

Formation of Different Titanium Oxide Morphology via Anodization and Its Effect on Hydrophilicity of the Substrate

Suman Kumari . Mantravadi Krishna Mohan

Department of Metallurgical and Materials Engineering, National Institute of Technology, Warangal, India.

ABSTRACT

In this article, studies have been carried out to produce Titanium Oxide (TiO₂) onto cp-Titanium (Ti) substrate by simple electrochemical anodization process. Effect of electrolytic bath composition on TiO₂ morphology was investigated by keeping all the other variables (voltage, Time period, pH, temperature and current density) constant. Anodization was carried out in four electrolytes, viz. 1 M H₂SO₄, 1 M H₃PO₄, 0.5 M HF and Ethylene Glycol (EG) mixed with 50% H₂O with the addition of 0.14 M NH₄F. TiO₂ morphology and its composition were examined with SEM and EDS. The contrast in surface morphology was observed for anodization carried out in Ethylene Glycol and HF electrolyte compared to that of carried out in H₂SO₄ and H₃PO₄. In the presence of fluoride ions, TiO₂ anodic film developed has porous/tubular morphology. Further, surface hydrophilicity was measured by simple Water Contact Angle (WCA) measurement technique.

© 2017 JMSSE and Science IN. All rights reserved

ARTICLE HISTORY

Received 21-04-2017

Revised 29-04-2017

Accepted 12-05-2017

Published 29-06-2017

KEYWORDS

cp-Titanium,
Anodization,
Inorganic electrolyte,
Organic Electrolyte,
TiO₂, WCA

Introduction

Titanium and Titanium alloys (Ti alloys) have attracted special attention in the field of biomedical materials owing to their excellent corrosion resistance, mechanical properties, biocompatibility and non toxic nature[1-2]. Ti is a trans-passive (or valve) metal thus instantly forms a thin TiO₂ layer (in the nm range) when exposed to environment. In order to exploit the properties of different TiO₂ morphology[3] it is important to orient them in a particular fashion onto the substrate. These well patterned and reproducible TiO₂ layers coated on Ti has great potential as biomedical material due to their biocompatibility and good wear resistance[4-6].

Several techniques have been explored over the years for deposition of TiO₂, such as, thermal oxidation, chemical methods, physical vapour deposition, anodization etc [7]. Among all these techniques, anodization is considered to be the cheapest, simplest and very popular technique to create ordered TiO₂ pattern on the substrate. Anodic oxidation allows the formation of much denser and thicker oxide layer. Many attempts have been undertaken in order to create different anodic oxide morphology and investigated their effect for reducing the bacterial growth, thus creating anti-bacterial surface, and enhanced cell adhesion. Morphology of anodic oxide films mainly depends on the choice of bath composition, voltage, current density, time period, pH and temperature [8-9].

The present work focuses on creation of different oxide morphology by varying the bath composition. Anodization was carried out for inorganic (H₂SO₄, H₃PO₄ and HF) and organic electrolyte (Ethylene Glycol with addition of NH₄F). Other parameters, e.g. voltage, time period and current density, were kept constant. The WCA measurements were carried out in order to investigate the effect of oxide morphology on the hydrophilicity of the substrate.

Experimental

Materials and Methods

The sample with dimensions 1cm x 1cm was cut from cp-Ti foil (with thickness 0.125 mm) procured from Good fellow, UK. The samples were prepared as prescribed in ASTM E8 standard for specimen preparation. The samples were mechanically polished with SiC abrasive papers (upto 2000 grits) followed by diamond polishing. Afterwards, samples were cleaned thoroughly with De Ionised (DI) water and blow dried. Etching was carried out with Kroll's reagent (DI : HNO₃ : HF :: 46 : 3 : 1) for 30 seconds and rinsed with DI water.

Anodization

Anodization process was carried out in a two electrode system (CH Instruments, USA [CH1600C], DC high voltage power supply from APLAB [Model-H0310], India) as shown in Figure 1, with cp-Ti as anode and stainless steel as cathode electrode in both, inorganic (H₂SO₄, H₃PO₄ and HF) and organic electrolytes (Ethylene Glycol) as shown in Table 1. The equipment used All the experiments were carried out at Room Temperature (RT). Anodized samples were rinsed and dried. The samples were annealed at 450 °C for 3 hours.

