

THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF TITANIUM DIOXIDE NANOTUBES SYNTHESIZED IN THE FLUORIDE-BASED ELECTROLYTE

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Abstract

Titanium is one of the biomaterials commonly used for prosthetic devices due to its bio-inert properties. The discovery of titanium dioxide nanotubes (TDNTs) has created a great interest in medical applications such as dental and orthopedic implants. The synthesizing of TDNTs can produce different morphology, sizes and mechanical properties of the nanotubes – depending on the applied method. In this study, an electrochemical anodization method was used for synthesizing the TDNTs. A 100 ml mixture of 99% of ethylene glycol (EG), 1% of deionized water and 1 wt.% of ammonium fluoride (NH₄F) was used as the electrolyte of the electrochemical cell. Parameters such as anodization time and the voltage applied were used to alter the morphology of the TDNTs formed. The produced nanotubes were analyzed and characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and microhardness tester. The SEM results showed that the formed diameter of nanotubes was mainly affected by the anodizing voltage. The wall thickness was found to be irrelevant to the parameters conducted in this study. The diameter of nanotubes formed with an anodizing voltage of 30, 45 and 60 V have the diameters ranging from 46 nm to 71 nm. All of the TDNTs samples formed have a wall thickness between 11 nm and 13 nm. With the use of EG and NH₄F as an electrolyte, the array of TDNTs with honeycomb structure was formed. In general, hardness test showed that the hardness of the nanotubes was inversely proportional with the anodizing time. The anodizing voltage only has little effect on the hardness of the nanotubes. The nanotubes formed by 60 V have about 3 to 5% lower hardness compared to those formed by 30 V for different anodizing times.

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Introduction

Titanium is a metal commonly used as a biomaterial in the prosthesis and biomedical devices. The oxide layer on titanium surface protects the titanium matrix from corrosion, and it is biocompatible. Due to these facts titanium has become a metal that is widely used in dental and orthopedic implants [1].

With the discovery of titanium dioxide nanotubes (TDNTs) in 1998 by Kasuga and co-workers [2], the application of TDNTs as bone and dental implants have become an interest due to the similarity of the surface morphology between the human bones and TDNTs. The TDNTs can help create a larger surface area to ensure good osseointegration. Other than that, the nanotubes can also serve as reservoirs for drug delivery system to prevent infection. Various routes including sol-gel, template-assisted, hydro/solvothermal approaches, and by electrochemical means (anodization) may achieve a synthesis of 1D TiO₂ nanotubes. Among these methods, anodization is a relatively more straightforward and economically feasible method.

The anodizing conditions are essential to alter the characteristic of nanotubes formed during the synthesis process. The length of the nanotubes formed is longer when using the organic solution compared to the aqueous solution as electrolytes [3]. Besides that, a more acidic electrolyte can form shorter nanotubes [4]. Another factor that could affect the length of nanotubes is the anodizing time where longer anodizing time produced longer nanotubes [2].

The concentration of fluoride ions in the electrolyte and the anodizing voltage applied can change the diameter of the TDNTs produced. The study done by *Zwilling et al.* [5] concluded that a small addition of fluoride ions is the key to form the TDNTs using anodization. A progressive increase in fluoride concentration can reduce the diameter of the nanotubes [6]. On the other hand, increasing the anodizing voltage increases the nanotubes diameters [7].

Recently many studies have reported antibacterial properties of Cu material coated titanium alloys [8]. The presence of Cu element improves the mechanical properties, bio-corrosion and antibacterial properties of Ti-Cu alloys for biomedical application [9]. As copper is one of the promising metal dopants for alloys in biomedical application, this research uses Cu as the cathode for the formation of TDNT.

Objectives

In real life situation, different types of prosthesis applied at different parts of the human body require specific physical characteristic especially the surface morphology and the hardness. Surface morphology is essential regarding bonding between the human bone cell and the coating itself. Appropriate surface morphology will enhance the cell-adhesion and hence improve the rate of recovering. As for the hardness, rigid contact may be provided at the implant area to have a sustainable design. This study investigates how the anodizing parameters (anodization time and anodization voltage) affect the surface morphology and hardness of TDNTs. Hence, suitable parameters can be ascertained to suit the need of the prosthesis.

