Effect of Applied Voltage on the Formation of TiO_2 Nanotube on Titanium Substrate using Anodizing Process

M. Ghanbari Haghighi[1,*], P. Parsi[1], Z. S. Seyedraoufi [1]

[1]*Advanced Materials Engineering Research Center, Karaj Branch ,Islamic Azad University, Karaj, Iran.*
Received: 31 January 2021 - Accepted: 11 April 2021

Abstract

In the anodizing process of active materials such as titanium, various parameters such as pH, temperature, applied voltage and time, electrolyte composition, etc. affect the formation of the oxide layer during anodising process. In this study, commercial pure titanium as substrate was used to evaluate the effect of voltage and anodizing process on titanium oxide (TiO2). Nanotubes obtained in 1% HF electrolyte from 10 to 30 volts at 60 to 120 minutes. According to field emission scanning electron microscopy studies, nanotube structure of titanium oxide was observed and the diameter and length of nanotubes increase with increasing anode process voltage, and nanotubes become non-uniform and irregular with increasing anode process voltage. Uniform nanotubes with a size of 27 to 32 nm were obtained at a voltage of 10 volts for 60 and 120 minutes. And by increasing the voltage of the anodizing process to 30 volts, a porous structure is formed.

Keywords: Nanotube, Titanium Oxide, Anodizing, Porosity.

1. Introduction

Among the various forms of titanium, nanotubes have attracted considerable attention due to their high surface-to-volume ratio, one-dimensional electrical conduit, and high ion exchange capacity. In 1998, Kazuga succeeded in synthesizing titanium nanotubes for the first time by a simple chemical hydrothermal method. Titanium dioxide nanotubes were then synthesized by other methods such as sol-gel. In 2001, Gang and colleagues first reported the production of regular, directional titanium nanotubes by anodic oxidation of titanium in an electrolyte solution containing hydrofluoric acid [1,2].

The production of titanium nanotubes by electrochemical anodizing process has received more attention than other methods due to its easy production and easy control in the direction of synthesized nanotubes. In recent years, many efforts have been made by researchers to improve and industrialize the production of nanotubes and provide a mechanism for how they are formed [3].

The electrolyte solution used to make TiO_2 nanotubes via anodizing process usually contains fluorine-based compounds such as HF, KF, NaF and NH_2F. The production of these substances based on chloride and bromide compounds has also been reported. Aqueous solutions were initially used as electrolytes, but then organic electrolyte solutions such as ethylene glycol and glycerol were tested. The morphology of titanium nanotubes strongly influences their application[3, 4].

In the anodizing process, various parameters such as the composition of the electrolyte solution, pH, voltage, time and temperature affect the morphology of titanium dioxide nanotubes [4,5].

Anodizing process is performed in an electrochemical cell, as shown in Fig. 1. In this method, pure titanium sheet is prepared and used as an anode. Another electrode (such as carbon, platinum, aluminum, or stainless steel) is placed in the cathode position. The nature of the electrolyte can also be acidic or alkaline. Then a certain electric current is established between the electrodes at a specific time with the help of an external source[5].

Due to the applied current, hydrogen is released at the cathode (negative electrode) and ions containing oxygen (and other negative ions) are also adsorbed towards the surface of the anode. The advantages of this method include low cost, single-stage, high ability to control process conditions and application in industry. There is widespread use of this method on an industrial scale and due to its nature, it is suitable for mass production [6,7].

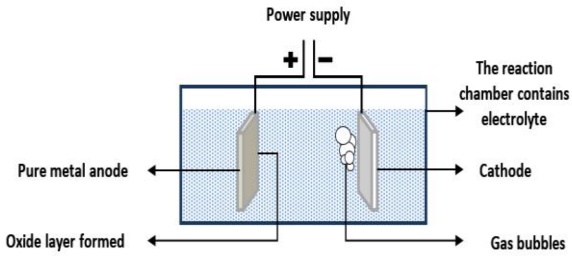

Fig. 1. Anodic oxidation process and its equipment [8].

