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Formation and Morphology Evolution of Anodic TiO_2 Nanotubes under Negative Pressure

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ABSTRACT

Anodic TiO_2 nanotubes (ATNTs) have attracted extensive interest in the past decade. ATNTs are generally fabricated by anodization of Ti foils under atmospheric conditions (0.1 MPa). To date, the growth kinetics of ATNTs remains unclear. Herein anodizations of Ti foils under negative pressure are designed to overcome this challenge. Longer nanotubes were fabricated under negative pressure, as compared to atmospheric conditions. Variations of the nanotube length and surface morphology of ATNTs provide evidences for oxygen bubble mould, in which the ionic current contributes to nanotube growth while the electronic current gives rise to the oxygen evolution. Nernst equation was firstly applied to simulate variations of electronic current and ionic current during anodization. The in-depth analysis of the morphology variations could help elucidate the formation mechanism, thus paving the way for the optimization of the synthesis process of ATNTs.

1. Introduction

Anodic TiO_2 nanotubes (ATNTs) and other porous anodic oxides have attracted considerable scientific interests due to their diverse applications in many fields [1–5]. The electrochemical anodization of valve metals and the formation mechanism of porous structures have been widely investigated for decades [6–10]. However, the fundamental exploration of growth mechanism behind the morphological complexities is limited, and the effects of electrochemical parameters (e.g., anodizing current, voltage) on porous nanostructures lack reasonable explanations and evidences in situ [10–12].

It is well known that two types of oxide films can be formed during anodization [10–13]. For the compact (barrier-type) film, the oxide growth comprises simultaneous migration of cations toward the electrolyte/oxide (E/O) interface and anions toward the oxide/metal (O/M) interface by a cooperative mechanism, forming the oxide at both E/O and O/M interfaces [12]. For the porous-type film, formation of nanostructures such as TiO_2 nanotubes is more complicated in view of their growth mechanism, due to additional critical factors such as field-assisted dissolution of oxide, ejection of cations into the electrolyte and stress generation [12]. Nevertheless, the first stages of the porous-type films (or nanotubes) are very similar to the formation of compact film [12]. That is, the relative thickness of barrier layer oxide is mainly determined by the transport numbers of anions and cations, which are 0.4 and 0.6 respectively in the case of amorphous barrier layers of TiO_2 and Al_2O_3 [13]. The generation of major pores (or nanotubes) can be ascribed to either a field-assisted plastic flow of barrier layer [14–16], or the field-assisted dissolution with growth and ionic transport [13]. A similarity between TiO_2 nanotubes and porous alumina that supports the flow model is the abnormally large thickness of the oxide that cannot be fully explained by field-assisted dissolution or the ejection of cations into the electrolyte [13]. Therefore, the main debate is whether nanotube growth occurs via field-assisted plastic flow combined with field-assisted ejection of the Ti^{4+} ions (i.e. ions are ejected into the electrolyte without oxide formation) or via field-assisted dissolution (i.e. preferential dissolution at the pore base where the electric field is stronger) [13]. As Garcia-Vergara et al. [14] concluded that the plastic flow is contrary to expectations of the dissolution model of pore formation. In the field-assisted ejection or preferential dissolution, anodic TiO_2 layers are considered to form merely at the O/M interface. The current (Faraday) efficiency is mainly determined by the transport numbers of anions and cations

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(ratio = 4:6) [13], so the current efficiency would not be higher than 50%. Furthermore, if there were an equilibrium between barrier oxide growth and field-assisted dissolution or field-assisted ejection of cations at the nanotube base throughout the anodizing process, the anodizing current efficiency (or oxide growing efficiency) should be defined as $\zeta \approx j_{grow}/j_{total} \approx 50\%$ (the oxide grow current j_{grow} and total current j_{total}) [17]. However, Proost et al. [18] reported a current efficiency value of 66% during anodization. Garcia-Vergara et al. [19] reported that the current efficiencies of porous alumina are 67%, 85% and 93% at the anodizing current densities of 5, 15 and 30 mA cm^{-2}, respectively [19]. These data illustrated that the pore development is consistent with the 'plastic flow' rather than the field-assisted dissolution or ejection [17,19]. As Thompson et al. [20] indicated that, experimental evidence for field-assisted dissolution, such as the impact of the electric field on the dissolution rate, has not been demonstrated. Hebert et al. [21] also proposed that, oxide dissolution rates are in fact very small, and oxide stress plays a prominent role in the formation of the pores [21].

In 1963, Hoar et al. [22] proposed that the total anodizing current consists of film forming current and pore forming current. In 1969, Diggle et al. [10] also concluded that both ionic current and electronic current contribute to anodizing current during anodization process. Unfortunately, these important viewpoints have been ignored for decades. Until 2009, Zhu et al. [23–26] have proposed a kinetics model for the porous anodic oxides, in which ionic current is related with the formation of the oxide while the electronic current leads to oxygen evolution. Other groups also concluded that electronic current and oxygen evolution have a key influence on the porous layer formation [6,11–13,27–32]. Curioni et al. [32] concluded that electronic conduction within the oxide produces oxygen evolution and does not contribute to oxide growth. Schmuki et al. [12] also indicated that ionic current and electronic current may be involved in the anodization process.

