ISSN : 0974 - 7494 Volume 8 Issue 6

Nano Science and Nano Technology
An Indian Journal

Full Paper

NSNTAIJ, 8(6), 2014 [193-197]

Synthesis and characterization of self-organized titania nanotube arrays by electrochemical anodization of titanium metal and Ti–6Al–4V alloy

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ABSTRACT

The current paper describes titania nano tubes (TNT), wires and rods that have been successfully grown by anodization in 0.5 wt% HF (Hydrogen Fluoride) electrolyte on Titanium metal and Ti-6Al-4V alloy, by varying the anodization voltage and keeping the temperature and time constant. The formed nenotubes,wires and rods were characterized by Environmental Scanning Electronic Microscope (ESEM), Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) technique.

KEYWORDS

Titanium;
Titanium alloy;
Electrochemical anodisation;
Titania nano tubes;
Nano wires;
Nano rods.

INTRODUCTION

TiO_2 nanotubes have attached tremendous attention due to the combination of a wide band gap semiconductive nature with high surface area, high surface activity and high sensitivity. Their excellent optical and electrical characteristics make them suitable for use in water splitting[1], dry-sensitized solar cells (DSSCs)[2,3] and photocatalysis[4]. Due to the specific ion interaction properties, TiO_2 nanotubes can also be used in electrocromic display devices[5]. Their biocompatibility further makes them important for biomedical applications[6]. For fabrication TiO_2 nanotubes, many approaches such as template based, hydrothermal, and sol-gel methods, have been exploited[7-9]. Recently self organized growth by anodisation has drawn much more attention[10-13] because of the advantages of simplicity and of vacuum and high temperature being unnecessary, while retaining quiet regular ordering. In the self-organized growth each individual TiO_2 nano tube is perpendicular to the membrane surface and the TiO_2 layer has a good ohmic contact with the Ti substrate.

Electrochemical anodization has been one common method of choice to synthesize titania nano tubes and is also applied for the fabrication of nano structured ceramic materials, and considerable attention has been given to the electro chemical deposition of ceramic coatings for biomedical applications. By changing the bath compositions and deposition parameters allows control over the morphology and porosity of the films[14]. The technique is relatively simple while still provides a high degree of control of nanotube dimensions. By controlling various anodization parameters (e.g. applied potential, electrolyte concentration, temperature) different titanium oxide structures can be synthesized. Similar approach has been applied in this paper where titania nanotubes (TNT), rods and wires have been successfully grown by anodization of titanium metal and Ti-6Al-4V alloy in a 0.5 wt% HF (Hydrogen Fluoride) electrolyte and their characterstics have been exam-

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ined with the help of ESEM,EDS and XRD techniques.

EXPERIMENTAL

The titanium metal and Ti-6Al-4V alloy samples prior to anodization were mechanically polished with different silicon carbide papers to obtain a mirror-like finish and was ultra sonically cleaned in deionized water and subsequently in acetone for 15 minutes each. Titania nano tubes,wires and rods were grown on titanium metal and Ti-6Al-4V alloy. The anodization was performed using a Aplab Regulated DC Power Supply L3205 in a electrolyte medium of 0.5wt% HF (hydrofluoric acid). Platinum wire was used as cathode. The electrolyte mixture was stirred during the process. The distance between the two electrodes was fixed at 26 mm. Nano tubes, wires and rods were grown on titanium metal and Ti-6Al-4V alloy at three different anodizing potentials i.e. 15V, 20V and 25V for a time period of 40 minutes at room temperature. Anodization voltage was kept constant throughout the process. The electrolytic solution (0.5 wt% HF) was changed after each process. The samples were then annealed at 500^0 C in a furnace for 3 hours. Surface morphology of titania nano tubes, rods and wires grown on titanium metal and Ti-6Al-4V alloy samples were observed by Environmental Scanning Electron Microscope (FEI Quanta 400). Energy dispersive spectroscopy (EDS) was used to determine the elemental composition of titania nano tubes, rods and wires grown on titanium metal and Ti-6Al-4V alloy samples. Crystallographic analysis of titania nano tubes, rods and wires grown on titanium metal and Ti-6Al-4V alloy samples were carried out by X-ray Diffraction (XRD) technique.

