

Fast migration of fluoride ions in growing anodic titanium oxide

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Abstract

The rapid inward migration of fluoride ions in growing anodic titanium oxide under a high electric field has been elucidated by anodizing a Ti–12 at% silicon alloy, where film growth proceeds at nearly 100% efficiency in selected electrolytes. Further, incorporated silicon species in the anodic film are immobile, acting as marker species. The migration rate of fluoride ions is determined precisely by three-stage anodizing, consisting of initial anodic film formation at a constant current density to 50 V in ammonium pentaborate electrolyte, subsequent incorporation of fluoride ions by reanodizing to 55 V in ammonium fluoride electrolyte and, finally, anodizing again in ammonium pentaborate electrolyte at high current efficiency. The resultant films were analyzed by glow discharge optical emission spectroscopy to reveal the depth distribution of fluoride ions and the location of the silicon marker species. The fluoride ions migrate inward at twice the rate of O^{2-} ions. Consequently, anodizing of titanium in fluoride-containing electrolytes develops a fluoride-rich layer that separates the alloy substrate from the anodic oxide, with eventual detachment of the film from the substrate.

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1. Introduction

Titanium oxide nanotube arrays, formed by anodic oxidation of titanium in fluoride-containing electrolytes, are the subject of current attention due to fundamental interest in the generation self-organized porous layers and their potential applications in photocatalysis, photoelectrolysis, photovoltaics and as sensors [1].

Formation of porous anodic oxides on titanium in hydrofluoric acid electrolyte was first reported in 1999 [2], with its nanotubular structure demonstrated by Grimes and co-workers in 2001 [3]. Further studies have focused on precise control of nanotube morphology, with the composition of the electrolyte playing a key role in controlling the morphology [4–10]. The superior properties of anodic titanium oxide nanotube layers, such as photocatalytic

and hydrogen sensing properties, as well as control of surface wettability, have also been demonstrated [1,11–16]. However, during formation of the porous anodic titanium oxide film, detachment of the film is often encountered, generating a layered anodic film [17].

The detachment of the anodic film may be associated with fluoride ions incorporated into the anodic film. Although the behaviour of fluoride ions during formation of anodic films on titanium in fluoride-containing electrolyte is not well understood, it is known that during anodizing of tantalum, the inward mobility of fluoride ions is twice that of O^{2-} ions, leading to the development of a thin layer of TaF_5 that separates the substrate from the anodic oxide film [18,19]. Poor adhesion of the resultant anodic film, associated with the fluoride layer, has also been demonstrated [18]. Thus, it is possible that film detachment on titanium is associated with the formation of a titanium fluoride layer between the oxide film and metal substrate that results from the fast inward migration of fluoride ions during anodic film growth under the high electric field.

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In the present study, the migration rate of fluoride ions during growth of anodic titanium oxide has been determined for the first time. In order to elucidate precisely the migration rate of fluoride ions, anodizing conditions have been selected that allow barrier type anodic film formation at high current efficiency. Normally growth of barrier type anodic films on high purity titanium at high current efficiency is limited to low voltages (~ 10 V), because of an amorphous-to-crystalline transition, with subsequent oxygen generation on further film growth [20,21]. The authors have revealed that the amorphous-to-crystalline transition is effectively suppressed to increased voltages by incorporation of foreign species from the substrate into the anodic oxide [22–27]. In particular, silicon species, incorporated from a Ti–Si alloy delay the transition to increased voltages; further, silicon species are immobile during film growth, thereby acting as marker species. From the depth distribution of the marker species, it is evident that the amorphous anodic titanium oxide grows at the metal/film and film/electrolyte interfaces by simultaneous migration of anions inward and cations outward respectively, with a transport number of cations of 0.39 ± 0.03 [24]. Further, from anodizing of a Ti–6 at% Si alloy in various electrolytes, the mobilities of a range of foreign species, derived from the associated electrolyte anions, have also been determined precisely [23,24]. Good correlation has been found between the migration rates of outwardly migrating species and their single metal–oxygen bond energies, such that species with strong metal–oxygen bonds migrate more slowly than titanium cations during film growth [24].

