

PHASE STUDY OF TITANIUM DIOXIDE NANOTUBES FABRICATED VIA ANODIZATION IN HF ELECTROLYTE

A'liya Abdul LAZIZ¹, Alaba O. ARAOYINBO^{1*}

Department of Mechanical Engineering Technology, Faculty of Engineering Technology, Universiti Malaysia Perlis
(UniMAP), 02100 Padang Besar, Perlis, Malaysia

Abstract

This study focused on the phase study of titanium dioxide (TiO₂) nanotube fabricated via anodization in HF solution. The objectives of this study is to observe the structure of nanotube formed after anodizing the titanium foil at different pH using field emission-scanning electron microscope and to analyze the different phases of TiO₂ heat treated at different temperature using X-ray diffraction tool. In order to form the TiO₂ nanotube, various parameters were used during the anodization process. The parameters include pH value of the HF solution, anodizing time, and applied potential. The pH of HF solution used is 1, 5 and 9 for 10 minutes time duration at 20 V. The TiO₂ nanotubes were heat treated at temperatures of 300, 500 and 700 °C with soaking time of 3 hours and cooling rate of 5 °C/min in a tube furnace to produce different phase of titanium dioxide. Phase identification from the titanium dioxide characterization indicates the presence of rutile and anatase peaks. The optimal condition for TiO₂ nanotubes formation was pH 5 with an applied potential of 20 V.

Keywords: sol-gel synthesis, nanomaterials, self-organization.

Introduction

Titanium dioxide is mostly available as a naturally occurring minerals e.g. rutile, anatase and brookite. The most common form of TiO₂ phase is rutile which is also the most stable when compared with the anatase phase [1]. The nanotube walls is observed to undergo a form of transformation into the anatase form and beneath the metal layer the tubes converts into the rutile phase upon heat treatment at higher temperatures [2].

Anodization of titanium foil is a promising approach to fabricate nanostructure porous oxides based on very simple process such as electrochemical anodic polarization [3]. Electrochemical anodization process is used to increase the thickness of the oxide layer on the surface of metal plates. The anodic electrode will increase corrosion resistance and wear resistance during anodizing process [4-6].

Anodization process is known to effect changes in the microstructure of the surface and crystal structure of the anodized metals. The anodized titanium layer is formed by passing a direct current through an electrolyte solution with the titanium foil serving as the anode. The current ejects hydrogen at the cathode (the negative electrode) and oxygen at the surface of the titanium anode, creating a build-up of titanium oxide. The voltage necessary for the successful anodization process in different solutions have been reported to be between 1 to 300 V dc. In the case of requiring thicker coatings higher voltages are often employed for solutions containing either organic acids or sulphuric acid. Titanium anodizing is usually performed in an acid solution which slowly etches the titanium oxide layer. The oxidation rate with the acid

action will form a nanoporous coating with 10-150 nm in diameter on the titanium surface. The significant conditions that can allow oxide layer fabrication involves the proper control of the electrolyte concentration, the type of acid used, temperature, and current [5-10].

Experimental

Titanium foils with dimensions 10 mm x 40 mm were cut and used for the anodization process. A 5 ml hydrofluoric acid was put into a 100 ml plastic beaker and stirred. The pH value of aqueous hydrofluoric acid solution was adjusted by adding sodium hydroxide. While adding the sodium hydroxide, the solution was stirred by using the magnetic stirrer.

The main parts of the process are composed of two electrodes and a stirrer. The titanium foil was used as the anode electrode (positive charge) while the platinum electrode as cathode electrode (negative charge) with distance of 3-3.5cm. The time for the anodization process is 10 minutes with 20 V potential. The process was repeated for hydrofluoric acid electrolyte with pH 1, 5, and 9.

The samples were rinsed with deionized water to remove the excess acid and dried with air gun. This step will reduce the contamination of hydrofluoric acid that may destruct the titanium dioxide nanotube structure. After the cleaning process, the samples were cut into 10 mm x 10 mm for morphology testing. In order to determine the morphology of TiO₂ nanotubes, the samples were characterized by using field emission-scanning electron microscope (FE-SEM) Nova Nano SEM from brand FET to identify the structure of TiO₂ nanotubes formed.

Three samples were cut with dimension 10 mm x 10 mm for the heat treatment. The temperature used are 300, 500, and 700°C with soaking time of 3 hours in a tube furnace at a cooling rate of 5°C /min.

Samples are then characterized with X-ray diffraction (XRD) machine D2 Phaser from Bruker. This characterization will show the rutile and anatase peak on the titanium dioxide foil after heat treatment. XRD patterns were recorded in the 2θ range of 10°- 80° with scanning speed of 5°/min.

