

Utilization of Electrolyte Solution in Nanotube Formation on Ti-6Al-4V Metal AlloyCharlena^{1*}, Tetty Kemala¹ and Armi Wulanawati¹¹Department of Chemistry FMIPA IPB, Gedung Kimia Wing 1 Lantai 3, Jl. Tanjung Kampus IPB Dramaga Bogor 16680*Corresponding Author: charlena.ipb@gmail.com**Abstract (English)**

Formation of nanotube morphology on the surface of Ti-6Al-4V metal did not occur homogeneously, so when it was coated with hydroxyapatite, it did not merge well. One of the factors that affected the inhomogeneously formed nanotube was the utilization of electrolyte solution. The research has been done to observe the effect of electrolyte solution in the formation of nanotube morphology on the surface of Ti-6Al-4V metal alloy. Electrolyte solution that was used was ethylene glycol, HF, and NH₄F with time variation of an hour, 2 hours, and 3 hours. Formation of nanotube morphology on the surface of Ti-6Al-4V metal alloy was done using anodization process. The result showed that in HF electrolyte solution which was anodized for an hour α and β phase that composed Ti-6Al-4V metal alloy was formed, meanwhile when using electrolyte solution of ethylene glycol + NH₄F for 2 hours showed that there were pores that opened on Ti-6Al-4V metal alloy surface. Nanotube morphology on the surface of Ti-6Al-4V metal alloy was formed using electrolyte solution of ethylene glycol + NH₄F which was anodized for 3 hours.

Keywords: *electrolyte solution, metal alloy, nanotube, Ti-6Al-4V*

Abstrak (Indonesian)

Pembentukan morfologi *nanotube* pada permukaan logam Ti-6Al-4V tidak terjadi secara homogen, sehingga ketika dilapisi dengan hidroksiapatit maka tidak dapat menyatu dengan baik. Salah satu faktor yang mempengaruhi *nanotube* yang terbentuk tidak homogen yaitu penggunaan larutan elektrolit. Untuk itu dilakukan penelitian dengan tujuan melihat pengaruh larutan elektrolit dalam pembentukan morfologi *nanotube* pada paduan logam Ti-6Al-4V. Larutan elektrolit yang digunakan adalah etilen glikol, HF dan NH₄F dengan variasi waktu 1 jam, 2 jam dan 3 jam. Pembentukan morfologi *nanotube* pada permukaan paduan logam Ti-6Al-4V dilakukan dengan menggunakan proses anodisasi. Hasil penelitian menunjukkan bahwa pada larutan elektrolit HF yang dianodisasi selama 1 jam terbentuk fase α dan β yang menyusun paduan logam Ti-6Al-4V, sedangkan menggunakan larutan elektrolit etilen glikol+NH₄F selama 2 jam terlihat adanya pori yang membuka pada permukaan paduan logam Ti-6Al-4V. Morfologi *nanotube* pada permukaan paduan logam Ti-6Al-4V terbentuk dengan menggunakan larutan elektrolit etilen glikol+NH₄F yang dianodisasi selama 3 jam.

Kata kunci: *larutan elektrolit, nanotube, paduan logam Ti-6Al-4V*

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INTRODUCTION

The research of implant material in orthopedic and dental field kept developing along with the increasing need for bone implant or bone damage

problem. Implant material that has been known to be used in orthopedic and dental field is metal. Type of metal which has been widely used for bone implant application is stainless steel, cobalt,

titanium and its alloy [1]. Titanium and its alloy such as Ti-6Al-4V has advantages compare to other metals which are its high biocompatibility, good endurance against corrosion, and good mechanical properties such as its hardness and wear resistance [2]. However, titanium and its alloy have a low bioactivity [3] so that it needs treatment on its surface.

Titanium and its alloy bioactivity can be enhanced through electrochemical modification on the Ti-6Al-4V metal surface, forming oxide layered nanotube that can increase osteointegrity and bioactivity because it stimulates osteoblast cells to attach on implant metal and grow the new bone cells [4]. Oxide layered nanotube on Ti-6Al-4V metal can be formed using anodization technique [5]. Anodization is the electrochemical coating process that can cause a material to form titanium oxide layer that has high endurance against corrosion and good hardness. The advantage of modification through anodization is its simplicity and it can produce oxide layer with higher hardness value than its parent metal. By choosing this method, we expect the oxide layer to have good thickness and hardness as well as good corrosion durability and wear resistance.

MATERIALS AND METHODS

Materials

Ti-6Al-4V metal alloy, ethylene glycol, NH_4F , $(\text{NH}_4)_2\text{SO}_4$, HF, ethanol, acetone, distilled water.

Synthesis of nanotube on Ti-6Al-4V using anodization method

Pre-treatment was needed before anodization process was used to form nanotube on Ti-6Al-4V metal alloy. Ti-6Al-4V metal was prepared with diameter 14 mm and thickness 2.5 mm. The metal was sanded, washed with acetone, ethanol, and distilled water using ultrasonication for 30 minutes. The metal was then soaked in the mixture of acid solution (3 mL HNO_3 , 1 mL HF, and 10 mL H_2O) for 2 minutes, rinsed with distilled water, and dried up [6].

