Fabrication of Titania Nanotubes by Electrochemical Anodization and their Characterization

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Abstract*— Titania nanotubes (TNTs) may be formed by various methods. Their prominent features include large specific surface area, ion exchangeability and photo catalytic potential. Their potential applications include bio implants, solar cells and photo catalytic water splitting. In the present work we have investigated the effect of voltage on the structure of Titania nanotubes grown on titanium substrate by electrochemical anodization method and explore their physical and structural properties. The aim was to get the ultrahigh aspect ratio (length/diameter). The electrolyte consisted of ethylene glycol, deionized water and ammonium fluoride. Titania nanotubes were characterized using Scanning Electron Microscopy (SEM).

Keywords*— electrochemical anodization, titania nanotubes, ammonium fluoride, ethylene glycol, SEM, XRD

I. INTRODUCTION

Titanium has gained much attention over the past few years because of its high corrosion resistance, low density and strong durability. Titanium has an atomic weight of 47.88 while its tensile strength varies from 210-1380 MPa. Titanium is as strong as some steels but 45% lighter therefore have high strength-to-weight ratio [1]. Titanium has low coefficient of thermal expansion as compared to steel, aluminum, copper and many other metals. These unique properties of titanium make it appropriate for biomedical applications. When exposed to air or oxidizing solutions, a passive oxide film is formed which makes it particularly resistant to corrosion. This passive layer is the compound of titanium and oxygen having formula TiO_2. This titanium oxide is suitable for a variety of applications. It has its applications in fields of solar energy, hydrogen gas sensors, water purification as well as in biomaterials. Different fabrication methods are used to obtain different morphologies of TNT's like nano fibers, nano rods, nanoparticles and nanotubes. Each method has its own practical importance. Aim of our work is to produce titania nanotubes using electrochemical anodization process at very low cost. It is an easy and fast process. Titania nanotubes fabricated using anodization technique will have large surface area and high reactivity. Smaller diameter nanotubes tend to be more brittle and harder to handle without breaking [2]. As a result of electrochemical anodization two different types of layers are formed depending upon the type of electrolyte. Our work includes the production of porous type layer of titania in aqueous and organic solutions consisting of Fluoride Ions. In porous type layer first of all barrier type layer forms which readily dissolves in fluoride and chloride based electrolytes. Ions react with both the metal and the oxide to form a titanium hexafluoride complex [TiF_6^{2-}] that is stable in water. On passage of anodization current nano porous, tubular and self-organized TiO_2 layers are formed perpendicular to the metal substrate under controlled conditions [2]. Size of nanotubes obtained varied from 20 to 60nm in diameter. Size of nanotubes depends upon anodization potential. At low voltage, nanotubes had not enough time for growth. Perfect ratio of voltage and time yield nanotubes with greater diameter and small thickness under constant temperature and pH.

II. ELECTROCHEMICAL ANODIZATION

Electrochemical self-ordering has been recognized as one of the most attractive synthetic approaches for fabrication of highly ordered nonporous nanotube materials. This method helps to modify the surface of the material by formation of nanotubes and offer the desirable surface characteristics. Advantages of this method includes production of TNT's with high aspect ratio, highly ordered nano structure and controlled TNT's dimensions by varying the parameters. It is comparatively easy and fast process for obtaining nanotubes. While other methods include template assisted method, hydrothermal and sol gel methods.

III. MECHANISM OF NANOTUBE FORMATION

A TiO_2 passive layer naturally exists on the surface of titanium. Titania nanotube formation has three growth stages during anodization. Stage one includes the formation of oxide barrier layer. The current at this stage is utilized for barrier layer formation and hence a decrease in current is observed. When constant voltage is applied on the sample during anodization, pits start forming on the surface. This is stage 2. The pits further grow into nanopores. Under the application of voltage and time, these pits and nanopores undergo continuous barrier layer formation and result in self-organized nanotubes [3]. The formation of titania nanotubes is the result of two processes i.e. field assisted anodic oxidation and chemical

dissolution. At first, anodic layer is formed during field assisted oxidation, reaction is given below.

$$H_2O \rightarrow O_2 + 4e + 4H^+$$
$$Ti + O_2 \rightarrow TiO_2$$

This TiO2 layer is then corroded by fluoride ions, which results in pitting. F^- Ions react with Ti^{4+} under the influence of electric field that is termed as chemical dissolution. Dissolution can be enhanced by increasing concentration of fluoride ions and water [4]. Localized dissolution of the oxide results in the formation of small pits represented by the following reaction [5].