Raw Materials

Titanium foil (Ti)

Titanium foil has been selected to be used as the starting material for the phase analysis in this study. The nanotube will form on the surface of the foil with thickness of 0.25 mm. Then, the foil is cut into 10 mm x 40 mm and used as the positive electrode during the anodization process.

Hydrofluoric Acid (HF)

Hydrofluoric acid was used for the anodization process at different pH value. The pH value was adjusted by adding aqueous sodium hydroxide.

Platinum electrode (Pt)

Platinum electrode was used in the anodization process as the negative electrode.

Sodium hydroxide (NaOH)

NaOH is used to adjust the pH value of HF acid solution.

Deionized water

Deionized water was used to clean the Titanium foil after anodization process. This is because the excess acid might be present on the Titanium foil which could further etch off the surface if not properly cleaned.

Results and Discussion

Morphology Observation

Fig.1 (a) and (b) shows the FE-SEM image obtained with voltage 20 V in pH 1 of HF solution for 10 minutes at current of 1.41 A with magnification of 10 kX and 200 kX. Fig.1 (a) shows the presence of TiO₂nanoparticles formed on the surface of the titanium foil as well as cracks also been detected in 10kX magnification. Fig.1 (b) shows the distribution of TiO₂ particles on the surface of the titanium foil at higher magnification. The nanotube structure is not seen in both magnifications but only TiO₂ particles are present.

The absence of nanotube structure during the anodization process at pH1 might be due to the etching of the titanium foil surface by the strongly acidic electrolyte. Hence, the growth of the tubes and the dissolution process is fast and cant sustain the propagation of the tubes. The crack observed on the surface of TiO₂ might be from the raw materials which had some scratches on the surface but not visible to the eyes.

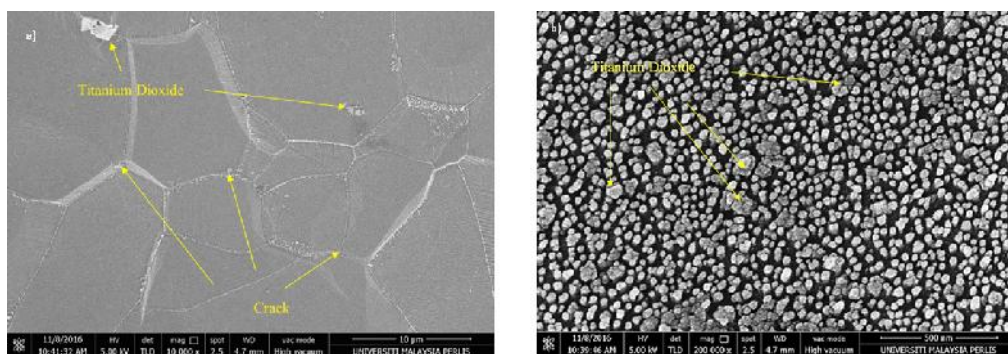


Fig.1 (a): FE-SEM image of surface structures obtained with 20 volts in pH 1 of HF solution for 10 minutes with magnification of 10 kX; **(b):** FE-SEM image of surface structures obtained with 20 volts in pH 1 of HF solution for 10 minutes with magnification of 200 kX.

Figure 2 (a) and (b) shows the FE-SEM image obtained with voltage 20 V in pH 5 of HF solution for 10 minutes at current of 0.28 A with magnification of 10 kX and 200 kX. Fig.2 (b) shows that the nanotubes were successfully formed on the titanium foil. The size of the nanotubes inner diameter is about 20 – 75 nm while the wall thickness is about 4.5 – 26.6 nm. The smallest size of nanotube inner diameter observed with size of 20.13 nm while the largest nanotube diameter identified is 73.01 nm. The TiO₂ nanotubes inner diameter size and wall thickness distribution is not uniformly formed.

In Figure 2 (a), the formation of the dark side in the FE-SEM image is because of the surface imperfection during the anodization process. From Figure 2 (b), TiO₂ nanotubes were successfully formed at pH 5 due to the acid condition which is weak acid which allows the formation of nanotubes. The surface was fully covered with the TiO₂ nanotubes structure with applied current of 0.28 A. Therefore, pH 5 is suitable for the formation of TiO₂ nanotubes as

the acidic electrolyte is mild and can sustain the dissolution and subsequent propagation and growth of the nanotubes.