SEM-EDAX Characterization

The morphology of oxidized specimen was investigated using Scanning Electron Microscope (*Tescan*, 2012). The SEM images were processed with *Vega3 LMU* software. The chemical analysis of surface was carried out utilizing EDAX (Energy Dispersive Spectroscopy) procured from *Oxford* company.

Water Contact Angle (WCA) Measurements

Water contact angle (WCA) measurements were carried out by placing a 10 µL drop of DI water. The droplet was imaged using *Coolingtech* microscope software. The contact angle was measured by *ImageJ* software. WCA measurements were carried out for polished and anodized Ti substrate. At least three measurements were carried out at different places for each substrate.

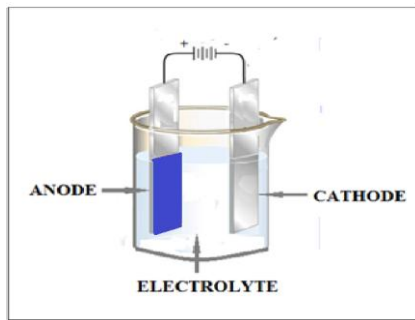


Figure 1: Two electrode anodization set-up

Table 1: Parameters for electrochemical anodization

S.No.	Electrolyte	Voltage (Volts)	Time period (minutes)	Current Density (A/cm ²)
1.	H ₂ SO ₄ (1M)	60 V	30	10
2.	H ₃ PO ₄ (1M)	60 V	30	10
3.	HF (0.5M)	60 V	30	10
4.	Ethylene Glycol (25 ml)+H ₂ O (25 ml)+NH ₄ F (0.14M)	60 V	30	10

Results and Discussion

Growth Kinetics and SEM-EDAX characterization

Mott-Cabrera (10) discussed the oxide film formed by anodic oxidation under electric field in late 1940s. The oxide growth is mainly governed by high-field conduction mechanism. The diffusion of cations through the metal-oxide interface into the oxide is considered as oxide growth rate determining step. During oxidation, both the rate of oxidation and rate of dissolution of oxide determine the thickness of oxide layer. According to this approach, the electrochemical oxidation of metal can lead to, either, stable continuous oxide layer, if the formed oxide is not soluble in the electrolyte, or, nanoporous/nanotubular oxide, if the oxide is soluble in electrolyte (Figure 2) [11-12].

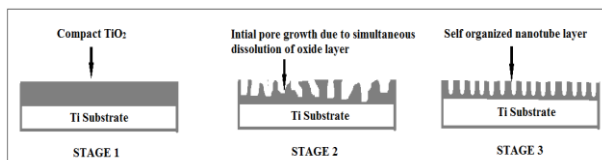


Figure 2: Stages of growth for nanotubular TiO₂

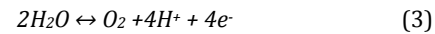
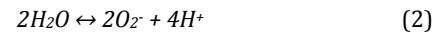
The anodic oxide growth was investigated in 1 M H₂SO₄ electrolyte (Figure 3). The oxide thickness linearly increases up to 70 V which was established in literature. The oxide layer after anodization in 1M H₃PO₄ electrolyte is regular, thick layer (Figure 4.). The anodization in H₂SO₄ and H₃PO₄ results in thick oxide morphology. During the initial stage of anodization, a thin compact TiO₂ layer is formed.

The main reactions leading to anodic oxidation of cp-Titanium are:

At the Ti/TiO₂ interface



At TiO₂/electrolyte interface:



At both interfaces:

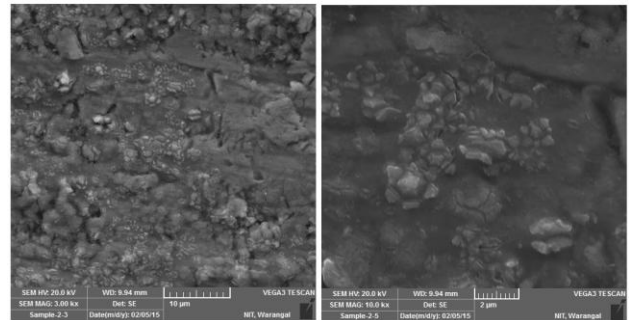
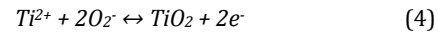