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_2^{-6} + 2H_2O$$

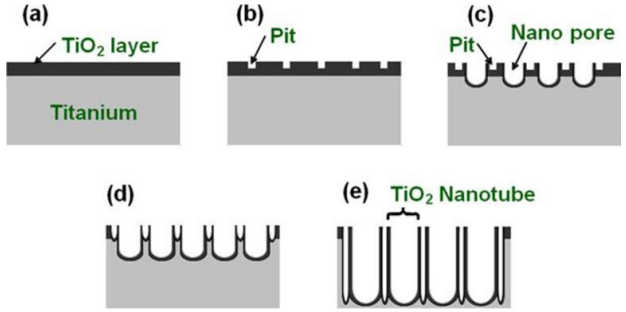

Fig.1. *Schematic illustration of TiO2 nanotube formation* [3]

Stage 3 consists of steady state growth of nanotubular oxide layer above the titanium surface. These pits then grow into pores and then nanotubes due to the continuous bore of fluoride ions into the titanium oxide layer. As a result, self organized titania nanotubes are obtained perpendicular to the titanium substrate. Porous oxide layer is formed in case of Al whereas nanotubular oxide layer is formed as a result of anodization of titanium [6]. Viscosity of electrolytes is an important parameter for uniform growth of nanotubes. Viscous electrolytes may result in non-uniform nanotubes and lower growth rates. For example, growth rate is low in glycerol having viscosity 945 cP at 25°C while considerable improvement was observed in ethylene glycol electrolyte having viscosity 16 cP at 25°C. This increase in growth rate is due to lower diffusion resistance in ethylene glycol solutions [5]. Nanotubes showed 10000% increase in length when anodized in NH_4F and ethylene glycol solution compared to those obtained in aqueous electrolytes [7]. Studies showed that high voltages are required for nanotube growth in non-aqueous electrolytes [8].

IV. Experiment

The fabrication of Titania nano tubes (TNTs) is carried out in an electrochemical cell. In this cell, our test specimen i.e. titanium is the working electrode and carbon is used as a counter electrode. Carbon acts as cathode while titanium acts as anode. The electrolyte consists of 97ml of ethylene glycol, 3ml deionized water and 0.3g ammonium fluoride. The pH initially obtained from this electrolytic composition is 7 i.e. neutral. Glycerol or ethylene glycol is usually added to increase the smoothness of the nanotube walls since they act as a buffer against the changing pH at the opening of the nanotube during synthesis [1]. Take 40ml of this electrolyte in a plastic beaker. The titanium substrate is prepared by first grinding the sample on emery paper ranging from 180-2000 grid size and then polishing using alumina paste. Rinse the samples using acetone and deionized water. Attach this polished titanium and carbon substrates with two separate copper wires with their ends attached to the alligator clips. Attach these alligator clip holders with DC power supply. Both the substrates are dipped in the electrolyte and the final arrangement is placed in a chemical fume hood. Turn on the DC supply for 1 hour. Once the anodization process is complete, take out the sample and rinse it with acetone. Different samples were prepared by using same process and varying the time and voltage.

V. Characterization of Titania Nanotubes

The morphology of Titania nanotube is characterize with the help of field emission scanning electron microscopy. FE-SEM results of samples prepared at 20 and 30 voltages for different hours are shown below.