Experiment

The materials used in these experiments are ethylene glycol (EG), ammonium fluoride (NH_4F), titanium foil, copper foil, ethanol ($\text{C}_2\text{H}_5\text{OH}$), acetone ($\text{C}_3\text{H}_6\text{O}$) and deionized water. The reagent grade ethylene glycol with 99.5% purity and reagent grade ammonium fluoride with 98% purity are purchased from Friendemann Schmidt Chemical. The copper foil (99.9% trace metals) with a thickness of 0.1mm and titanium foil (99.7% trace metals) with a thickness of 0.127mm are purchased from Sigma-Aldrich Chemistry.

The titanium foils used for anodization were ground with different SiC emery papers and followed by polishing with 6 μm and 1 μm diamond paste to produce an optically reflective surface. Then it was immersed in acetone and sonicated in an ultrasonicator for 15 minutes. Subsequently, the titanium foil was washed and immersed in deionized water followed by 15 minutes of sonication. After that, the titanium foil was immersed in ethanol and sonicated for 15 minutes. Lastly, the titanium foil was washed and dried in the ambient room.

In the setup of the electrochemical cell, the titanium foil was connected to the anode of a DC power supply with a clip wire whereas the copper foil was connected to the cathode of the DC power supply with a wire. Copper foil was used in cathode because it is cheap and has been reported to be able to exhibit good biocompatibility for biomedical application [10, 18]. Both the foils were then immersed in a beaker containing 100 ml of electrolyte. The electrolyte is made up of 99 % of ethylene glycol, 1% of deionized water and 1wt% of ammonium fluoride. A magnetic stirrer was used to stir the electrolyte continuously throughout the anodizing process.

Once the electrochemical cell was set up entirely, the titanium and copper foil was connected to DC power supply with 30V. The anodization time was set for 1 hour, 3 hours and 5 hours respectively for different runs. The experiment was repeated by changing the applied voltage to 45V and 60V with an anodizing time of 1 hour, 3 hours and 5 hours respectively. All anodized samples were characterized by scanning electron microscopy (SEM), x-ray diffractometer and microhardness tester.

Results and Discussion

Microstructural analysis

The TiO_2 nanotubes formed were viewed by using the high-resolution scanning electron microscope (HRSEM). The SEM micrographs for each voltage are shown in Fig. 1 to Fig. 9 for the anodizing times of 1 to 5 hours. The dimensions of wall thickness and tube diameter were measured by software's tool when the desired micrographs were captured.

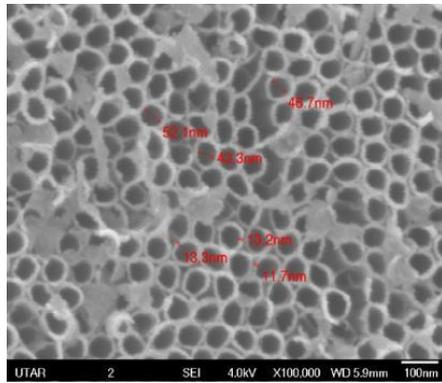


Fig. 1. 30 V and 1-hour anodizing time.

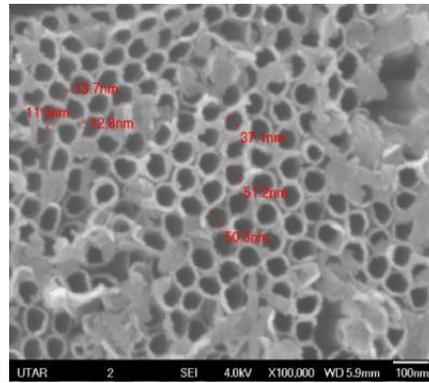


Fig. 2. 30 V and 3 hours anodizing time.

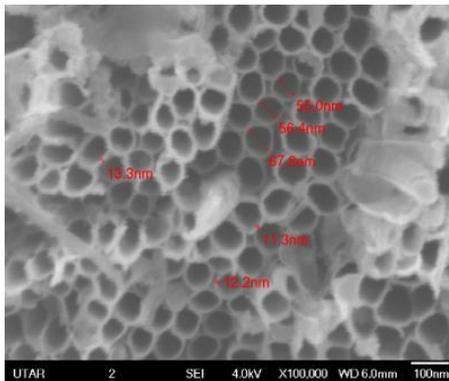


Fig. 3. 30 V and 5 hours anodizing time.