*Corresponding author
Email address: mohsen.ghanbari@gmail.com

So far, similar activities have been performed in this field. Goodarzi et al [8]. investigated the effect of electrolyte solution pH on the structure of titanium oxide nanotubes using the anodizing process and found that titanium oxide nanotubes at pH = 1.5 have a larger diameter and a thinner wall than Nanotubes are formed at pH = 3, which may be due to the higher dissolution rate of the oxide at lower pH. Behzadipour et al [9], studied the anodizing process in modifying the surface of nanoscale titanium implants and found that bone growth was higher in the anodized specimen with a hollow surface morphology than in the anodized specimen. In summary, they concluded that bone formation around the anodized implant could lead to better osseointegration. The need for fluoride ions to form nano porous structures on low-voltage titanium surfaces was first reported by Zwilling [10, 11]. Nano tube formation had not been reported until then. In 1999, Grimes succeeded in making self-regulating titanium anodized nanotubes at a voltage of 10 to 40 volts in HF solution.
Pishkar et al [12]. investigated the effect of time on the morphology of titanium oxide nanotubes by anodizing method and found that the process of nanotube formation starts in the first moments and with increasing time, the length of nanotubes increases.
The competition between these reactions will determine the final shape of the titanium oxide nanostructures. According to the time-flow diagram, the process of formation and growth of these nanotubes can be explained. According to Fig. 2., in step 1, after one hour, a layer of metal oxide is formed on the surface of the titanium. Conduction is reduced and there is a sharp drop in current.

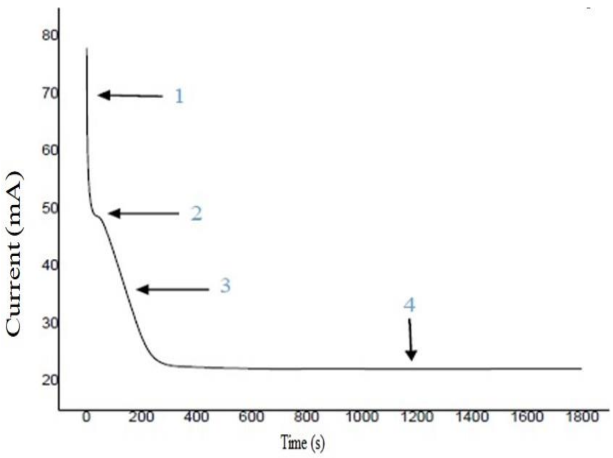

Fig. 2. Flow diagram in terms of time during the anodizing process [12].

As the time increases, the structure of the cavities is formed, which is the beginning of the nucleation of the nanotubes, and as can be seen from the diagram, in phase 2, the flow has started to increase.
In the third stage, the current is reduced, which indicates the beginning of the growth of nanotubes and increase their length. In step 4, the oxidation current reaches a constant value, which indicates the equilibrium of the nanotube growth process [12].
In this study, the mechanism of oxide layer formation in the anodic oxidation process is not completely clear. There are various theories in this regard, the existing theories are often different that do not include all the properties of anodic oxidation.

2. Materials and Methods

This research requires cleaning and reducing the surface roughness of pure titanium sheet. This is done by mechanical grinding using abrasive paper with grit 100 to 2500, then the samples are mechanically polished, then to remove grease and polishing wax remaining on the surface, the samples are soaked in acetone solvent and immersed in ultrasonic for 20 minutes.
Degreasing was performed. The thickness of the samples is 1 mm and all samples are cut with dimensions of 1 * 3 cm. In this study, in order to remove oxides on the surface of the sample, it was first deoxidized by immersion in (3%) HF + (10%) HNo3 + H2O solution for 5 seconds and then rinsed. To perform anodizing in this study, the electrolyte was combined with HF1% Vol. used. In order to increase the oxygen concentration, oxygen was injected into the electrolyte by the aquarium air pump during the anodizing process. 8 samples were anodized at different voltages and times according to Table. 1. All samples were rinsed after the anodizing process and then dried by a hot air dryer.

Table. 1. Specifications of samples.