RESULTS AND DISCUSSIONS

Anodization of titanium metal and Ti–6Al–4V alloy at 15 V results a nano rod like structure. An increase in cell voltage from 15 V to 25 V has resulted in an increase in average pore diameter from 30 nm to 150 nm. At an anodization voltage of 20 V, an oxide layer has been formed on the surface due to interaction of the metals with O^{2-} or OH^- ions. The oxide layer has been removed in certain areas due to localized dissolution of the oxide only a sponge like porous structure is observed at 25 V, whereas at 20 V nano tubular structure has been formed. Anodization process results in formation of TiO_2 nano tube like structure when it is performed at an anodization voltage 20 V for 20-30 minutes at room temperature. The pore size of the tubes was found to be in the range from 25 to 65 nm.

The surface morphology of nano tube arrays obtained on titanium metal at 20 V and annealed at 500^0 C for 3 hours is shown in Figure 1. It can be seen that the nano tubes are uniform over the surface. The nano tubes are approximately 400 nm in length. The surface morphology of nano wires obtained on Ti-6Al-4V alloy at 25 V is shown in Figure 2. It can be seen from the image that the nano wires are uniform over the surface. The surface morphology of nano rods obtained on Ti-6Al-4V alloy at 20 V is shown in Figure 3. It indicates that nano rods and wires formation is dependent on the applied potential in the anodization process.

The EDS data of titania nano tubes arrays obtained on titanium metal at 20 V and annealed at 500^oC is provided in Figure 4. The EDS data confirms the presence of titanium and oxygen. Similarly, EDS data of mixed titania nano wires and rods synthesized by anodization of Ti-6Al-4V alloy annealed at 500^oC is given in Figure 5. The EDS data confirms the presence of titanium, aluminum, vanadium and oxygen.

The X-ray diffraction measurements have been carried out to examine the crystallinity of titania nano tubes,

