MATERIALS CHARACTERIZATION 71 (2012) 58–65

Available online at www.sciencedirect.com

SciVerse ScienceDirect

www.elsevier.com/locate/matchar

Effect of anodization parameters on the structural morphology of titanium in fluoride containing electrolytes

K. Indira[a,b], *S. Ningshen*[b], *U. Kamachi Mudali*[b], *N. Rajendran*[a,*]

[a]*Department of Chemistry, Anna University, Chennai-600 025, India*
[b]*Corrosion Science and Technology Group, Indira Gandhi Center for Atomic Research, Kalpakkam-603 102, India*

ARTICLE DATA

Article history:
Received 24 October 2011
Received in revised form
11 June 2012
Accepted 20 June 2012

Keywords:
TiO_2 nanopore
Anodization
Anatase
Pore diameter

ABSTRACT

In the present work, formation of titania nanopores on titanium substrate was investigated in aqueous (sulphuric acid) and neutral organic (glycerol) electrolytes containing different concentrations of HF (0.1–0.2 M). The surface morphology, topography and phase structures were analyzed using scanning electron microscopy, atomic force microscopy and X-ray diffraction techniques, respectively. Under optimized electrolyte conditions, titania nanopore is obtained with the average pore diameter of 64 nm and 84 nm for aqueous and organic electrolytes, respectively. Atomic force microscope investigation shows that the porous layer forms under a competition of titania formation and oxide dissolution up to a limiting thickness of ~75 nm and 100 nm respectively for aqueous and organic electrolytes. The porous structure was observed at 0.15 M HF concentration. It was found that depending on the electrolytes the pore diameter alters and also its concentration effected the porous structures formation. Compared to aqueous electrolytes, organic electrolytes showed larger diameter pores. From the X-ray diffraction measurement it is evident that the as prepared titania nanopores are amorphous in nature, whereas the anodized heat treated titania nanopores are in anatase phase.

1. Introduction

The field of nanopores is undergoing an explosive growth, fueled by breakthroughs in various synthesis methods and the promise of unique applications. In recent years, significant interest has been shown in the synthesis of nanoporous metal oxide thin films because of its promising application as micro and nano-devices [1]. Among the various nanostructured oxide materials, titania (TiO_2) based nanopores have attractive features like enhanced ion-exchangeable ability, nontoxicity, environmental safety, photocatalytic properties and higher surface-to-volume ratio. In this category, the electrochemical formation of self-organized porous structures has been reported for various types of materials such as Al [2,3], Si [4], Hf [5], Ru [6], Nb [7], Fe [8], Ni [9], W [10] and Ti [11]. Among these, TiO_2 nanoporous structures play a promising role in the field of photocatalysis [12], solar cells [13], corrosion resistance [14], sensors [15], and especially in the biomedical field [16]. Titanium and its alloys have been used extensively for applications ranging from bone-implant materials and aerospace to chemical industries because of their excellent corrosion resistance. Such a high and remarkable corrosion resistance is attributed to a very stable passive oxide film formed on the surface of titanium. The native oxide film has thickness of few nanometers. In the case of anodic oxidation, the oxide thickness can be enhanced up to micrometer range [14]. The color and thickness of oxide layer depends mainly on the anodization process and electrolyte employed for the anodization [17].

Numerous methods such as anodization [18,19], sol–gel processing [20], evaporation [21], template based method [22]

---

[*] *Corresponding author*. Tel.: +91 44 2235 8659; fax: +91 44 2220 0660.
E-mail address: nrajendran@annauniv.edu (N. Rajendran).

1044-5803/$ – see front matter © 2012 Elsevier Inc. All rights reserved.
doi:10.1016/j.matchar.2012.06.005

and ion-beam synthesis [23] are available for the preparation of metal oxide (TiO_2) nanopores. Among these, electrochemical anodization is a simple and cost effective technique that is widely used because it is controllable and reproducible. It is also possible to tune the size and shape of nanopore arrays to the desired dimensions. In addition, this method produces strongly adherent nanoporous TiO_2 layer on the substrate, which is more desirable for many practical applications.

The present study involves the synthesis of the nanoporous TiO_2 layer by electrochemical anodization technique in two different electrolytes: (i) mixture of HF and H_2SO_4 and (ii) mixture of HF and glycerol. Furthermore, the concentration of the HF was varied between 0.1 and 0.2 M. The aim of the present investigation is to study the influence of different electrolytes and its concentration on the pore diameter and the structural morphology of anodized Ti.

2. Materials and Methods

Highly pure Analytical Reagent (AR) grade chemicals viz., hydrofluoric acid (HF, 40%), sulphuric acid (H_2SO_4, 88%), and glycerol (99%) were used for the experiment. Deionized water was used for making the electrolyte solutions. Commercially pure-Ti sheet (99.8% purity) of 0.05 cm thickness was obtained from M/s Ti Anode Fabricators Pvt. Ltd, Chennai, India and was used for the fabrication of TiO_2 nanopores.