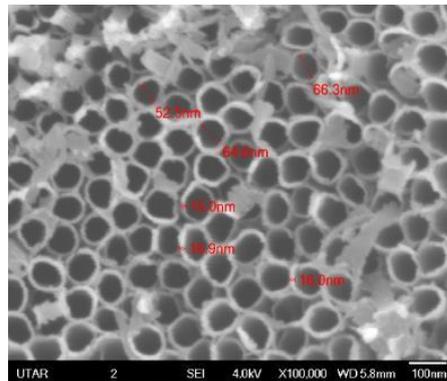


Fig. 4. 45 V and 1-hour anodizing time.

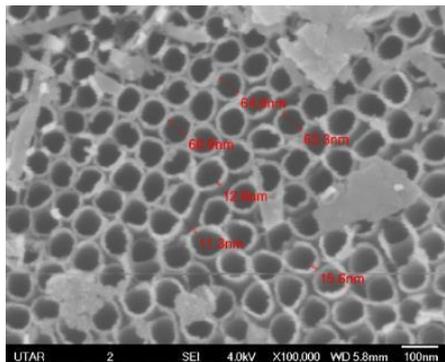


Fig. 5. 45 V and 3 hours anodizing time.

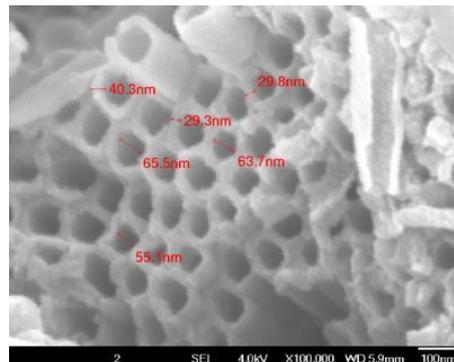


Fig. 6. 45 V and 5 hours anodizing time.

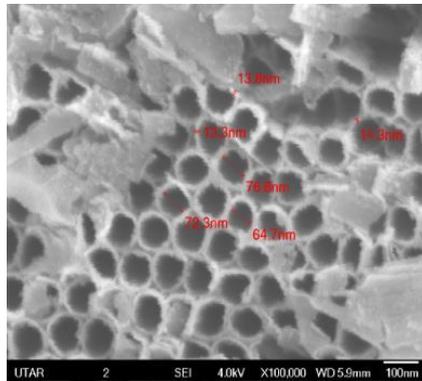


Fig. 7. 60 V and 1-hour anodizing time.

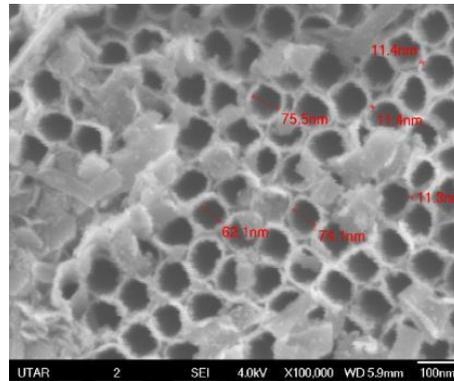


Fig. 8. 60 V and 3 hours anodizing time.

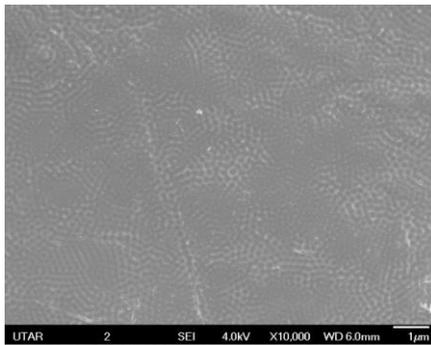


Fig. 9. 60 V and 5 hours anodizing time.