Table Head	**Inner diameter (nm) of titania nanotubes obtained at different voltages for different time parameters**		
Sample number	***Voltage (V)***	***Time (hrs.)***	***NTs obtained (nm)***
1	20	1	37.07
2	30	1	62.57
3	20	2	48.32
4	30	2	52.79
5	20	3	No TNTs
6	30	3	No TNTs

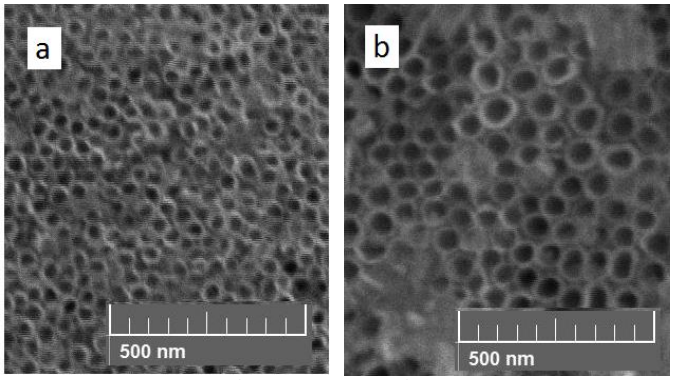

Fig.2. *FE-SEM images of samples anodized for 1 hour at (a) 20V (b) 30V*

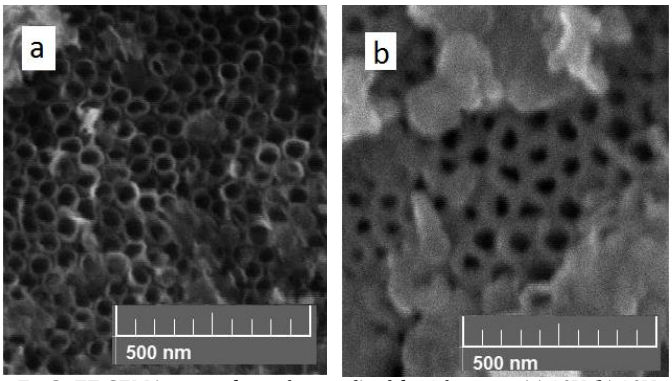

Fig.3. *FE-SEM images of samples anodized for 2 hours at (a) 20V (b) 30V*

The most important parameter that controls diameter of nanotubes is anodization potential. Fig 2 (a)-(b) represents the increase in diameter of nanotubes with the increase in voltage at 1 hour. The minimum diameter obtained was at 20V when anodized for 1 hour. Same increasing trend was observed in samples prepared at anodizing potential of 20 and 30V for 2 hours time (shown in fig 3 (a)-(b)). Temperature and pH were kept constant for all these samples. Diameter of nanotubes is in direct relation with anodization potential i.e. diameter increases with the increase in voltage. Temperature is inversely related while fluoride content is directly related to wall thickness [6].

Wall thickness of titania nanotubes depend on fluoride ion concentration in electrolyte and temperature. However it also depends upon voltage and electrolyte conductivity. Liu and coworkers proposed that the efficiency and surface area of nanotube arrays can be determined by using the following formula [9]

$$P = 1 - \frac{2\pi W(W + D)}{\sqrt{3}(2W + D)2}$$

P = porosity of TNTs arrays
W = wall thickness
D = inner diameter

As application changes the efficiency of nanotubes changes in accordance with that application. For example for photo-catalysis for gaseous reactants, the most efficient diameter is 20 nm while the wall thickness varies from 20-30nm. Macak studied that in NH_4F containing electrolyte, diameters ranging from 20 to 300nm can be obtained by varying the voltages between 2 to 40V. At potentials higher than 40V the nanotubes obtained are not uniform and self-organized [8]. Titania nanotube growth is directly related to anodization time, voltage and fluoride ion concentration in electrolyte. For example, longest nanotubes of 1000 µm length were obtained in nine days while 5 µm long tubes were obtained when titanium was anodized for 17 hours at same parameters [4].

The biocompatibility of Titania nanotubes was tested by Indra and coworkers by immersing anodized titanium sample in hank's solution. After 7 days of immersion a bonelike apatite layer was formed on the surface of titania nanotubes. This treated sample showed very low corrosion current density and very high corrosion resistance than the untreated sample of titanium [10]. Hence, titania nanotubes are the best suited materials for bio implants because of their high corrosion resistance even after implantation.

VI. Conclusion

It was investigated that electrochemical anodization method is one of the cost effective method for the production of nanotubes. The formation of Titania nanotubes was a sensitive process and even small variations in anodization time and potential changed the results. It is concluded that optimum conditions and the perfect ratio of time to voltage yield nanotubes with high aspect ratio.

VII. Acknowledgment

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VIII. References

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