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Formation mechanism of anodic titanium oxide in mixed electrolytes

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ABSTRACT

The formation mechanism of anodic TiO_2 nanotubes (ATNTs) remains mysterious and complicated. Usually, ATNTs are fabricated in pure NH_4F electrolytes rather than mixed electrolytes and Ti anodizations are carried out under potentiostatic rather than galvanostatic conditions. In this work, anodizations under the potentiostatic and galvanostatic conditions are conducted. The formation processes of titanium oxide film in different mixed electrolytes are explored in detail. By changing the mass ratios of oxalic acid and ammonium fluoride, different kinds of anodic titanium oxide films are fabricated: the compact anodic titanium oxide (CATO) films, transient-state anodic titanium oxide films and porous films (ATNTs). A distinct transform from CATO films into ATNTs was observed. Cavities within oxide and hemispheric bottoms are found, confirming the presence of oxygen bubble mould. Based on the electronic current and ionic current model, a consistent formation mechanism for three kinds of anodic titanium oxide films in mixed electrolytes is proposed.

1. Introduction

Anodic TiO_2 nanotubes (ATNTs) [1,2] have received attention due to special nanostructure and mysterious mechanism. ATNTs are traditionally fabricated in fluoride-containing electrolytes [3–6]. The accepted mechanism is the field-assisted dissolution (FAD) theory ($TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O$) for the formation of pores in anodic titanium oxide films [6–9]. However, TiO_2 nanotubes can also be obtained in $AgNO_3$ and HNO_3 electrolytes without fluoride [10,11]. These facts make the FAD theory or the $[TiF_6]^{2-}$ effect somewhat problematic [12]. Furthermore, during anodizing process, the FAD theory claims that total anodizing current includes oxide growth current and dissolution current [9]. However, Thompson et al. [13] indicated that the dissolution process is chemical in nature and cannot contribute to the anodizing current. Therefore, Hebert et al. [14,15] indicated that there is no model that has clearly explained the relationships between anodizing curves and film morphologies during potentiostatic anodization. The above FAD process cannot give reasonable explanation to the formation of the hemispheric bottoms and cylindrical nanopores [16–18].

There are two different kinds of anodic oxide films for Ti anodization, the compact anodic titanium oxide (CATO) films and porous TiO_2 nanotubes, which can be fabricated in fluoride-free solutions [12,17–19] and fluoride-containing solutions [3–9], respectively. The traditional theory indicates that the formation mechanisms for the two films are different [7–9,12,17,18]. In fact, the barrier oxide layer formed before nanotubes in fluoride-containing solutions is actually same as the CATO films formed in fluoride-free solutions [19–22]. The FAD theory was proposed based on the fluoride-containing electrolytes [6–9,12], which cannot explain TiO_2 nanotubes obtained in fluoride-free electrolytes [10–12]. Few reports investigate the formation of nanotubes based on mixed electrolytes or compare these two kinds of films above.

In the present work, CATO films and ATNTs obtained from fluoride-containing and fluoride-free electrolytes were compared in detail. The formation mechanism for anodic TiO_2 films is explored based on variation of film morphology and anodizing curves. Furthermore, the transform process from compact anodic oxide to nanotube arrays was observed and investigated. In the mixed electrolytes with oxalic acid, closed nanotube embryo and hemispherical bottoms were first observed. The present results indicate that the increase of $H_2C_2O_4$ content leads more ionic current and voltage rise while the increase of NH_4F current leads more electronic current accompanied by oxygen evolution.

2. Experimental

Titanium foils (100 μm thick, purity 99.6%), were polished in the mixed solution with HF (≥40%), HNO_3 (65%–68%) and DI water (1:1:2 in volume). Then, the samples were rinsed by DI water and dried in the air.

The electrolytes were ethylene glycol solutions with 3 wt% water.