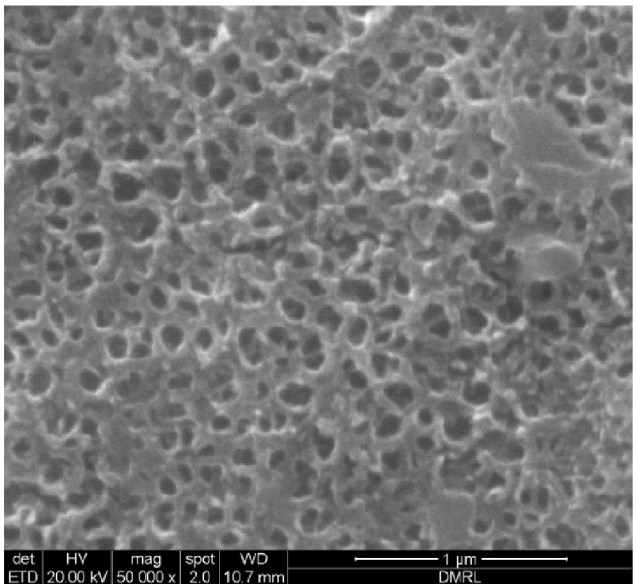

Figure 1 : Surface morphology of the nano tubes obtained on titanium metal

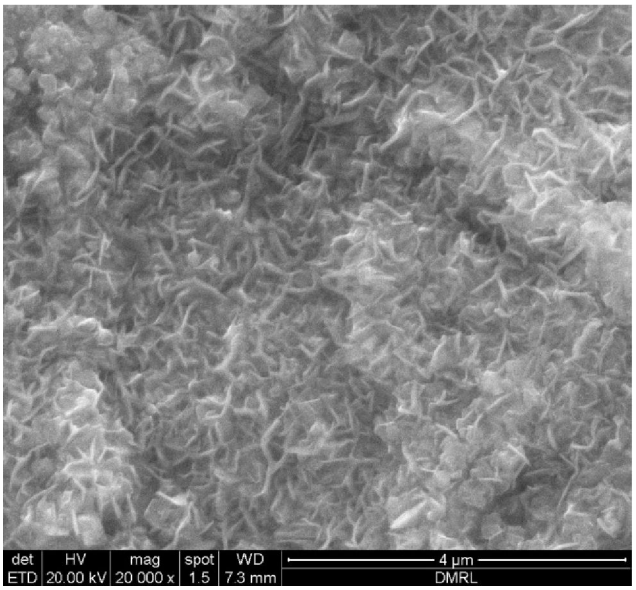

Figure 2 : Surface morphology of the nano wires obtained on Ti-6Al-4V alloy

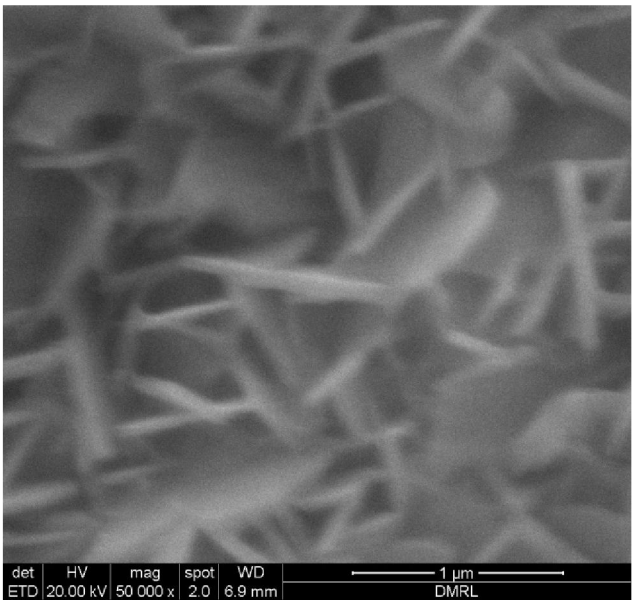

Figure 3 : Surface morphology of the nano rods obtained on Ti–6Al–4V alloy

rodes and nano wires grown on the titanium metal anodized at 15 V, 20 V and 25 V. Figure 6 shows the X-ray diffraction patterns of titania nano tubes which has been obtained on the titanium metal samples annealed at 500^0 C for 3 hours.

Similarly, X-ray diffraction measurements have been carried out to examine the crystallinity of titania nano wires and rods for Ti-6Al-4V alloy samples anodized at 15 V, 20 V and 25 V. Figure 7 shows the X-ray diffraction patterns of titania nano wires and rods which have been formed on the Ti-6Al-4V alloy annealed at 500^0 C for 3 hours.

THE MECHANISM OF NANO TUBE AND ROD FORMATION

The growth of nano tubes and rods on titanium metal and Ti-6Al-4V alloy is affected due to selective dissolution of less stable elements[15-17]. The Ti–6Al–4V alloy has a dual phase α + β microstructure. The α phase is enriched with element Aluminium, whereas β phase is enriched with element Vanadium. Due to this difference in chemistry of these phases, formation of the nano tubular oxide layer is not uniform in alloys as β phase is etched preferentially by the electrolyte. Similarly, the process of nano tube formation on α phase is similar to anodization of pure titanium metal sample[18].

The overall reactions for the anodization of titanium can be represented as follows[19]:

$$2H_2O = 4H^+ + O_2 + 4e^-$$

$$Ti + O_2 = TiO_2$$

Initially, an oxide layer is formed on the surface of titanium as a result of the above reactions. In the presence of fluoride ions, the oxide layer dissolves locally and a nano tube is created from small pits that are formed in