Figure 3: SEM micrograph of TiO₂ for anodization carried out in 1 M H₂SO₄

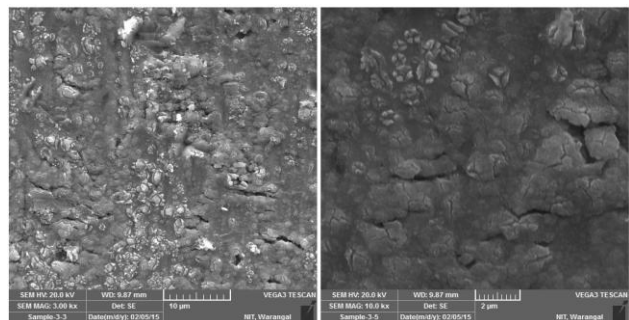


Figure 4: SEM micrograph of TiO₂ for anodization carried out in 1 M H₃PO₄

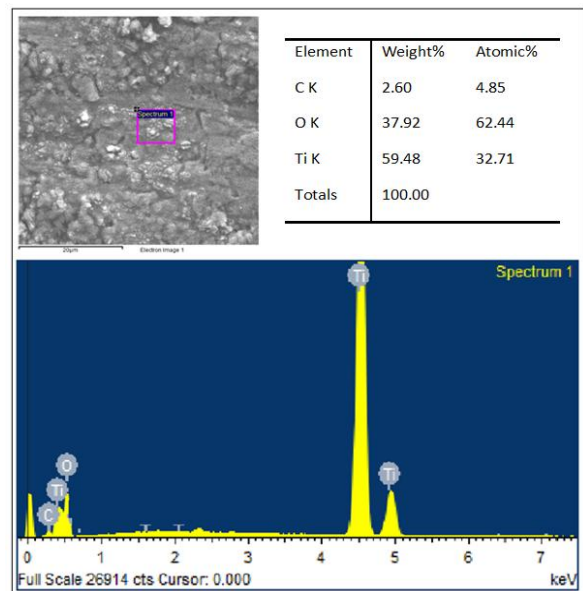


Figure 5: EDAX studies of TiO₂ for anodization carried out in 1 M H₂SO₄

The Ti²⁺ and O₂⁻ ions formed during the reactions are driven through the formed TiO₂ layer by externally applied electric field. As long as the electric field is high enough to drive the ions through oxide, a current will flow and the oxide will continue to grow. The EDAX confirmed the presence of TiO₂ for anodization carried out in H₂SO₄ and H₃PO₄ electrolytes as shown in Figure 5 and 6 respectively.

For samples anodized in 0.5 M HF, as shown in Figure 7, SEM images show some cracks and pits on the surface, while the SEM image at higher magnification shows porous structure. SEM micrographs for Ti specimen anodized in organic electrolyte, i.e. mixture of EG and H₂O, with the addition of NH₄F is shown in Figures 8 and 9. As, it can be seen, the oxide morphology is quite different from the surface anodized in inorganic electrolytes. The micrographs show the formation of nanotubes on the surface. The presence of TiO₂ was confirmed with EDAX (Figures 10 and 11).