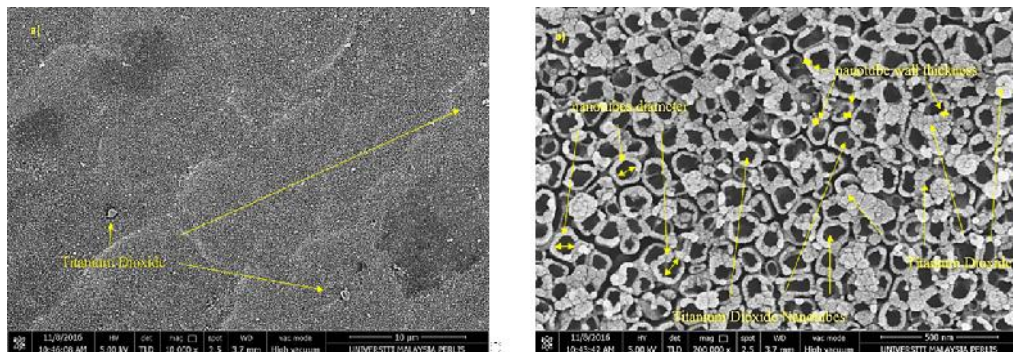


Fig.2 (a): FE-SEM image of surface structures obtained with 20 volts in pH 5 HF solution for 10 minutes with magnification of 10 kX; **(b):** FE-SEM image of surface structures obtained with 20 volts in pH 5 HF solution for 10 minutes with magnification of 200 kX.

Fig. 3 (a) and (b) shows the FE-SEM image obtained with applied voltage of 20 V in pH 9 of HF solution for 10 minutes and with a current of 0.08 A with magnification of 10 kX and 200 kX. Fig.3 (a) shows the TiO₂ nanoparticles with magnification of 10 kX. The surface is not smooth and have many agglomerated-like particles been observed while Fig.3 (b) shows no tubes formed on the Ti-foil surface.

The nanotubes were not produced at this pH and with a low current value was recorded. The current value for pH 9 is 0.08 A which is lower than the current value for pH 5 which is 0.28 A. When the current value is low, the chemical etching rate is lower which leads to the lower oxide layer formation on titanium foil. The thick barrier layer decreases and the pore form cannot grow into nanotubes.

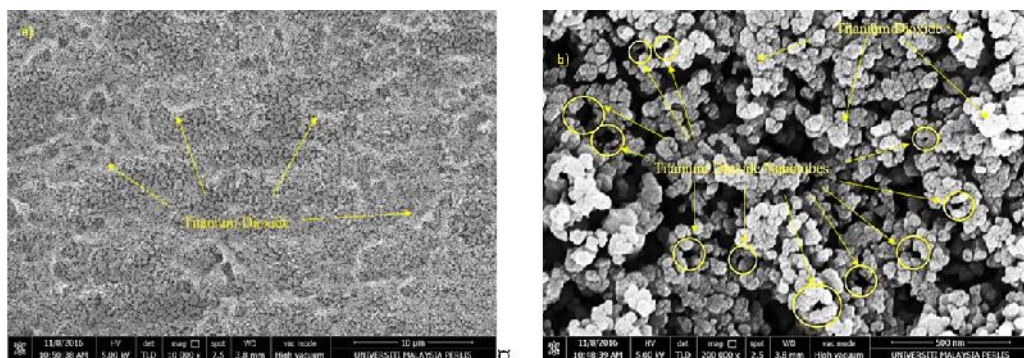


Fig. 3 (a): FE-SEM image of surface structures obtained with 20 volts in pH 9 HF solution for 10 minutes with magnification of 10 kX; **(b):** FE-SEM image of surface structures obtained with 20 volts in pH 9 HF solution for 10 minutes with magnification of 200 kX

Phase Analysis

The TiO₂ nanotubes fabricated via anodization process at pH 1, 5 and 9 of HF electrolyte was characterized with XRD. Fig. 4 shows the XRD patterns of raw TiO₂ nanotubes fabricated via anodization process with pH 1, 5, and 9 of HF electrolyte without heat treatment. Most of the peak observed was titanium peak formed.

Fig. 5 shows the XRD patterns of TiO₂ nanotubes fabricated via anodization process with pH 5 of HF electrolyte and heat treated at different temperatures of 300, 500 and 700 °C with 3 hours soaking time and cooling rate of 5°/min. Based on Fig. 5, many of the peaks present was observed to be anatase phase structures when the TiO₂ nanotubes was heat treated at 300 °C and 500 °C. As the temperature is increased to 700 °C, many of the amorphous crystallizes into rutile phase as shown in 2θ of 27.92°, 36.61°, 38.73°, 40.43°, 53.36°, 56.96° and 70.94° that are assigned to (110), (101), (200), (111), (210), (211), (210) and (310) lattice plane while the anatase peak only shown once at 2θ of 22.84° which is assigned to (101) lattice plane.

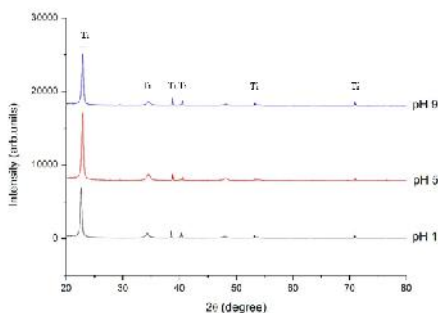


Fig. 4. XRD patterns of raw TiO₂ nanotubes fabricated via anodization process with pH 1, 5, and 9 without heat treatment.