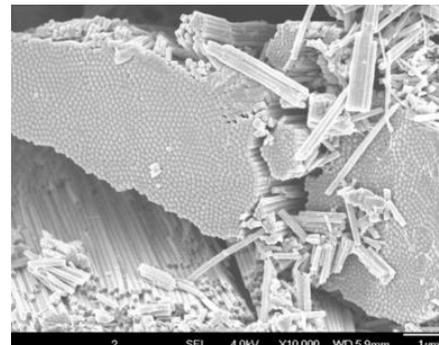


Fig. 10. Broken pieces of nanotubes formed under 60V with 5 hours of anodizing time.

The nanotubes are a well-aligned 1D structure in a specific growth direction (Fig. 1-10). The nanotubes formed under 45 V have thicker wall compared to those samples synthesized under a voltage of 30 V. Besides that, the nanotubes wall thickness is increasing proportionally to voltage. This observation is in line with the finding in Bauer et al. [7] whereby the authors found that the wall thickness of nanotubes linearly depends on the applied voltage. Also, the wall thickness of the nanotubes in the sample anodized with 45 V for 5 hours has increased by 160% compared to those anodized for 3 hours. This phenomenon could be due to the longer anodizing time at a higher voltage which leads to the extensive formation of the TiO_2 coating on the nanotube's wall. This finding is inline with the observation reported in Bauer et al. [7], whereby the authors found that the wall thickness of nanotubes linearly depended on the applied voltage [11].

For the nanotube arrays formed with 60 V of applied voltage, the surface structures were more irregular and rough. The well-aligned structure can only be obtained in some small areas. As for the sample of 60 V with 5 hours of anodizing time, the nanotubes were all covered up. The self-organized alignment of the nanotubes is still present even if there are many broken pieces of the nanotubes on the coating (Fig. 10).

A similar observation was reported by Qingyun et al. [12]; they found that the appearance of tubes was lost and discrete, hollow, cylindrical tube-like features was created. At the voltage higher than 40 V, the structure of nanotube is lost. This losing of nanotube structure could be attributed to over dissolution of tubes by fluoride ions [13]. Hence, the formation of the self-organized TiO₂ nanotubes coating is less effective under high voltage [14].

Calculating the average diameter of the nanotubes in each sample allows studying the effects of experimental parameters on the formed TiO₂ nanotubes morphology (Fig. 11).

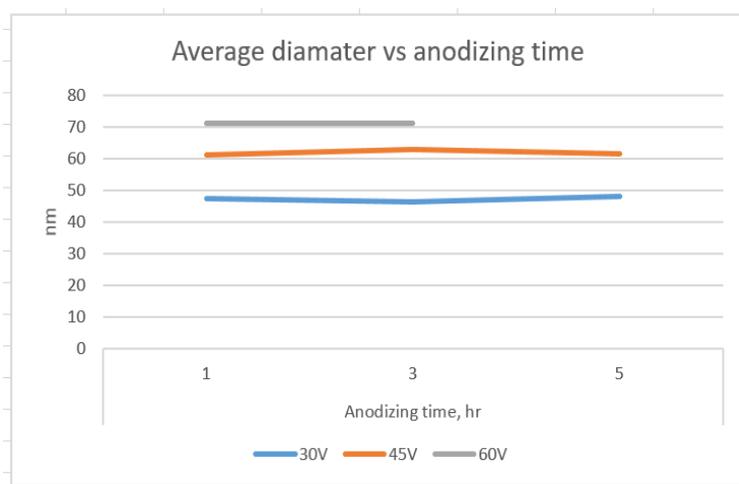


Fig. 11. Graph of average diameter vs. anodization time at different voltages.

The average diameter of the TiO₂ nanotubes increases gradually from 30, 45 to 60 V. At 30 V of the applied voltage, the average diameter of the nanotubes is from 46 to 48 nm for all anodizing times. For 45 and 60 V, the average diameter is 61 and 71 nm, respectively. In general, it is evident that the anodization time does not significantly affect the diameter of TiO₂ nanotubes [15].

Fig. 12 shows the average wall thickness as a function of anodizing time at different voltages. The wall thickness of the TiO₂ nanotubes formed was not significantly affected by the anodization time of 3 hours and below. The average wall thickness of all the samples ranges from 12 to 16 nm. Nevertheless, the sample under 45 V with 5 Hours of anodizing time was found to insistent with the trend; this could due to the result of the instability of the anodizing condition.