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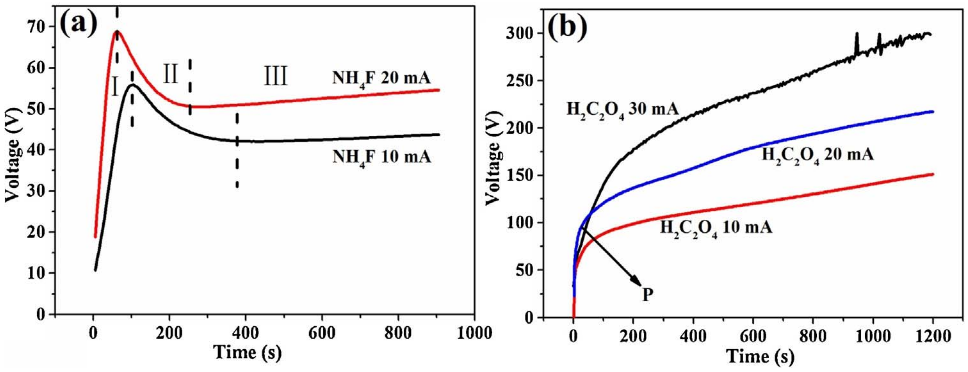

Fig. 1. Voltage-time curves obtained in two single electrolytes severally with (a) 0.5 wt% NH_4F and (b) 0.5 wt% $H_2C_2O_4$ under constant currents.

Besides, different mass ratios of oxalic acid and ammonium fluoride were added into the solutions. Anodization was carried out by employing a two-electrode electrochemical cell, in which the polished Ti foils acted as anode and a Pt mesh acted as cathode. One-step anodization is adopted in this work. The pretreated samples were all anodized in corresponding electrolytes at 20 °C. The anodizing area of Ti foil was maintained constant (~ 4 cm^2). All samples were examined by the field-emission scanning electron microscope (FESEM, Zeiss Supra 55).

3. Results and discussion

Fig. 1a shows voltage-time curves obtained in 0.5 wt% NH_4F electrolyte under constant current (10 mA, 20 mA) anodization. During anodization, the current resulted from the ionic migration is ionic current while the current resulted from electronic migration is electronic current. For a typical voltage-time curve obtained in galvanostatic anodization, there are three stages, similar as those in potentiostatic anodization. At stage I, the barrier oxide keeps growing, and then voltage rises and arrives at maximum; the total anodizing current is mainly composed of ionic current, and ionic current contributes to barrier oxide layer growth. At stage II, when the barrier oxide grows to the critical thickness, electronic current rises sharply and gives rise to oxygen evolution. The critical thickness represents the thickness of barrier oxide at the inflection point of the anodizing curve. After the barrier oxide reaches the critical thickness, the electronic current will occur. As the total anodizing current is constant and composed of ionic current and electronic current, ionic current decreases a lot, leading to the drop of voltage. At stage III, the electronic and ionic currents achieve a balance and stable growth for nanotubes will maintain at this stage. Obviously, FAD theory and dissolution current cannot apply in galvanostatic anodization. Fig. 1b shows voltage-time curves obtained in 0.5 wt% $H_2C_2O_4$ electrolyte under constant current (10 mA, 20 mA, 30 mA). As shown in Fig. 1b, the voltage increases gradually in pure $H_2C_2O_4$ electrolyte as CATO films keep growing without the formation of nanotubes. Oxide grows in the electrolyte/oxide (E/O) and oxide/Ti (O/Ti) interfaces and therefore CATO films keep thickening along with voltage rise [21]. Based on FAD theory, the inflection point (P) in Fig. 1b should be attributed to the occurrence of dissolution current. In fact, the FAD process does not exist in fluoride-free electrolytes. As a result, the inflection point P as shown in Fig. 1b is irrelevant to FAD process. In fact, it is the occurrence of electronic current that leads to drop of oxide growth efficiency and results in the inflection point when the barrier oxide grows to the critical thickness, whether the electrolyte is fluoride-free or not. In our previous work, the separation of the total anodizing (J_{total}) has been achieved and the theoretical formula for electronic current (J_e) and ionic current (J_{ion}) has been given [21,22]. Diggle et al. [23] have proposed that the ionic conductance is in the dominant position at initial anodization while electronic conductance predominates at late anodization. Chong and Zhang et al. [21,22] indicated that total anodizing current is composed of ionic current and electronic current ($J_{\text{total}} = J_{\text{ion}} + J_e$). For galvanostatic anodization, the total anodizing current is constant and ionic current predominates at initial anodization ($J_{\text{total}} \approx J_{\text{ion}}$); the oxide growth efficiency $\eta = J_{\text{ion}}/J_{\text{total}} \approx 100\%$. After the electronic current occurrence at critical thickness, $\eta = J_{\text{ion}}/J_{\text{total}} \approx (J_{\text{total}} - J_e)/\ J_{\text{total}} = 1 - J_e/J_{\text{total}} < 100\%$. The drop of oxide growth efficiency leads to the formation of the inflection point P as shown in Fig. 1b.