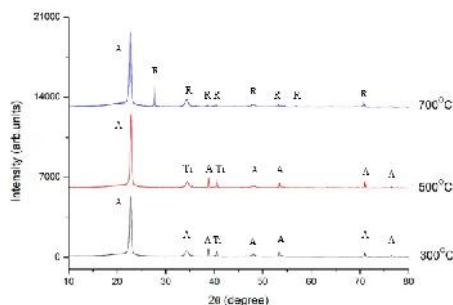


Fig. 5. XRD patterns of TiO₂ nanotubes fabricated via anodization process with pH 5 and heat treated with different temperature at 300 °C, 500 °C, and 700 °C.

Conclusion

The TiO₂ nanotubes was characterized by using field emission-scanning electron microscope with magnification of 10 kX and 200 kX to observe the morphology of TiO₂ nanotubes. The pH value of hydrofluoric (HF) electrolyte used are 1, 5 and 9. The titanium dioxide (TiO₂) nanotubes were successfully fabricated via anodization at pH 5 of HF electrolyte at 20 V for 10 minutes. The samples for pH 1, 5 and 9 were heat treated at 300 °C, 500 °C and 700 °C with 3 hours soaking time and cooling rate of 5°/min. The phase of TiO₂ nanotubes were analysed by using x-ray diffraction (XRD) machine. The sample phase was characterized from 10° – 80° with step rate at 5°/min. Anatase peaks were obtained when the TiO₂ nanotubes were heat treated at 300 and 500 °C, while the rutile structure was formed when heat treated to 700 °C.

Acknowledgements

This research was supported by Universiti Malaysia Perlis (UniMAP), supervised by Dr. Alaba Oladeji Araoyinbo and coordinated by Associate Prof Dr. Mohd Mustafa Al Bakri Abdullah.

References

- [1] F. Rodai, K. Hiroharu, G. Harrison, W. Pamiko, *Preparation of high quality nitrogen doped TiO₂ thin film as a photo catalyst using a pulsed laser deposition method*, **J. Thin Solid Films**, **454**, 2004, p. 162.
- [2] J. Zhao, X Wang, T Sun, L Li, *In situ templated synthesis of anatase single-crystal nanotube arrays*, **Nanotechnology**, **16**, 2005, p. 2450-2454.
- [3] H. Tsuchiya, M. Macak, L. Taveira, E. Balaur, A. Ghicov, K. Sirotna, P. Schmuki, *Self-organized TiO₂ nanotubes prepared in ammonium fluoride containing acetic acid electrolytes*, **J. Electrochemistry Communications**, **7**, 2005, p. 576-580.
- [4] M. Huang, Y. Wu, H. Feick, N. Tran, E. Weber and P. Yang, *Catalytic Growth of Zinc Oxide Nanowires by Vapor Transport*, **J. Adv. Mater.**, **13**, 2001, p. 113.
- [5] I. Csaki, G. Popescu, R. Stefanoiu, *Reactive Vacuum Infiltration Aluminium based Composite Hardness Variation with in situ Reaction Completion Level*, **Revista de Chimie**, **65**, 2, 2014, pp. 206-209.
- [6] G.L. Gheorghievici, C.T. Rusu, E. Voicila, I.M. Nafliu, A.M. Cimbru, S.K. Tanczos, *Titanium Dioxide for Biomedical Uses I. The controlled production of nanoparticles by hydrothermal synthesis moderated by dimedone*, **Revista de Chimie**, **68**, 1, 2017, pp. 11-15.
- [7] E. Joseph, **Coating and Surface Treatment Systems for Metals**, Finishing Publications Ltd. and ASM International, 1997, p. 34-38.
- [8] S. Mahshid, M. Askari, and M. S. Ghamsari, *Synthesis of TiO₂ nanoparticles by hydrolysis and peptization of titanium isopropoxide Solution*, **Journal Mater Process Technical**, **189**, 1-3, 2007, pp. 296-300.
- [9] L. Gang, W. Xuewen, C. Zhigang, C. Hui-Ming, and L. Gao Qing, (2009), *The Role of crystal phase in determining photocatalytic activity on nitrogen doped TiO₂*, **Colloid Interface Science**, **329**, pp. 331-338.
- [10] H. Xu, X. Wang and L. Zhang, (2008), *Selective preparation of nanorods and micro-octahedrons of Fe₂O₃ and their catalytic performances for Thermal decomposition of ammonium perchlorate*, **Powder Technology**, **185**, 2, pp. 176-180.

Received: June 12, 2017

Accepted: September 3, 2017