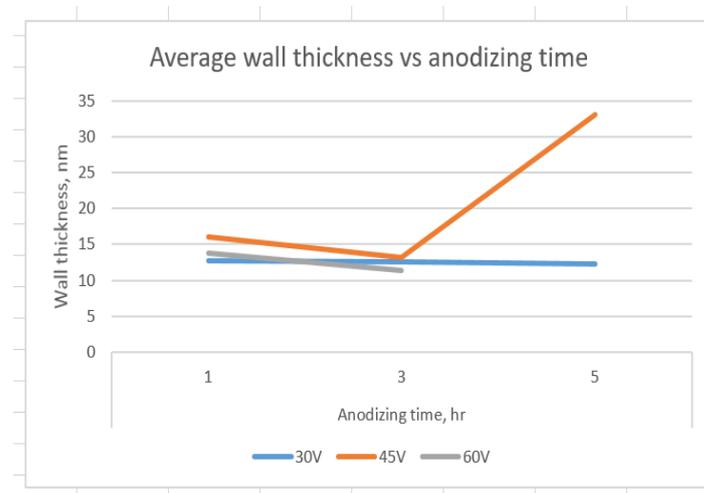


Fig. 12. Graph of average wall thickness vs. anodization time at different voltages.

The data indicates that the optimal anodizing time for thin wall thickness is 3 hours and below. The average wall thickness of all the samples, for these times, is around 12 to 16 nm. Nevertheless, there is an alien data which is the sample under 45 V with 5 hours of anodizing time. The data indicates that the optimal anodizing time for thin wall thickness is 3 hours and below.

X-Ray Diffraction (XRD) Analysis

The samples are investigated using the X-Ray Diffraction (XRD), to determine the composition of the anodized titanium foil. Firstly, the significant peaks can be obtained by observing the x-ray card data of titanium.

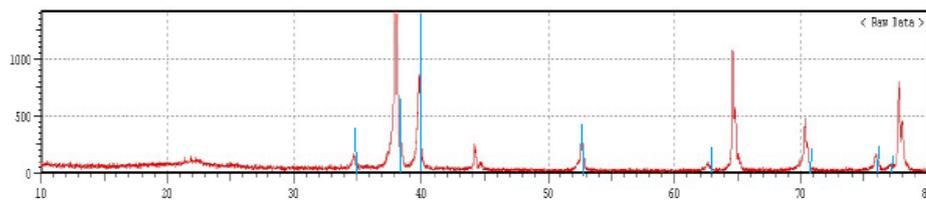


Fig 13. The X-ray card data of titanium (blue line), and XRD result of the original titanium foil (red line).

As shown in the Fig. 13, the three most significant peaks of the titanium are approximately located at 35°, 38.5°, and also 40° [16]. Next, the peaks of the x-ray card data are used to compare with the XRD result of the original titanium foil.

By comparing all the peaks of both spectra in Fig. 13, we can observe that the intensity of the peaks is different. However, the location of the peaks is similar to each other as the three most significant peaks of original titanium foil fall at about 38°, 40° and also 65° to indicate the presence of Ti. XRD tests were carried out on all samples to compare the peaks with that of the original titanium foil [17].

By comparing the XRD results of the nanotubes formed under 30 V, the three most significant peaks are all located at the same degrees which are about 38°, 40° and also 70°. However, the intensity decreases as the anodization time increases from 1 hour to 3 hours, and increases again at the 5 hours of anodization time. The decreasing of the intensity of titanium indicates that the composition of the titanium is gradually decreasing.

For the XRD results of the nanotubes formed under 40 V of applied voltage, the trend of intensity is similar to the samples of 30 V. The intensity decreases at first from 1 to 3 hours and grows back at 5 hours. Nevertheless, the location of the three most significant peaks is matching with the XRD result of the original titanium foil which is 38°, 40° and 70°.

As for the samples of nanotubes formed under 60V of applied voltage, the intensity decreases as the anodization time increases. The location of 3 most significant peaks is about 38°, 40° and also 71°. However, the last sample shows a very inconsistent result with more significant peaks compares to the other samples. This could be due to the failure in forming the nanotubes structure which in turn affects the overall composition of the sample.

