the solution increasing, the size of the "flower-like" structures turns to nonuniform, and some big crystalline grains with the diameter larger than 3 μm are emerged (Fig. 4d and e).

The chemical composition of anodic oxide films of five samples was detected by XPS. The results show that, with the high oxidation potential of 30 V, Ti^{4+} is the only state that can be detected for the titanium element of potentiostatically grown films, while the O 1s spectra can be fitted with 3 peaks, corresponding to O^{2-}, OH^{-} and H_2O, respectively. Fig. 5 displays the percentage contents of O^{2-}, OH^{-} and H_2O for the five anodic oxidized samples. It is clear that the percentage contents of the O^{2-} species increase and the OH^{-} and H_2O species decrease progressively with the replacement of the sample, which means that the dehydration of anodic titanium oxide films is encouraged by the accumulation of Ti^{4+} in the electrolyte. To the best of our knowledge, the bound water (OH^{-} and H_2O) is a source of disorder in the anodic oxide film, which is unfavourable for the crystallization.

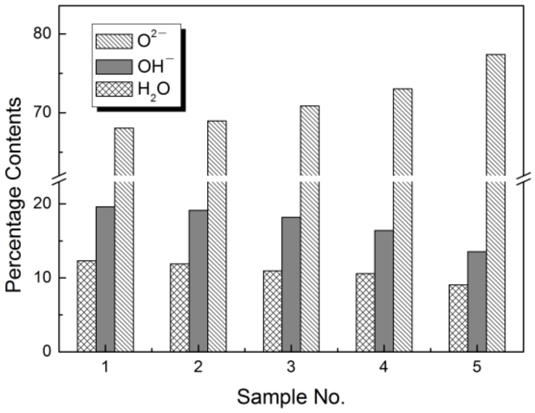

Figure 5. Percentage contents of O^{2-}, OH^{-} and H_2O for five anodized titanium samples.

3.3. Effect of the Ti^{4+} incorporation in solution

The chrono-amperometric curves of titanium anodization for the five samples, filtered by smoothing approaches, are presented in Fig. 6. It can be found that the anodizing of the five samples has been performed in the same process, except that the steady-state current density increases with the sample number. It is reported that, after the initial stage of titanium anodization, the current response is mainly contributed by the ionic migrations across the film [21]. In other words, with the accumulation of Ti^{4+} in the solution, the ionic migrations during the titanium anodization process are enhanced.

For titanium anodization under potentiostatic conditions, TiO_2 micro-crystals are emerged at the very beginning stage of anodizing process due to very high local current density at the local defect sites of sample surface. Subsequently, these micro-crystals will act as ionic conducting channels and grow up to "flower-like" structures [9]. With the accumulation of Ti^{4+} in the solution, the ionic migrations during titanium anodization are enhanced, and as a result, the size of the "flower-like" crystalline grains will be enlarged. Moreover, the Ti^{4+} dissolved in the solution also has an effect on the formation of the primal TiO_2 micro-crystals at the initial stage of titanium anodizing. The ionic conductivity of some micro-crystals can be modified by the dissolved Ti^{4+} in the electrolyte, this may be why the size of the "flower-like" structures turns to more nonuniform with the replacement of the sample. Similarly, with the accumulation of Ti^{4+} in the electrolyte, the dehydration and crystallization process of anodic titanium oxide films can be also promoted by the enhancing of ionic migrations. Thus, the crystallinity and the percentage contents of O^{2-} species are higher for the anodized Sample 5 as compared to the previous samples.

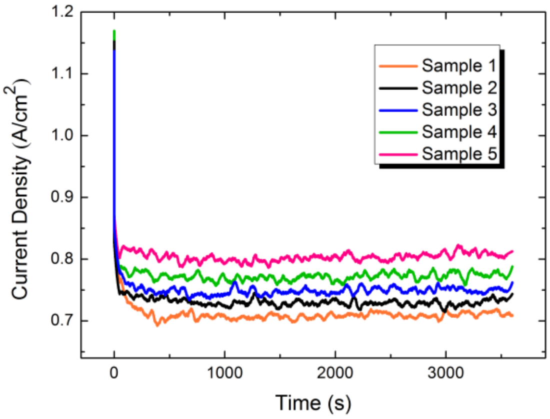

Figure 6. Chrono-amperometric curves of titanium anodization for five samples.

Nevertheless, the open question could be that why the ionic migrations are encouraged by the accumulation of Ti^{4+} in the solution? To the best of our knowledge, the conductivity of the electrolyte may play an important role. With the dissolving of Ti^{4+} in the electrolyte, the conductivity of the solution can be more or less increased. As a result, the current density and then the ionic migrations during titanium anodization will be enhanced with the increasing of Ti^{4+} in the solution (Fig. 6). This could be a plausible assumption without concerning the fact that the conductivity of the sulfuric acid solution is very high already [22]. Thus, the above question will be discussed from the point of the ionic migration mechanisms of titanium anodization.

It is revealed that the anodic titanium oxides are developed not only at the oxide/solution interface by the migration of titanium ions outward, but also at the mental/oxide interface by the migration of anions (O^{2-}, OH^-) inward [23, 24]. Furthermore, according to the point defect mode (PDM) proposed by Macdonald et al., the movement of ions across the mental oxide film is performed by vacancy motion, due to the preponderance of Schottky defects [25]. For the anodization of valve metal, the anion vacancies are generated at the metal/film interface and consumed at the film/solution interface, while the cation vacancies are produced at the film/solution interface and consumed at the metal/film boundary, in which the generation of the cation vacancies at the film/solution interface occurs by dissolving the metal ions into the electrolyte [25]. In the present study, the GFAAS results clearly show that the amount of the dissolved Ti^{4+} increases significantly with the replacement of the sample (Fig. 1b). That is to say, more cation vacancies will be produced with the increasing of Ti^{4+} concentration in the solution, and as a result, the ionic migrations during titanium anodization will be also enhanced.

4. CONCLUSIONS

The influence of the dissolved Ti^{4+} in the solution on the formation and crystallization of anodic titanium oxide films has been studied. The results show that the crystallization and dehydration process of the anodized films are encouraged and the formed “flower-like” crystalline grains on sample surface are enlarged by the accumulation of Ti^{4+} in the solution. We believe our works will be helpful for the study on the formation process and crystallizing mechanisms of anodic titanium oxide films, hence provide a useful inspiration for the preparation of functional titanium anodized films, such as the doping of other metal ions in titanium oxide layers.

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