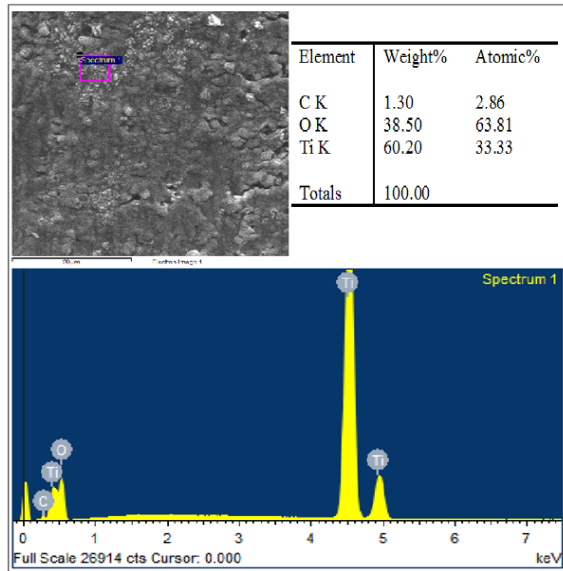


Figure 6: EDAX studies of TiO₂ for anodization carried out in 1 M H₃SO₄

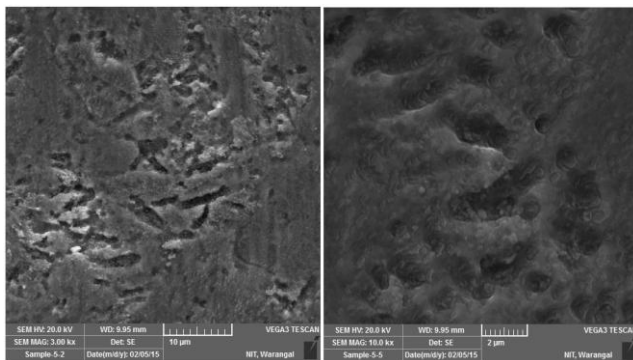


Figure 7: SEM micrograph of TiO₂ for anodization carried out in 0.5 M HF

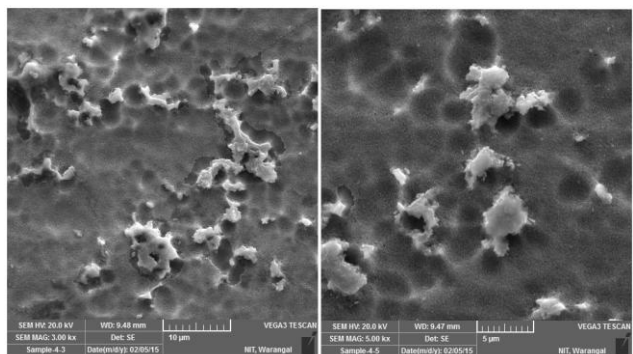


Figure 8: SEM micrograph of TiO₂ for anodization carried out in EG:H₂O (50:50) with the addition of NH₄F

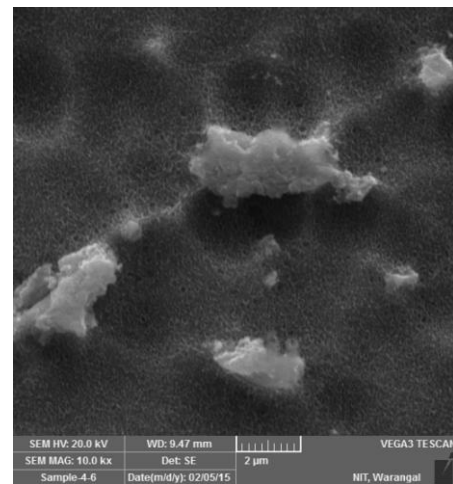


Figure 9: Higher magnification SEM micrograph of TiO₂ for anodization carried out in EG:H₂O (50:50) with the addition of NH₄F

