



Roles of mechanical stress and lower-valent oxide in the formation of anodic titanium dioxide nanotube layers

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ABSTRACT

Self-organized TiO₂ nanotube arrays are characterized by gaps that separate the layers of oxide surrounding cylindrical pores. Nanotube layer growth is thought to involve oxide flow induced by mechanical stress associated with anodization. The mechanism of TiO₂ nanotube initiation was studied with in situ stress measurements during anodization in ethylene glycol-water-fluoride solutions. Compressive stress changes due to initial growth of barrier oxide films were detected, along with significantly larger tensile and compressive stress changes that followed the appearance of gaps between nanotubes at the metal-oxide interface. Interrupted anodizing experiments revealed that the latter stress changes are due to chemical processes or open-circuit electrochemical reactions. Further evidence for such reactions was deduced from the calculation of apparent Ti valences below four from measurements of Ti metal consumption during anodization. The gaps between nanotubes are thought to result from local oxide delamination at the metal interface induced by oxide flow, and the large compressive stress change is attributed to chemical oxidation of Ti⁺³ ions in the nanotube walls. This previously unrecognized chemical oxidation reaction may suggest new avenues to control nanotube layer growth and properties.

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1. Introduction

Self-organized anodic oxide nanotube layers are produced by electrochemical oxidation of Ti in fluoride-containing electrolyte solutions in which the oxide is soluble. Nanotubes order in a hexagonal array with the tube axis perpendicular to the metal surface. The nanotube dimensions can be controlled through the applied voltage and solution composition [1,2]. Extensive research on TiO₂ nanotubes has been carried out to explore applications such as solar cells, photocatalytic and photoelectrochemical water splitting, batteries, electrocatalysis, and biomedical materials and devices [2,3]. Parallels exist between the morphology and growth of nanotube layers and porous anodic alumina, another anodic oxide widely used in nanomaterials fabrication, which also consists of hexagonally ordered arrays of cylindrical pores [4,5]. While the oxide between pores of porous alumina forms a continuous matrix, gaps separate the circular outer surfaces of adjacent nanotubes. The electrochemistry of Ti anodization also appears to be more complex

than that of Al, as oxides with lower oxidation states than TiO₂ can be formed [6].

The growth mechanism of self-organized nanotube arrays is still actively debated [7,8]. Creation of both nanotube layers and porous anodic alumina requires the use of solutions in which the rates of metal dissolution and ionic migration through the oxide are balanced [9]. Solutions used for growth of nanotube layers achieve sufficient dissolution rates through fluoride-catalyzed Ti⁺⁴ ion dissolution from the oxide. In porous anodic alumina, considerable evidence exists that pore growth is assisted by mechanical stress-assisted oxide flow from the pore base into the pore walls [10–13]. Stress-driven flow of TiO₂ from the base to the walls of nanotubes is also suggested by evidence that the oxide volume expansion factor (ratio of the thicknesses of formed oxide and consumed metal) exceeds the Pilling-Bedworth ratio (ratio of oxide to metal volumes according to the stoichiometry of the anodization) [14–16]. Monitoring of stress changes during anodization is a powerful source of insight into interfacial reactions during anodizing, as stresses due to volume changes accompanying anodization reactions can be detected [12,17–21]. Stress measurements can reveal the driving force for oxide flow-assisted nanotube growth. Also, the in situ nature of stress measurements is important to

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identify reactions that form potentially unstable reaction products such as lower-valence oxides that may be involved in the anodization mechanism.

Here we report an investigation of the initial growth of TiO₂ nanotube layers using in situ stress measurements by curvature interferometry [22,23]. To our knowledge, the present research is the first study of stress evolution during formation of TiO₂ nanotube layers. Anodization is carried out at constant potential in solutions of water and ammonium fluoride in ethylene glycol, a procedure in widespread current usage. Experiments with interrupted polarization are reported that elucidate the effect of open-circuit processes on stress evolution. Surprisingly, it is found that non-Faradaic reactions dominate the stress response during nanotube layer growth. We show that nanotube layer formation involves direct electrochemical oxidation of Ti to Ti(III) followed by chemical oxidation of Ti(III) oxide to TiO₂. The direct involvement of chemical oxidation in anodization may suggest new possibilities for controlling nanotube layer growth and possibly the material properties of nanotubes.