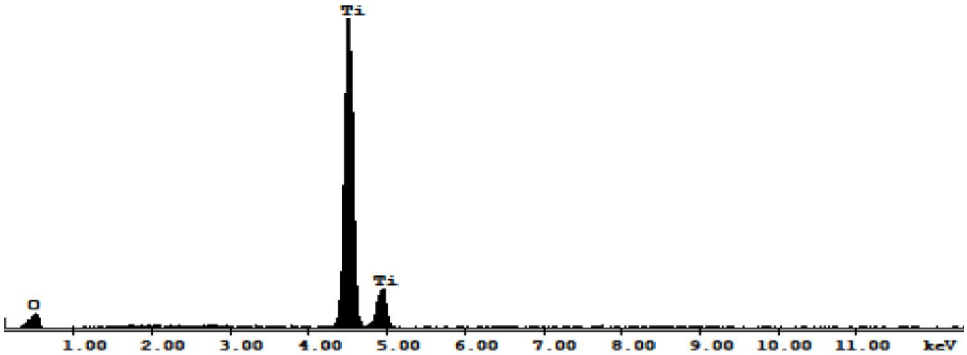

Figure 4 : EDS data of titania nano tube arrays obtained on titanium metal

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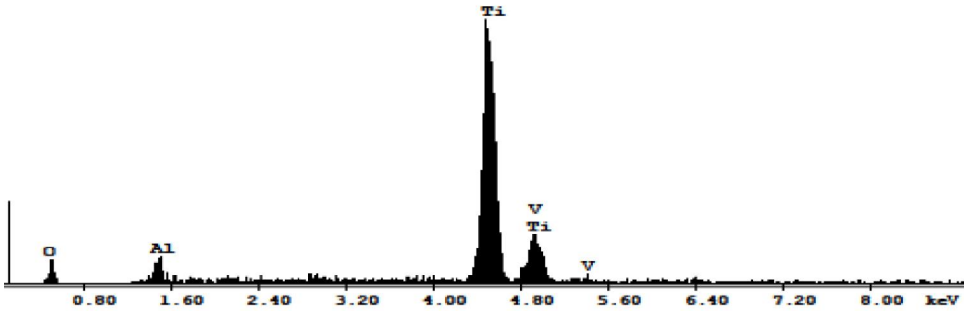

Figure 5 : EDS data of mixed oxide nano tube arrays obtained on Ti–6Al–4V alloy

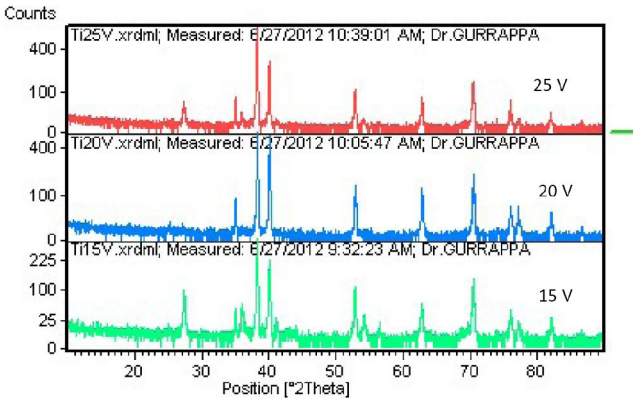

Figure 6 : XRD patterns of nano tubes synthesized on titanium metal at different voltages

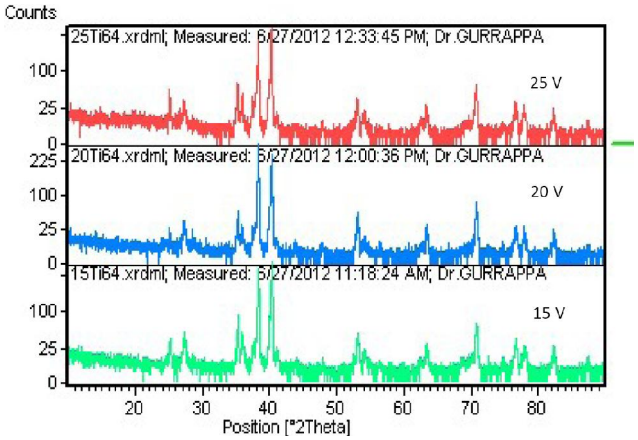

Figure 7 : XRD patterns of nano wires and rods synthesized on Ti-6Al-4V alloy at different voltages

the oxide layer. These pits are created from the following reactions between TiO_2 and HF:

$$TiO_2 + 4H^+ + 6F^- = TiF_6^{2-} + 2H_2O$$

The chemical dissolution reduces the thickness of the oxide barrier layer at the bottom of the pits and allows the electrochemical etching process to continue (field assisted oxidation and dissolution). At the bottom of the pits, both the chemical dissolution and the electrochemical etching take place. The oxide layer at the bottom of the pits is relatively thin; and the thin layer, in turn, increases the electric field intensity, resulting in further pore growth. In addition, chemical dissolution removes the top of the shallow pore column and this forms the unanodized metallic region between the pores. The channels formed in these regions separate the pores from each other.

CONCLUSIONS

1. Self-organized titania nano tubes, rods and wires have been successfully synthesized under an applied anodized voltage of 15 V, 20 V and 25 V in 0.5 wt% HF by anodization of titanium metal and Ti–6Al–4V alloy.
2. The average inner diameters of nano tubes at applied anodizing voltage 15 V, 20 V and 25 V voltage resulting nano tubes are straight, with a pore size ranging from 65 to 100 nm.
3. Surface morphology of titania nano tubes, rods and wires obtained on titanium metal and Ti-6Al-4V alloy samples have been observed by Environmental Scanning Electron Microscope
4. Energy-dispersive spectroscopy (EDS) results confirmed the elemental composition of titania nano tubes, rods and wires.
5. Crystallographic analysis of titania nano tubes, rods and wires grown on titanium metal and Ti-6Al-4V alloy samples have been confirmed by X-ray Diffraction (XRD) technique.

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