Fig. 2 shows CATO films obtained in $H_2C_2O_4$ electrolyte under constant current (10 mA, 20 mA, and 30 mA). For curves of 10 mA and 20 mA in $H_2C_2O_4$ electrolyte, voltage still increases after the inflection point without fluctuation, which reflects the stable growth of compact oxide. However, when the applied current is up to 30 mA, the voltage-time curve tends to fluctuate, which is attributed to the sharp rise of electronic current and oxygen evolution. The surfaces of CATO films obtain under 10 mA and 20 mA are flat while that for 30 mA shows many concaves as shown in Fig. 2. These concaves in Fig. 2f reflect the breakdown state [24–27], as the voltage is close to the breakdown voltage and almost all anodizing current turns into electronic current gradually with evolution of large quantities of oxygen on oxide surface ($4OH^- - 4e^- = 2H_2O + O_2$ or $2O^{2-} - 4e^- = O_2$) [27–29]. These concaves on the oxide surface in Fig. 2f result from oxygen evolution rather than dissolution [27,28]. From the cross-section of CATO films obtained under 30 mA shown in Fig. 2e, none nanotubes can be seen as the oxygen evolution only exists on the oxide surface.

In conclusion, the differences between voltage-time curves of NH_4F and $H_2C_2O_4$ electrolytes are attributed to the presence of electronic current. In NH_4F electrolyte, electronic current is much easier to occur along with oxygen evolution within oxide, while for fluorine-free electrolytes, electronic current can only occur companied with oxygen evolution on oxide surface near breakdown state. Oxygen bubbles within oxide act as mould and lead to the nanotube embryo formation. To confirm this, anodization in mixed electrolytes was designed.

Fig. 3a shows the voltage-time curves obtained in different electrolytes. In electrolyte only with 0.5 wt% $H_2C_2O_4$, the voltage keeps rising. In comparison, the voltage-time curve for electrolyte with 0.4 wt % $H_2C_2O_4$ and 0.1 wt% NH_4F demonstrates an inflection point near 600 s. Before the inflection point, these two curve tendencies are very similar, which reflects the same growth manners of compact oxide layer. The inflection point indicates the significant drop of oxide growth efficiency ($\eta = J_{\text{ion}}/J_{\text{total}} \approx (J_{\text{total}} - J_e)/J_{\text{total}} = 1 - J_e/J_{\text{total}}$), which is attributed to the occurrence of electronic current due to the addition of 0.1 wt% NH_4F, rather than chemical dissolution, as FAD process does not contribute to anodizing current [13,21,26,30]. Fig. 3b–d show FESEM images of CATO films obtained in the mixed electrolyte (0.4 wt % $H_2C_2O_4$ and 0.1 wt% NH_4F). Obviously, there is still no porous structure but distinct bulge and hemispheric bottom can be observed, which are caused by oxygen evolution. The oxygen bubble acts as a mould, leading to the formation of hemispheric bottom as shown in Fig. 3d. Therefore, it is indicated that oxygen evolution arises once the electronic current occurs. Moreover, oxygen evolution can take place anywhere, on oxide surface in Fig. 3b and c, and within the oxide in