2. Experimental methods

Titanium samples were rectangular coupons cut from 0.89 mm thick 99.7% purity sheet (Alfa Aesar). The Ti surface to be anodized was polished to a 600 grit finish, and the opposite side of the coupon was polished to a mirror finish to provide a reflective surface for interferometric measurements. After polishing samples were cleaned by immersion in ultrasonic baths containing acetone, isopropanol and methanol for 10 min each, and then washed in distilled and deionized water and dried in an air stream. Samples were then mounted in a Teflon two-electrode electrochemical cell with platinum wire counter electrode, with the cell potential applied with a potentiostat (Gamry Reference 3000). Contact to the solution was through a 1 cm × 2.5 cm window, with the back side of the Ti coupon facing the optical system. Solutions consisted of ammonium fluoride and water in ethylene glycol, prepared using reagent grade chemicals. After alignment of the optical system components the interferometric signals were allowed to stabilize. The cell voltage was applied immediately upon introducing solution into the cell. Anodizing was at constant potential with no initial voltage ramp. Usually stress measurement was continued on open circuit after the anodizing period. Scanning electron microscopy (SEM) analysis was carried using a field-emission instrument (FEI Quanta 250-SEM).

The phase shifting curvature interferometry method and its application to measure stress changes during Al anodizing were described previously [22,23]. Changes in sample curvature during dissolution or anodizing are monitored, and the curvature change related to the near-surface force per width according to the Stoney thin-film approximation,

$$\Delta F_w = \frac{E_s h_s^2}{6(1 - \nu_s)} \Delta \kappa \quad (1)$$

Here $\Delta \kappa$ is the curvature change, ΔF_w is the change in force per width, and E_s , ν_s and h_s are and are respectively the elastic modulus, Poisson's ratio and thickness of the Ti sample. The force per width is the in-plane biaxial stress σ_{xx} integrated through the sample thickness,

$$F_w = \int_0^{\infty} \sigma_{xx} dz \quad (2)$$

where the x axis is parallel to the Ti surface, and the z axis extends

toward the bulk metal from the surface. Force per width is referenced to the initial state of the sample at the beginning of anodic polarization, and compressive and tensile force changes are respectively negative and positive in sign.

3. Results

3.1. Titanium valence during nanotube formation in glycerol-fluoride solutions

Significant correspondences will be demonstrated between the present transient stress measurements and prior observations of interface morphology evolution during nanotube formation. Fig. 1 shows current transients and SEM images of film cross sections during the initial period of anodization at 20 V in 0.35 M NH₄F-glycerol, as reported by Berger et al. in a paper giving a detailed account of events during nanotube initiation [15]. The morphology changes in Fig. 1 are broadly typical of those in other fluoride baths, and will be used as a basis to interpret the stress measurements [1,24–26]. After application of the anodizing voltage, a compact barrier oxide layer forms in the first 0.5 min while the current decays. At about 1 min, roughly 20 nm wide pores appear in the outer part of the barrier layer and subsequently grow in depth. Different pore diameters would be produced at applied potentials other than 20 V, owing to the characteristic increase of tube diameter with potential [1]. The pores are thought to grow by localized oxide dissolution [25]. When the pores penetrate close to the metal interface at 1.7 min, oxide along the interface between the pores appears to detach from the metal. Oxide detachment forms interfacial voids between the oxide and metal, since oxide over the delaminated area remains intact with no indication of pores permitting entry of solution. Images at later times demonstrated nanotube growth after the minimum current density at 2.2 min, with the characteristic gaps separating nanotubes originating at the interfacial voids [27]. In agreement with this interpretation, some investigators also find that gaps initiate by solid-state void formation [28,29], while others propose that the gaps form by oxide dissolution [30]. A high-resolution TEM study by Nguyen et al. found that the metal interface was shielded from solution by transverse ridges of oxide connecting nanotubes, and concluded that tube separation and gap formation must occur by interfacial void coalescence instead of dissolution [29].

Berger et al. used lithographic masks to create unreacted reference surfaces on their samples, thus enabling measurement of the depth of metal consumed during anodization [15]. They reported oxide volume expansion calculated from the consumed metal thickness, but did not relate the measured metal consumption to anodic charge density. Fig. 2 shows the apparent Ti valence n_{app} (number of electrons involved in anodic oxidation) determined using the integrated charge density and consumed Ti depth from Ref. [15], for anodization in 0.175 M and 0.35 M NH₄F. Values of n_{app} for barrier oxide growth at less than 0.5 min are scattered around an average of 4, hence consistent with formation of TiO₂. At times of 1.7–2.0 min in both solutions, n_{app} decreases sharply to values of 2–2.5. The decrease of n_{app} coincides with the initiation of nanotubes in Fig. 1, i. e. the appearance of voids at the metal interface between pores. After the current minimum, n_{app} increases slowly to steady-state values close to 3 in both solutions which are maintained during nanotube layer growth. Since nanotube layers consist of TiO₂, apparent valences less than 4 can be explained in two ways: (i) direct anodic oxidation of Ti to lower-valence oxides such as Ti₂O₃, followed by conversion of these oxides to TiO₂ in a chemical step; or (ii) direct anodic oxidation of Ti to TiO₂ accompanied by significant rates of cathodic reactions (despite the high applied

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