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Control of morphology and composition of self-organized zirconium titanate nanotubes formed in $(NH_4)_2SO_4/NH_4F$ electrolytes

Kouji Yasuda[1], Patrik Schmuki*

Department of Materials Science, Institute for Surface Science and Corrosion (LKO), University of Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany

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Abstract

We investigated the formation of self-organized zirconium titanate nanotubes by anodizing a Ti-35Zr alloy in 1 M $(NH_4)_2SO_4$ + 0.1–2.0 wt.% NH_4F electrolytes. The morphology and composition of the zirconium titanate nanotube are controlled by the applied electrochemical conditions. The outer diameter of nanotubes is controlled by the anodization potential in the range between 1 and 100 V (versus Ag/AgCl). Tubes with diameters from 14 to 470 nm can be grown. The nanotube length correlates with the anodic charge up to a length where significant dissolution of the nanotube layer is observed. The wall thickness, composition of the nanotubes and porosity of the nanotube layer are significantly affected by the fluoride ion concentration. The length limiting factor of the nanotube growth is found to be the diffusion of ionic species in the electrolyte.

Keywords: Zirconium titanate; Complex oxide; Nanotubes; Control; Self-organized

1. Introduction

Electrochemical processes can be an excellent tool to produce one-dimensional structures due to the provision of a two-dimensional reaction interface and a precise control of critical reaction parameters. The occurrence of lateral self-organized phenomena on the reaction interface can therefore be used to grow three-dimensional nanostructures by electrochemical methods. Especially, the electrochemical formation of self-organized porous nanostructures has attracted much interest, since they possess wide applications in biological nano-patterning, high-density recording media and templates for nanomaterials. Recently, the formation of self-organized oxide nanotube layers has been achieved on various valve metals including titanium [1–5], zirconium [5–7], hafnium [8], niobium [9], tungsten [10] and tantalum [11]. Self-organized oxide nanotube formation was also succeeded for several alloys, Ti-Al-Nb [12], Ti-Al-V [12], Ti-Nb-Ta-Zr [13], Ti-Nb [14] and Ti-Zr [15]. For the Ti-Zr alloy, our previous work showed that zirconium titanate (ZT, $Zr_{1-x}Ti_xO_2$) nanotubes can be produced by an anodization in $(NH_4)_2SO_4 + NH_4F$ electrolytes [15]. ZT is a complex oxide applied to microwave resonant components and frequency-stable oscillators [16–18] using its low-loss and temperature-stable dielectric properties. Other applications of ZT include catalysts [19], pigments [20], refractory ceramics [21], sensors [22] and optical devices [23,24]. Typically, ZT is produced via solid-state reaction of the component oxides, sol–gel methods or the hydrolysis of metal alkoxides, and its morphology was restricted to bulk or powder. A formation of the nanotubular shape may lead to new functionalities of ZT such as photoluminescence and cathodeluminescense, and a control of morphology and composition is significantly important for a property control. Furthermore, both the Ti-Zr alloy [25] and the ZT complex oxide [26–28] have a solid solution behavior over the entire composition range and wide compositions, respectively. The existence of a wide range as solid solution is promising for control of the composition in the process. The present work investigates the feasibility to control the diameter, wall thickness, length, porosity and composition of ZT nanotubes by changing electrochemical conditions in $(NH_4)_2SO_4 + NH_4F$ electrolytes.

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* Corresponding author. Fax: +49 9131 852 7582.
E-mail address: schmuki@ww.uni-erlangen.de (P. Schmuki).

[1] On leave from: Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Kyoto 606-8501, Japan.

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2. Experimental

Ti-Zr alloy plates (50:50 wt.%, 65:35 mol%, ATI Wah Chang Co.) were degreased prior to electrochemical experiments. The pretreatment was first conducted by polishing with silicon carbide abrasive paper and diamond and silica abrasives successively. And then, the polished samples were sonicated in acetone, isopropanol and methanol successively, followed by rinsing with deionized water and drying in nitrogen stream. The electrolyte was 1 M $(NH_4)_2SO_4$ (99%, anhydrous, Sigma–Aldrich Co.) solution with an addition of 0.1–2.0 wt.% NH_4F (98%, anhydrous, Sigma–Aldrich Co.) at ambient temperature.