2.1. Synthesis of Titania Nanopores

Prior to anodization of the surface, titanium samples were grounded on both sides with silicon carbide paper up to 1000 grit. Final polishing was done using alumina paste (1 μm size from M/s Chennai Metco Pvt. Ltd, India) in order to produce a smooth surface. The polished samples were washed, degreased with acetone and thoroughly rinsed with distilled water. The samples were ultrasonicated in a mixture of acetone, 2-propanol and ethanol followed by pickling in a mixture of 0.9 M HF and 3.0 M HNO_3 solution. Before anodization, each specimen was rinsed in distilled water and dried in air at room temperature. All anodization experiments were carried out at room temperature for 1 h using two-electrode electrochemical anodization cell consisting of Ti (1.5 cm × 1.5 cm) as anode and Pt (coupon of 4.5 cm × 4 cm × 0.06 cm thickness) was used as the cathode. Both the electrodes were connected to a Direct Current (DC) voltage source (Aplab, Model H0615) and the anodization voltage was kept constant at 40 V. Two electrolytes were used for anodization viz aqueous and organic electrolytes. The concentration of the aqueous and organic electrolytes consisted of 0.13 M H_2SO_4 and 0.13 M glycerol respectively with 0.1, 0.15 and 0.2 M HF. After the anodization, the samples were rinsed in deionized water and dried.

2.2. Surface Morphological and Phase Structural Measurements

The surface topography of anodized samples was investigated using Atomic Force Microscopy (AFM) (NT-MDT, Russia). All the topographical measurements were carried out in semi-contact mode. The pore diameter and length were measured using AFM image analysis tools (NOVA Image Analysis Software 1. 0. 26. 1443). Similarly, surface morphology of anodized samples was obtained using Scanning Electron Microscopy (SEM) (Quanta 200 Model, The Netherlands). X-ray diffraction (XRD) patterns of anodized Ti were performed using a diffractometer (STOE Make, France) with radiation of a Cu target (Kα, $\lambda = 1.54056$).

2.3. Annealing of Anodized Ti

The anodized Ti samples were annealed at 450 °C in vacuum furnace with 1.0×10^{-5} mbar pressure for 3 h at the heating and cooling rate of 30 °C/min. Since, the as prepared porous TiO_2 films are amorphous, thus, annealing at high temperatures was carried out to induce crystallinity.

3. Results and Discussion

3.1. Effect of Electrolyte and its Concentration

The formation of pore on the surface of Ti depends on the electrolyte, its concentration and applied voltage. It has been reported by Gong et al. [24] that the pore diameter increases with increasing the applied voltage. It has also been reported that the fluoride ion concentration alters the formation and morphology of the resulting anodized titania samples [25].

Fig. 1 shows the AFM and SEM images of as polished and pickled Ti samples before anodization. The as polished samples showed only polishing lines (Fig. 1a and c) and no nanoporous surface was observed after pickling which is shown in the Fig. 1b and d. Fig. 2 shows the current transients (I–t curves) recorded at constant voltage of 40 V during anodizing process in a mixture of 0.15 M HF with 0.13 M glycerol. The initial drastic current drop is due to the formation of compact oxide layer. During anodization, the color of the titanium oxide was changed from blue to whitish green and pink swiftly. The color change is due to the increase in oxide film thickness. After some time, the current gradually increases, which is due to the reaction between the oxide layer and fluoride ion, in turn form hexafluorotitanium complexes, then remained stable; detailed mechanism is explained in the following section. It has been reported [26] that the anodization in the organic electrolyte produces very smooth curves without any fluctuations in current. It was due to the lower diffusivity and concentration of ions in the organic electrolyte.

Figs. 3 and 4 show the SEM micrographs and AFM topographs for the anodized Ti specimen in aqueous electrolyte containing different concentrations of HF. At low concentration of fluoride ion in the electrolyte, a compact oxide layer was formed with the film thickness of 3000 nm (inset in Fig. 3a). However, with increasing the concentration of fluoride to 0.15 M distinct pores were observed. At high concentration of fluoride (0.2 M HF), distorted images were observed due to the enhanced dissolution of the oxide layer. The pore diameter was found to be in the range between 60 and 72 nm. The average pore diameter was found to be 64 nm (Fig. 5a) while the inter pore distance was about 160 ± 2 nm. A line profile (which was derived using the AFM image analysis tool) analysis of the sample anodized in aqueous electrolyte containing 0.15 M HF is shown in Fig. 5b using pore length of the anodized Ti which was calculated and presented in Fig. 5c. The pore length was in the