As a conclusion, the formation of TiO₂ nanotubes is not efficient for an extended period of anodizing time. This can be proven by the results of the XRD which show inconsistency at 5 hours of anodizing time. This situation is similar to the HRSEM test which shows irregularity of average diameter and also walls thickness at the 5 hours of anodizing time.

Micro Hardness Test

The setting of the microhardness tester is set to 0.5 kg of force with a dwell time of 10 seconds. With the aim of getting results with higher accuracy, the hardness of each TiO₂ nanotubes sample is measured at three different locations on the surface. The average Vickers hardness value (HV) will then be calculated. The average hardness values of samples are plotted in Fig. 14 below.

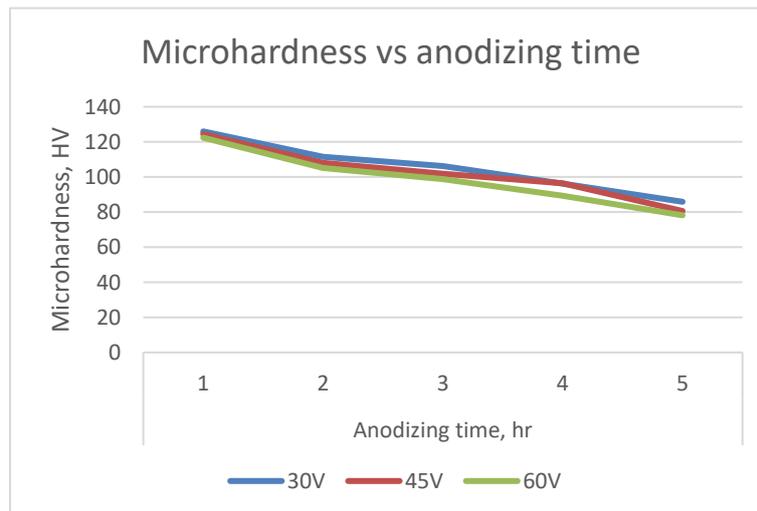


Fig. 14. Graph of average hardness vs anodizing time at different voltages.

From the Fig. 14, it is observed that the average hardness value decreases as the anodizing time increases. According to the research by *Haring, Morris and Hu* [19], the diameter of the TiO₂ nanotubes increases as the voltage applied to the anodization increases, which is verified in our results. The strength of the nanotubes with larger diameter was reported to be weaker compared to the strength of the nanotubes with a smaller diameter, assuming the wall thickness remains constant [19]. Also, during high anodizing voltage, the rate of movement of ions towards the electrode increases. Eventually, the potential difference between cathode and anode slowly increases which will result in higher rate of anodization. Consequently, the hardness of the nanotubes decreases when the rate of nanotubes formation increases.

Conclusions

The objective of this study is achieved successfully by forming the TiO₂ nanotubes at different parameters of anodization time, and the applied voltage by using the electrochemical anodization method.

The micrographs of the formed nanotubes can be observed under the high-resolution scanning electron microscope (HRSEM). The self-organized structure of the TiO₂ nanotubes coating can be seen. This proves that the self-organized TiO₂ nanotubes can be formed via the electrolyte with the mixture of ethylene glycol, deionized water, and ammonium fluoride. Next, the average diameter of the TiO₂ nanotubes of each sample is calculated. The average diameter does not increase with the anodization time, but higher anodizing voltage will increase the average diameter. At the same time, the average wall thickness of the samples is also calculated, and the result shows that wall thickness is affected by both the parameters. Nonetheless, there is some inconsistency of result in the samples with a more prolonged period of anodizing time. The formation of TiO₂ nanotubes coating is not suitable for the more prolonged period of anodizing time and also at a voltage higher than 30 V.

As for the X-ray diffraction analysis, the three most significant peaks of each sample are successfully matching with the XRD result of original titanium foil. This shows that the composition of the titanium foil after the anodization process remains constant. Moreover, the intensity of the peaks decreases as the anodization time increases which indicates that the composition of titanium decreases. Lastly, the microhardness test of the samples gives consistent results. The hardness value of the samples decreases as the anodization time and the voltage applied increase. This could be associated with the higher forming rate of TiO₂ nanotubes under a higher voltage applied.

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