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Influence of Anodization Time and Voltage on the Parameters of TiO₂ Nanotubes

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Abstract. A vertically aligned titania nanotube layer was obtained by electrochemical anodic oxidation in the electrolyte contained 0.4 wt% solution of NH₄F in 54 ml of ethylene glycol and 5 ml of deionized water, after titanium was chemically cleaned/etched with a mixture of HCl, H₂O and HNO₃ solution for removing the natural oxide films. The morphology and composition of the titania nanotube layer were examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The anodization of TiO₂ nanotubes was done using 60 V for 240 min and 30 min, and 30 V for 30 min. The diameter of the titania nanotubes was about 52–156 nm, the wall thickness about 32–53 nm and the height about 0.9–6.3 μm. The pore size of TiO₂ nanotubes influences the dissolution rate of CaP thin films and Young's modulus, which is significantly lower than that of the Ti substrate. Our future challenge will be investigation of the microstructure and mechanical behavior of titania nanotubes with CaP film.

1. Introduction

Titanium and its alloys are increasingly used in orthopedic and dental implants due to their excellent mechanical properties, high corrosion resistance, and good biocompatibility. However, titanium is a bioinert material, therefore, investigation of hybrid bioactive coatings formation on the Ti surface is required [3]. Titanium nanotubes can be used as one of the components for these coatings.

The advantage of using TiO₂ nanotubes is that they can be grown directly on the Ti surface by a cost-effective technique as anodic oxidation. In addition, the nanoindentation results indicate that the Young's modulus of the TiO₂ nanotubes is significantly lower than that of the Ti substrate. Also, it is well known that important disadvantage connected with hydroxyapatite (HA) coating is poor adhesion strength at the HA/Ti interface. It is suggested that TiO₂ nanotubes with a 3-D micro/nonporous structure may enhance apatite formation when compared to dense TiO₂ [2].

There are a few methods for HA coatings fabrication on the surface of titanium oxide nanotubes. Various methods are available to prepare such coatings. Radio frequency (RF) magnetron sputtering has several advantages. It can produce uniform and reproducible thin films with the properties that can be tuned by changing the operational parameters. Whereas sputter deposited calcium phosphate (CaP) coatings have much to offer in this regard, in the as-deposited state they are inherently amorphous and readily undergo rapid dissolution [1]. The authors of the study [1] reported that the nanotubes parameters can affect the dissolution rate of CaP films deposited on the nanotubes arrays and attendant cell behaviour.

To our knowledge, a systematic investigation of the microstructure and mechanical behaviour of self-assembled, vertically aligned nanotubes coated with HA film has not yet been reported. The



preparation of the vertically aligned titanium nanotubes is needed for a design of the hybrid HA/TiO₂ coating on Ti substrate.

The purpose of this study is to obtain titania nanotubes with different dimensions and investigate the effect of anodization parameters, such as anodization time and voltage, on the titanium nanotubes dimensions and growth rate in a NH₄F electrolyte solution.

2. Materials and methods

2.1. Fabrication of titanium nanotube layer

TiO₂ nanotubes were fabricated using the technique of anodization. The anodization process involved is as follows: two electrode systems comprising Ti foil (2 x 5 cm) as the anode and cathode. The samples were chemically cleaned/etched with a mixture of HCl, H₂O and HNO₃ solution for removing the natural oxide films, in the proportion of 1:1:2 respectively, and after that the samples were rinsed in the deionized water and dried in air.

The electrolyte contained 0.4 wt% solution of NH₄F in 54 ml of ethylene glycol and 5 ml of deionized water. The anodization was performed using constant current voltage power. The distance between the anode and cathode was 2.5 cm. After anodization all the samples were washed in de-ionised water and dried in the environment prior to further investigation.

2.2. Characterization

The morphological study of non-detached titania nanotubes was done using a field emission scanning electron microscope (SEM, Quanta 200D). The length, inner diameter and wall thickness of the tubes were measured by segmenting SEM micrographs and using image analysis software (xT microscope Control). Micrographs for quantitative analysis were taken from at least three different locations on each sample. Characterization of the coating/substrate cross sections was carried out by fracturing the coating by bending, and examination of the detached TiO₂ coating. SEM was used to examine both the bottom of the coating as well as the Ti substrate. The elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDXS, Quanta 200D). The images are presented in Figures 1-3.

3. Results and discussion

Figure 1, 2 and 3 reveal a top view and cross-sectional SEM images of TiO₂ nanotubes anodized at 60 V for 240 min, 30 min and at 30 V for 30 min, respectively, in NH₄F -containing electrolyte. A uniform structure of thin-walled TiO₂ nanotubes was obtained. The anodization resulted in vertically oriented titania nanotubes arrays.