Based on field-assisted dissolution or ejection, pore formation is attributed to the chemical dissolution process ($TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O$) [33–35], during which no gas evolution is involved. Therefore, anodization process and morphology evolution of ATNTs should not be affected by ambient pressure [36]. No report on the influence of ambient pressure has been found heretofore. Herein, the influence of ambient pressure on the formation and morphology evolution of ATNTs was investigated. The present results show that longer nanotubes were fabricated under negative pressure, as compared to atmospheric conditions, which put the field-assisted dissolution theory into question. Furthermore, fundamental exploration of Ti anodization and quantitative analysis were conducted based on oxygen bubble mould and electrochemical anodization reaction. Nernst equation was firstly applied to explain electrochemical reactions during anodization. The present results can provide unique insights into the fabrication of TiO_2 nanotubes and help to better understand the growth kinetics of the porous anodic oxides.

2. Experimental details

The commercial Ti foils (100 μm thick, purity 99.5%, Shanghai Shangmu Technology Co. Ltd.) were polished using a mixture solution of HF (40%), HNO_3 (65%) and deionized water (1:1:2 in volume) for 10 s, after which the samples were rinsed thoroughly by deionized water and dried in the air. The polished Ti foil was then anodized at 18 °C. The anodizing area of Ti anode was maintained constant (4.0 cm^2). A Pt mesh was used as cathode and the ratio of the anodic area to the cathodic area is 4:52. The electrochemical cell containing anode and cathode was put into a vacuum oven. A vacuum pump was used to exhaust air from the oven until the gauge pressure reached −0.08 MPa (The actual pressure was 0.02 MPa). The negative pressure was maintained constant during the whole anodization process. All pretreated Ti foils were anodized at constant voltage (50 V, 60 V) in ethylene glycol (EG) solutions containing 0.4 wt% NH_4F. The distance between anode and cathode was maintained at 1.5 cm. Each experiment was repeated for three times. The current density-time curves were recorded automatically using Chroma Programmable DC power supply (62006P-300-8). The TiO_2 film morphologies were characterized by field-emission scanning electron microscope (FESEM, Zeiss Supra 55). Nanotube lengths were measured directly on the FESEM.

3. Results and discussion

3.1. Current density-time curves and surface morphology of ATNTs obtained under 0.1 and 0.02 MPa

Fig. 1 shows the current density-time curves of ATNTs obtained in electrolyte with 0.4 wt% NH_4F at 50 and 60 V under 0.1 and 0.02 MPa, respectively. Fig. 2 shows the FESEM images of the ATNTs obtained under 0.1 and 0.02 MPa, respectively. The anodizing current under 0.02 MPa is larger than that under 0.1 MPa, as shown in Fig. 1. Fig. 2 shows the average tube length of nanotubes fabricated at 50 and 60 V under 0.1 and 0.02 MPa, respectively. Longer nanotubes were obtained under 0.02 MPa, which is consistent with the higher anodizing current. The results indicate that the ambient pressure has a significant influence on the nanotube length of ATNTs. However, the traditional field-assisted dissolution model cannot explain this phenomenon. Based on the field-assisted dissolution model, the growth rate of nanotubes depends on the corrosion rate of F^- anions and it is irrelevant with ambient pressure. Herein, the influence of ambient pressure on

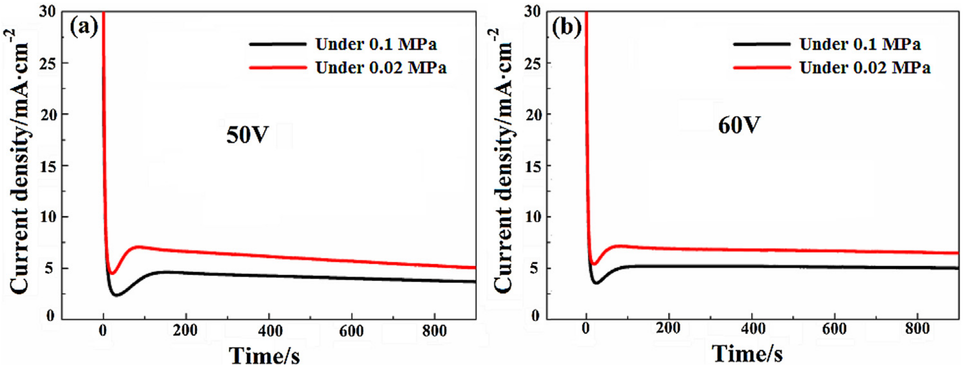

Fig. 1. Comparison between current density-time curves of ATNTs under 0.1 and 0.02 MPa at (a) 50 V and (b) 60 V, respectively.