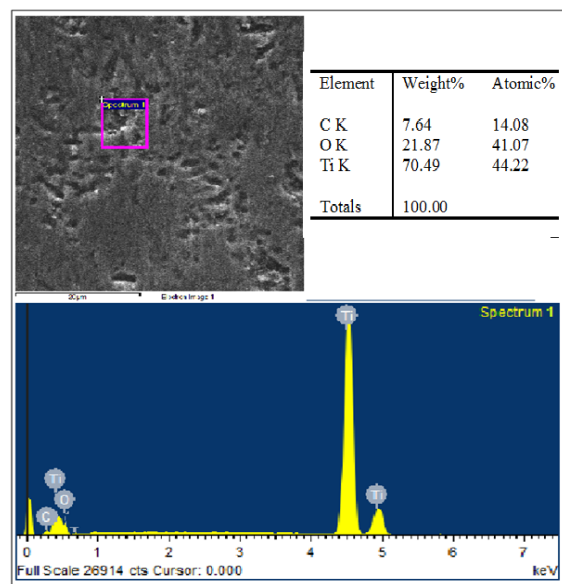


Figure 10: EDAX studies of TiO₂ for anodization carried out in 0.5 M HF

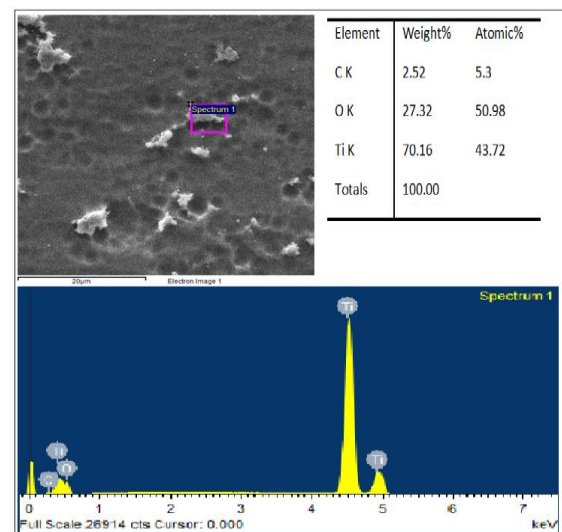


Figure 11: EDAX studies of TiO₂ for anodization carried out in EG:H₂O (50:50) with the addition of NH₄F

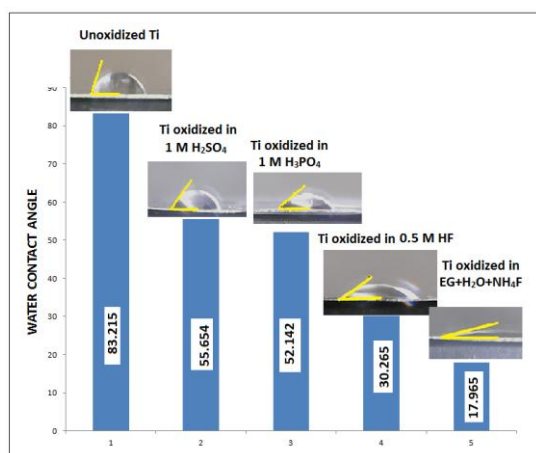
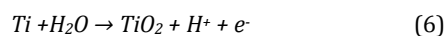
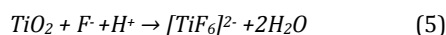


Figure 12: Bar graph showing the Water Contact Measurements for different oxide morphology

In fluoride containing electrolytes, current densities are higher than those in fluoride-free electrolytes. The dissolution reaction of the anodic oxide layer is induced by F⁻ ions. The formation of TiO₂ nanotubes is clearly affected by the fluoride in the electrolyte. This is due to additional chemical dissolution of the electrochemically formed oxide layer due to soluble [TiF₆]²⁻ complexes. In the first step, the current density decreased sharply due to oxide formed on the surface with low conductivity. The current density start to increase by active chemical dissolution reaction due to F⁻ ions from the electrolyte[11]. The porous structure is formed as a result of localized chemical dissolution of the oxide by [TiF₆]²⁻ according to the reaction



This leads to a higher field at the bottom of the pore that drives further oxidation, and field assists dissolution where Ti ions come out of the metal and dissolve in solution. Finally, the current reaches a steady state. However, if there are no F⁻ ions in electrolyte, the oxide layer is composed of only compact layer instead of nanotubular layer according to equation 2 because acidification from [TiF₆]²⁻ is not established at the electrolyte/oxide interface. So Ti⁴⁺ can be complexed to [TiF₆]²⁻ before reacting with a hydroxide layer.

This layer consists of some statistically break down sites where next to compact oxide dissolution occurs. After 1-3 min, these pore nucleation events are apparent on the entire surface. After 3-10 min., from the beginning of anodization, the pores have random appearance. In this period, pronounced dissolution at the pore bottom takes place making them significantly deeper. Further, no remnant TiO₂ layer from the stage 1 is present on the surface. After additional, 20 min have passed, the porous structure starts to readily convert into nanotubular structure (in the presence of fluoride ions).