A three-electrode system was used for electrochemical experiments. The working electrode was a Ti-Zr alloy plate exposed to an electrolyte with an area of 1 cm^2 using an O-ring. The counter and reference electrodes were a platinum gauze and a Haber–Luggin capillary with a Ag/AgCl (1 M KCl) electrode, respectively. Electrochemical measurements were performed by using a high-voltage potentiostat (IMP 88 PC, Jaissle). Anodization was conducted by sweeping potential from the open circuit value (approx. 0 V versus Ag/AgCl) to an anodization potential at a rate of 50 mV s^{-1}, and then keeping the anodization potential for a fixed time. After the anodization, the sample surface was rinsed with deionized water followed by drying in nitrogen stream.

The morphology of the samples was observed by field emission-type scanning electron microscopy (FE-SEM, S-4800, Hitachi) and transmission electron microscopy (TEM, CM300 UT, Philips, 300 kV). The composition was measured by energy dispersive X-ray spectroscopy (EDX, Genesis 4000, EDAX). Depth profiles of X-ray photoelectron spectroscopy (XPS, PHI 5600, Perkin-Elmer, Mg Kα) were used to determine the dissolution rate by measuring the thickness of compact oxides which were soaked in 1 M $(NH_4)_2SO_4$ + 0.5 wt.% NH_4F electrolytes for different durations.

3. Results and discussion

3.1. Formation of nanotube layers

Fig. 1(a) shows the current–time behavior during the potential sweep from 0 to 20 V (versus Ag/AgCl) and the subsequent constant potential anodization at 20 V for 2 h in 1 M $(NH_4)_2SO_4$ + 0.5 wt.% NH_4F solution. During the initial potential sweep, after an increase in anodic current an active–passive transition takes place resulting first in a perforated and porous surface oxide layer, and finally the current drops to a steady value while a self-organization process creates a highly ordered oxide structure [3]. During extended constant potential anodization, the current decreases due to an increase in the diffusion length for the ionic species (this will be discussed more detail in Section 3.3). The morphology of the nanotubes obtained after the anodization is shown in Fig. 1(b and c). A layer has been formed that consists of highly

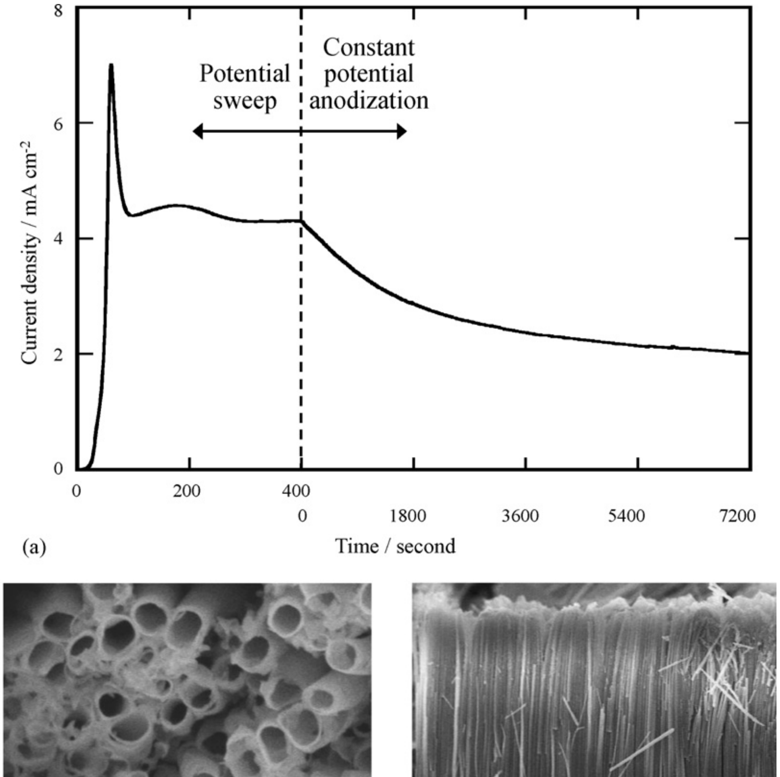

Fig. 1. (a) Current–time curve for the anodization of Ti-Zr alloy during the potential sweep from 0 to 20 V at a rate of 50 mV s^{-1} and the constant potential anodization at 20 V for 2 h in 1 M $(NH_4)_2SO_4$ + 0.5 wt.% NH_4F solution. (b) Surface and (c) cross-sectional SEM images of the obtained nanotube layer.