Sample Code	Process voltage (volts)	Process time (minutes)
A1	10	60
A2	10	120
B1	20	60
B2	20	120
C1	24	60
C2	24	120
D1	30	60
D2	30	120

To analyze the surface and cross-sectional morphology of the samples, FESEM analysis (MIRA3 TESCAN field emission scanning electron microscope) with secondary electron detector was used. The surface of the sample were coated with a thin layer of gold. Also, the average diameter of nanotubes was taken by Image J software for all samples.

3. Result and Discussion

Scanning electron microscope image of morphology of samples A1 and A2 is presented in sections a and

b of Fig. 3. The microstructure of both samples consists of uniform titanium oxide nanotubes.
The diameter of these nanotubes is about 27 nm in sample A1 and about 32 nm in sample A2.

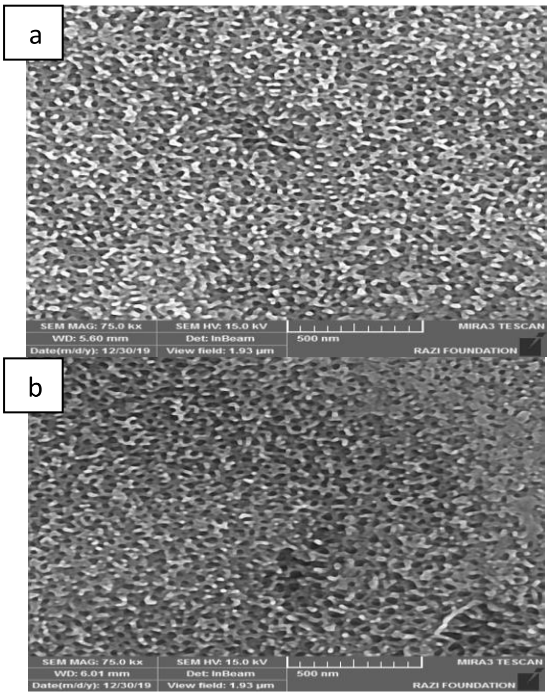

Fig. 3. FESEM microstructure of samples a-A1 and b-A2.

Scanning electron microscope image of morphology of specimens B1 and B2 is presented in sections a and b of Fig. 4. The microstructure of both samples consists of almost uniform titanium oxide nanotubes. The diameter of these nanotubes is about 71 nm in sample B1 and about 86 nm in sample B2.

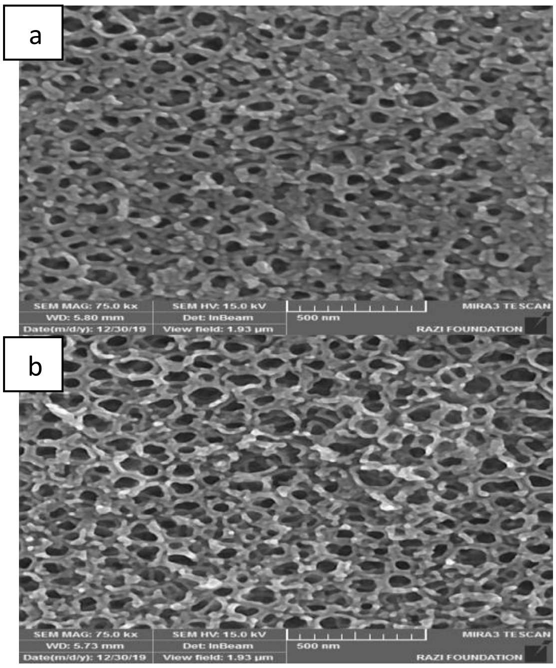

Fig. 4. FESEM microstructure of samples a-B1 and b-B2.

Scanning electron microscopy image of morphology of samples C1 and C2 is presented in sections a and b of Fig. 5. The microstructure of both samples consists of non-uniform and porous titanium oxide nanotubes. The diameter of these nanotubes is about 106 nm in sample C1 and about 108 nm in sample C2.