In the present work, silicon-stabilized amorphous anodic titanium oxide has been grown to 50 V at high current efficiency in fluoride-free electrolyte (Fig. 1a). Subsequently, fluoride ions are incorporated into the anodic film by anodizing in ammonium fluoride electrolyte to 55 V (Fig. 1b). The depth distribution of fluoride ions after further anodizing in the fluoride-free electrolyte (Fig. 1c) has been determined by glow discharge optical emission spectroscopy (GDOES). The depth of fluoride ions with respect to the thickness of the anodic film, (d/d_0), at a formation

voltage, E , is determined by the migration rate of fluoride ions relative to that of O^{2-} ions, $u_{\text{F}^-}/u_{\text{O}^{2-}}$, and the transport numbers of cations, t_+ , and anions, t_- , using the following equation:

$$\frac{d}{d_0} = \left(t_+ + \frac{u_{\text{F}^-}}{u_{\text{O}^{2-}}} t_- \right) \left(1 - \frac{55}{E} \right) \quad (1)$$

2. Experimental

Ti–12 at% Si alloy films, approximately 200 nm thick, were prepared by dc magnetron sputtering on a silicon wafer. The target consisted of a 99.9% pure titanium disk of 100 mm diameter and 6 mm thickness; two square silicon plates, with 15 mm sides, were placed symmetrically on the region of the target that is sputtered. In order to generate deposited films of uniform composition and thickness, the substrate holders were rotated around the central axis of the chamber as well as their own axis.

The deposited films were anodized to 50 V at a constant current density of 50 A m^{-2} in stirred 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 293 K. Fluoride ions were then incorporated into the initial anodic oxide by reanodizing to 55 V at 10 A m^{-2} in 0.1 mol dm^{-3} ammonium fluoride electrolyte. Finally, the specimens were anodized further to 80 or 100 V at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte. The growth of the anodic film in the ammonium pentaborate electrolyte proceeded at nearly 100% efficiency [24]. For comparison, the deposited films were also anodized to 50 V in 0.1 mol dm^{-3} ammonium fluoride electrolyte at 293 K.

Depth profiles of the anodized specimens were generated using a Jobin-Yvon 5000 RF instrument in a neon atmosphere of 900 Pa by applying RF of 13.56 MHz and power of 50 W. A neon plasma, rather than the generally used argon plasma, was necessary to excite the most intense fluorine line of 685.60 nm [28]. Light emissions of characteristic wavelengths were monitored throughout the analysis with a sampling time of 0.01 s to obtain the depth profiles. The wavelengths of the spectral lines used were 365.350, 288.158, 685.602, 130.217 and 249.678 nm for tita-

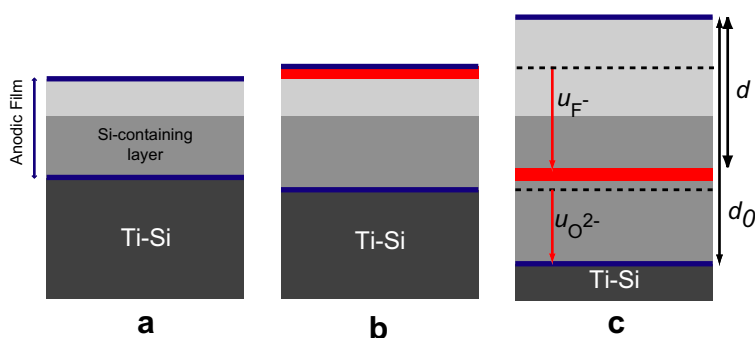


Fig. 1. Schematic diagrams showing the distributions of the silicon marker species and fluoride ions in the films used for determination of the migration rate of fluoride ions: (a) film formed to 50 V in ammonium pentaborate electrolyte; (b) fluoride incorporation by subsequent anodizing to 55 V in ammonium fluoride electrolyte; and (c) after further anodizing in ammonium pentaborate electrolyte.

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