Water Contact Angle Measurements

The wettability of different TiO₂ and unoxidized Ti was characterized by water contact angle measurements. The WCA measurements are shown in Figure 12 for all the anodized samples. As polished specimen exhibited the highest WCA, i.e., 83.215. The formation of TiO₂ reduced the values for water contact angle irrespective of oxide morphology. The Ti substrate anodized in inorganic

electrolyte (1 M H₂SO₄ and 1 M H₃PO₄) shows the contact angle values as 55.654 and 52.142 respectively. The anodization in electrolytes containing fluoride ions resulted in much lower WCA values. The porous TiO₂ morphology obtained for anodization in 0.5 M HF exhibited the WCA value of 30.265, which shows that the surface is more hydrophilic in nature compared to unoxidized or substrates oxidized in inorganic electrolyte. The formed nanotubes showed the least values for WCA measurements. It shows that the nanotube morphology is the most hydrophilic surface among all the substrates.

Conclusions

The bath composition is a crucial factor in determining TiO₂ morphology during electrochemical anodization. The anodization is 1 M H₂SO₄ and 1 M H₃PO₄ resulted in the formation of compact oxide, while anodization in 0.5 M HF created porous morphology. When anodization was carried out in organic electrolyte (EG+H₂O with the addition of NH₄F), nanotubes were formed on the surface.

The hydrophilicity of the substrate depends on the substrate surface morphology. The polished Ti substrate was hydrophobic in nature, while the nanotubular TiO₂ shows most hydrophilicity with a contact angle of 17.965.

References

- Liu X, Chu PK, Ding C. Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Mater Sci Eng R Reports*. 2004, 47(3-4), 49-121. doi:10.1016/j.mser.2004.11.001.
- Gotman I. Characteristics of metals used in implants. *J Endourol*.1997,11(6), 383-389. doi:10.1089/end.1997.11.383
- Lee Bg, Choi Jw, Lee Se, Jeong Ys, Oh Hj, Chi Cs. Formation behavior of anodic TiO₂ nanotubes in fluoride containing electrolytes. *Trans Nonferrous Met Soc China (English Ed)*. 2009,19(4), 842-845. doi:10.1016/S1003-6326(08)60361-1.
- Das K, Bandyopadhyay A, Bose S. Biocompatibility and in situ growth of TiO₂ nanotubes on Ti using different electrolyte chemistry. *J Am Ceram Soc*. 2008, 91(9), 2808-2814. doi:10.1111/j.1551-2916.2008.02545.x.
- Macak JM, Hildebrand H, Marten-Jahns U, Schmuki P. Mechanistic aspects and growth of large diameter self-organized TiO₂ nanotubes. *J Electroanal Chem*. 2008, 621(2), 254-266. doi:10.1016/j.jelechem.2008.01.005.
- Sul YT, Johansson CB, Jeong Y, Albrektsson T. The electrochemical oxide growth behaviour on titanium in acid and alkaline electrolytes. *Med Eng Phys*. 2001, 23(5), 329-346. doi:10.1016/S1350-4533(01)00050-9.
- Liu X, Chu PK, Ding C. Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Mater Sci Eng R Reports*. 2004, 47(3-4), 49-121. doi:10.1016/j.mser.2004.11.001.
- Tian T, Xiao XF, Liu RF, She H De, Hu XF. Study on titania nanotube arrays prepared by titanium anodization in NH₄F/H₂SO₄ solution. *J Mater Sci*. 2007, 42(14), 5539-5543. doi:10.1007/s10853-006-1104-6.
- Diamanti M V, Pedferri MP. Effect of anodic oxidation parameters on the titanium oxides formation. *Corros Sci*. 2007, 49(2), 939-948. doi:10.1016/j.corsci.2006.04.002.
- N. C. and N. F. Mott, "Theory of the oxidation of metals," *Reports Prog. Phys.*, 1949, 12 (1), 163.
- Apolinário a, Quitério P, Sousa CT, et al. Modeling the Growth Kinetics of Anodic TiO₂ Nanotubes. *J Phys Chem Lett*. 2015, 6(5), 845-851. doi:10.1021/jz502380b.
- Macak JM, Tsuchiya H, Ghicov A, et al. TiO₂ nanotubes: Self-organized electrochemical formation, properties and applications. *Curr Opin Solid State Mater Sci*. 2007; 11(1-2), 3-18. doi:10.1016/j.cossms.2007.08.004.