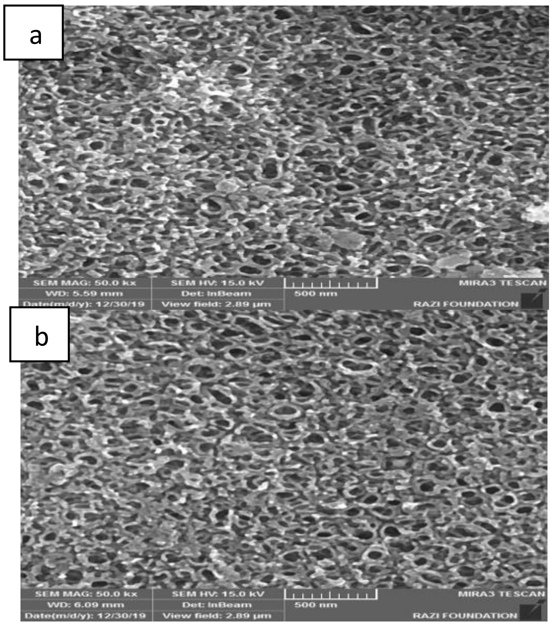

Fig. 5. FESEM microstructure of samples a-C1 and b-C2.

Scanning electron microscopy image of morphology of samples D1 and D2 is presented in sections a and b of Fig. 6. The predominant microstructure of both samples is titanium oxide porosity. And a small amount of non-uniform titanium oxide nanotubes are formed.

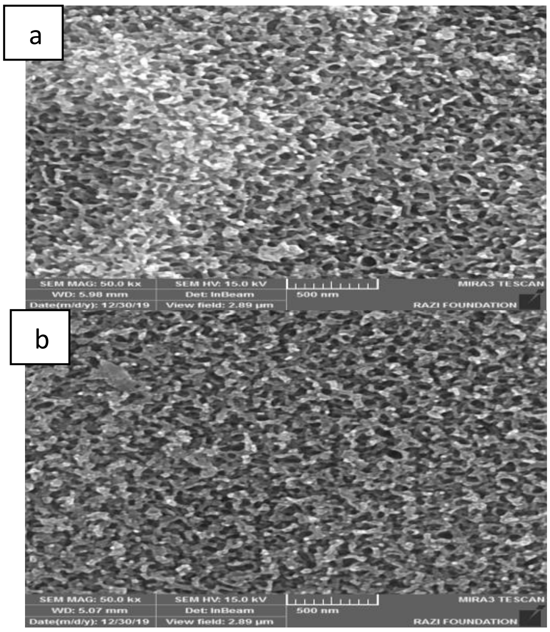

Fig. 6. FESEM microstructure of samples a-D1 and b-D2.

Scanning electron microscopy image of the cross section of sample A1 and C2 is presented in sections a and b of Fig. 7. The thickness of the coating or the length of the nanotubes in sample A1 is about 174 nm and in sample C2 is about 320 nm.

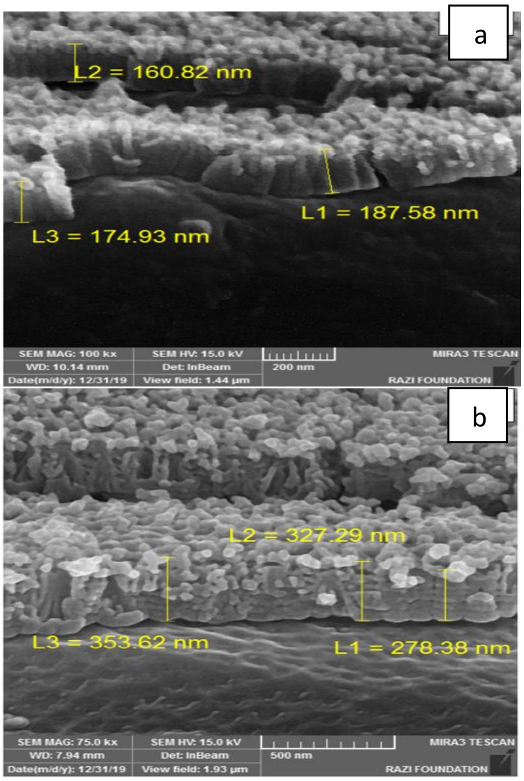

Fig. 7. Sample cross section A-A1 and B-C2.