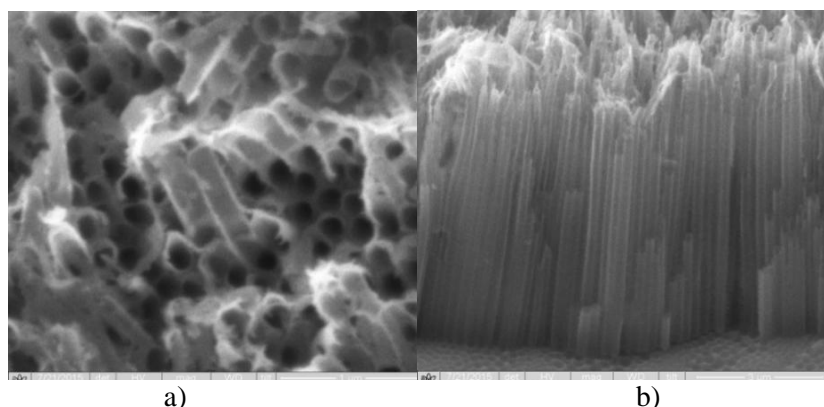


Figure 1. (a) Top view and (b) cross-sectional SEM images of TiO₂ nanotube arrays formed by anodic oxidation of Ti in NH₄F - containing electrolyte, at the potential of 60 V for 240 min

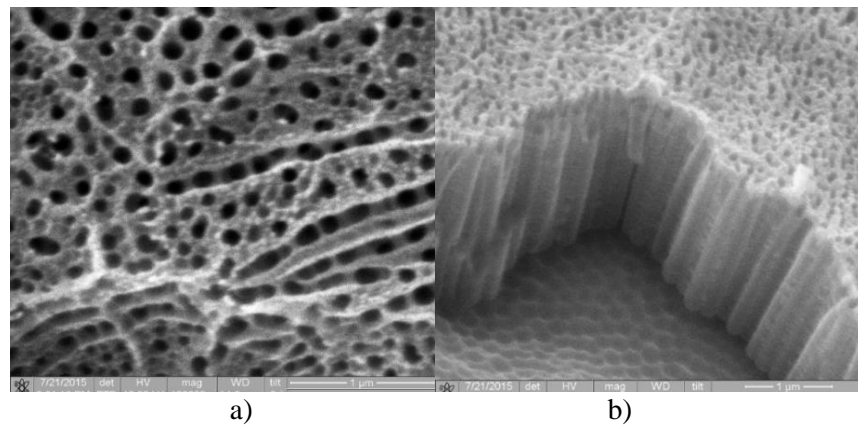


Figure 2. a) Top view and (b) cross-sectional SEM images of TiO_2 nanotube arrays formed by anodic oxidation of Ti in NH_4F -containing electrolyte, at the potential of 60 V for 30 min

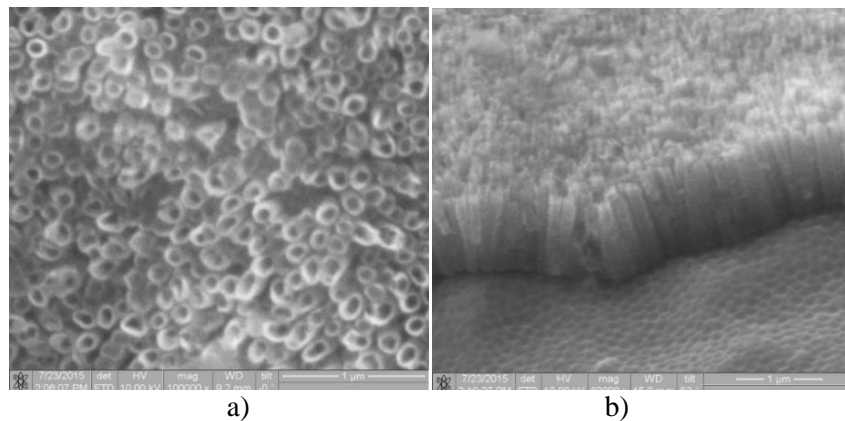


Figure 3. a) Top view and (b) cross-sectional SEM images of TiO_2 nanotube arrays formed by anodic oxidation of Ti in NH_4F -containing electrolyte, at the potential of 30 V for 30 min

Table 1 shows the quantitative measurements of the important dimensions of the nanotubes. An increase in anodization time and voltage had a significant effect on nanotubes diameter, wall thickness and length. An increase in tube dimensions with increasing in the anodization time, from 30 min to 240 min or increasing anodization voltage, from 30 min to 60 V, was observed. The alteration of the corresponding length (0.9–6.3 μm) and wall thickness (32–52 nm) of the nanotubes was achieved by varying the anodization time (30–240 min) and voltage (30–60 V).