According to the flow-time diagram, the process of formation and growth of these nanotubes can be better explained. When a layer of metal oxide forms on the surface of the titanium, the conductivity is reduced and there is a sharp drop in current (Step 1). As time goes on, the structure of the pores is formed, which is the beginning of the nucleation of the nanotubes, and as can be seen from the diagram, in step 2, the flow begins to increase.
In step 3, the current is reduced, which indicates the beginning of the growth of nanotubes and increase their length. In step 4, the oxidation current reaches a constant value, which indicates that the growth process of the nanotubes is in equilibrium.
At the beginning of the second stage, field-assisted dissolution overcomes chemical dissolution, and due to the local dissolution of the oxide by current, small cavities are formed.
As the voltage increases, the amount of local current density on the oxide surface increases, causing larger initial cavities to form. The final diameter of the pipes strongly depends on the size of the initial cavities.
Therefore, according to Fig**.** 8**.**, with increasing voltage, the diameter of the produced nanotubes also increases.

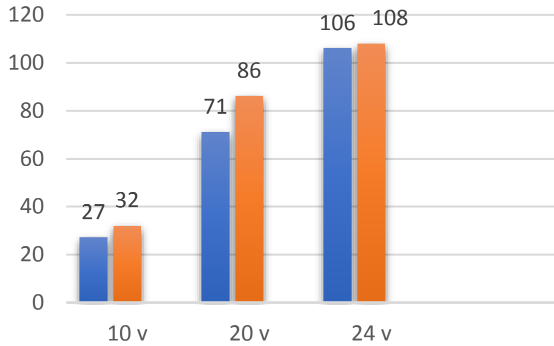

Fig. 8. Changes in nanotube diameters with respect to different voltages and times.

4. Conclusion

In this study, commercial pure titanium anodizing was performed on HF electrolyte under applied voltages of 10 to 30 volts for 60 and 120 minutes. The following results were obtained after scanning electron microscopy:
1. As the voltage of the anodizing process increases, the diameter of the nanotubes increases.
2. As the voltage of the anodizing process increases, the length of the nanotubes increases.
3. Uniform nanotubes with a size of 27 to 32 nm were obtained at a voltage of 10 volts for 60 and 120 minutes.
4. With increasing voltage, the anodizing process of nanotubes becomes non-uniform and irregular.
5. By increasing the voltage of the anodizing process to 30 volts, a porous structure is formed.

References

[1] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, Form. Titanium Oxide Nanotube., Langmuir., 14, (1998), 3160.
[2] T. Maiyalagan, B. Viswanathan, and U. V. Varadarju, Bull. Mater. Sci., 29, (2006), 705.
[3] D-J.Yang, H-G.Kim, S-J.Cho and W-Y.Choi, Mater. Lett., 62, (2008), 775.
[4] T. Hoseinzadeh, Z. Ghorannevis and M. Ghorannevis, A Mater. Sci. Process., 123, (2017), 1.
[5] S. Bauer, S. Kleber, and P. Schmuki, Electrochem. Commun., 8, (2006), 1321.
[6] D. Gong, C. A. Grimes, O. K. Varghese, W. Hu, R. S. Singh, Z. Chen and E. C. Dickey, J. Mater. Res., 16, (2001), 3331.
[7] R. Xu, J. Zhao, J. Tao, Xixin Wang and Y. Li, J. Appl. Electrochem., 38, (2008), 1229.
[8] M.Goodarzi,A.Afshar,H.Dolati,S.Pouladvand" 8th Iranian Cer. Cong., (2011).
[9] D.Behzadipour, R.Mohammadi and T. Mesgaar, The Conf. on Nanosci. and Nanotechnol., (2013).
[10] A. Mazzarolo, M. Curioni, A. Vicenzo, P. Skeldon and G. E. Thompson, Electrochemica. Acta., 75 (2012), 288.

[11] D. Gong, C.A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, and E. C. Dickey, J. Mater. Res., 16, (2001) 3331.
[12] Pishkar, Ghorannevis, Soltanabadi “National Conf. on Nanostructures, Nanostruct. Sci. and Nanoengineering, (2017).