Table 1. Dimensions of TiO_2 nanotubes fabricated via anodic oxidation of Ti in NH_4F -containing electrolytes.

Anodization voltage (V)	Anodization time (min)	Nanotubes dimensions (nm)		
		Tube length	Inner diameter	Wall thickness
60	30	1410±60	98.23±15.92	52.43±25.62
60	240	6270±360	155.95±27.96	32.78±7.89
30	30	909±50	52.96±10.12	50.70±10.50

SEM images of the cross-sections allowed to reveal the coating thickness. It appeared that there was a significant increase in the coating thickness with time between 30 and 240 min. However, the results showed that the average growing rate for the anodization time of 30 and 240 min is 47.0 and 26.1 nm per min, respectively. But the average growing rate for the anodization voltage of 30 and 60 V was 30.1 and 47.0 nm per min, respectively. The growth process of the nanotubes was discussed and several possible mechanisms for the formation of nanotubes were proposed in [2], [5] and [6].

The authors of the paper [2] showed that pore size influenced the mechanical properties and elastic modulus. Nanoindentation results yielded progressively higher values of elastic modulus for thinner films [2].

Mutreja et al. showed that prolonged availability of the as-deposited CaP can be provided by the use of a substrate surface comprising titania nanotubes. Moreover, nanotubes pore size and length affected the rate of CaP dissolution and attendant cell behaviour. The authors of the study [1] reported that the highest levels of ALP activity of osteoblast measured at 21 days occurred on CaP thin films deposited onto titania nanotubes with an average pore size of 30 ± 7.5 nm and tube length of 1.3 ± 0.2 μm .

EDS pattern of TiO_2 nanotubes prepared at the electron energy of 15 keV is shown in Figure 4.

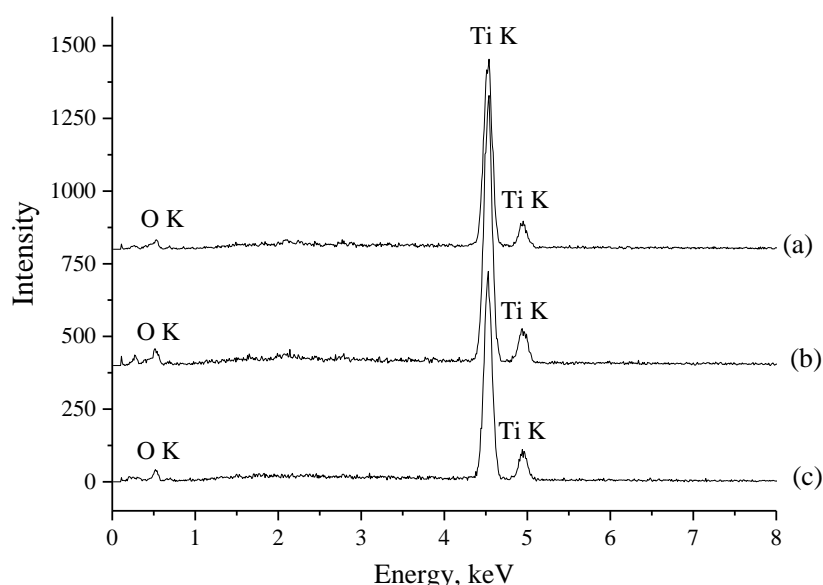


Figure 4. EDS pattern of titanium nanotubes were obtained at: a) 60 V for 240 min, b) 60 V for 30 min, c) 30 V for 30 min.

4. Conclusion

The electrochemical anodization method allows to produce amorphous TiO_2 nanotubes. Annealing results in their transformation into crystalline nanotubes. Based on a comprehensive study of the surface features prepared using a range of processing voltage and time settings, nanotubes with three significantly different pore sizes and lengths were obtained by performing electrochemical anodization at 60 V for 240 min, 30 min and 30 V for 30 min, respectively.

The quantitative microstructure characterization and elemental composition of TiO_2 nanotubes on Ti substrate are reported. The following conclusions can be drawn:

- 1 Nanotubes were prepared using anodic oxidation, in the NH_4F -containing electrolyte.
- 2 The dimensions of titania nanotubes increased with increasing in the anodization time. However, the average growth rate decreased with increase in the anodization time.

- 3 Increase in the anodization voltage leads to the increase in the nanotubes dimensions and their growth rate.
- 4 The variation of anodization conditions did not affect the chemical composition of TiO₂ nanotubes.

The investigation of the microstructure and mechanical behavior of vertically aligned titania nanotubes coated with HA films will be investigated in the future.

Acknowledgements

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