The formation of nanotube using anodization method was done by preparing 2 electrodes, Ti-6Al-4V plate at anode cell and Pt plate at cathode cell which was connected to power supply. In this

study, some electrolyte solutions were used with anodization time variation (1,2, and 3 hours). For the first treatment, both electrodes were dipped in 200 mL electrolyte solution containing NH_4F 0.4% (b/v), H_2O 5% (v/v), and ethylene glycol 95% (v/v) and stirred at 180 rpm using magnetic stirrer. For the second treatment, electrodes were dipped in HF 5% (b/v) [7]. For the third treatment, electrodes were dipped in 1 M $(\text{NH}_4)_2\text{SO}_4$ with the addition of NH_4F 0.5% (b/v) for 1 and 2 hours [8]. For the fourth treatment, electrodes were dipped in 0.6% NH_4F in ethylene glycol and distilled water (9:1) with voltage of 20 V for 3 hours. Anodization process produced hydrogen gas bubble around Pt wire at 20 V DC [6]. After anodization, obtained plate was rinsed slowly with distilled water, dried and calcinated at 500 °C for 3 hours [9]. Anodization product was characterized using stereo microscope and SEM.

RESULT AND DISCUSSION

Anodization process was occurred through electrolysis cell, which is the occurrence of oxidation reaction on positively charged anode and reduction reaction on the negatively charged cathode [10]. The oxide layer was formed on oxidized anode. On the anodization circuit, Ti-6Al-4V metal was functionalized as anode so that the oxide layer was formed on its surface and Pt metal was functionalized as cathode at DC current that was connected to power supply. Anodization circuit was showed in Figure 1.

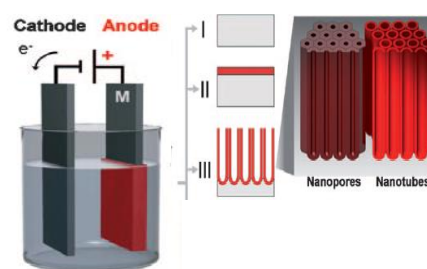


Figure 1. Anodization Circuit.

Before anodization process, metal was prepared by sanding its surface to smooth the metal surface. The next step was to eliminate the contaminant on metal by sonication in acetone:ethanol:distilled water separately with duration 15 minute each. In this study, anodization was carried out at the voltage of 20 Volts because

at the voltage over 40 volts, nanotube would disappear or could not be formed, meanwhile if the voltage was under 20 volts, nanotube pores would be sparse. According to Ghicoy *et al.* [11], the optimal potential value for nanotube pores formation was 20 V. Ti-6Al-4V metal alloy surface was observed using stereo microscope and SEM.

The Result of Ti-6Al-4V Metal Alloy Characterization Using Stereo Microscope.

The characterization using stereo microscope showed that, there were two Ti-6Al-4V metal alloys that were detected having nanotube, which were the sample that were dipped in HF solution and the sample that was dipped in ethylene glycol + NH₄F. Sample with HF electrolyte solution treatment for 1 and 2 hours showed the presence of nanotube, but the one with 1-hour anodization time, had more distinct nanotube. Nanotube presence was also observed on the sample which was dipped in ethylene glycol + NH₄F solution and anodized for 2 hours, meanwhile the sample with 1-hour anodization time, did not show the presence of nanotube. This was the result of characterization using stereo microscope.

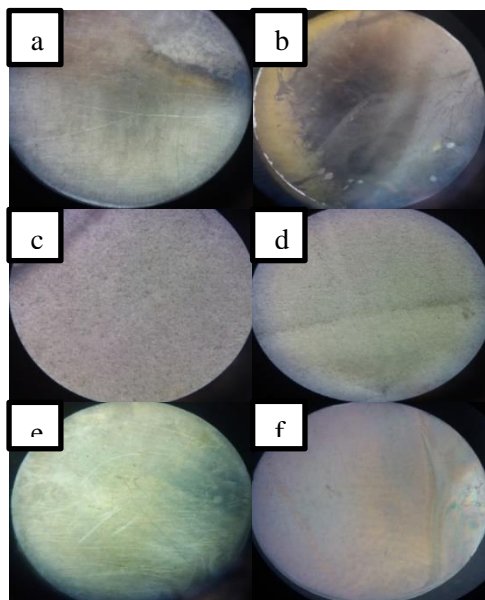


Figure 2. Stereo microscope characterization images for sample in electrolyte solution (a) (NH₄)₂SO₄+NH₄F 1 h (b) (NH₄)₂SO₄+NH₄F 2 h

(c) HF 1 h (d) HF 2 h (e) ethylene glycol+NH₄F 1 h (f) ethylene glycol +NH₄F 2 h.

Stereo microscope image for Ti-6Al-4V metal alloy surface which was anodized in NH₄F + ethylene glycol electrolyte solution for 3 hours, showed only scratches on the surface of the metal alloy but there were no nanotube pores formed. Nanotube observation using stereo microscope was less favorable than the observation using SEM.

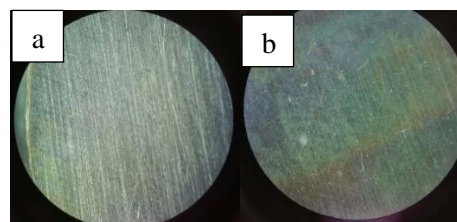


Figure 3. Stereo microscope characterization images of Ti-6Al-4V surface with (a) anodization and (b) without anodization.

The Result of Ti-6Al-4V Metal Alloy Characterization Using SEM

SEM analysis on Ti-6Al-4V metal alloy was done to see the formed nanotube morphology. There were two phases on the metal samples, α and β phases. Phase α was the phase which was rich in Al metal (HCP), meanwhile phase β rich in V metal (BCC) [8]. SEM characterization showed that there were two phases (α and β) in sample which was anodized using HF solution. This result was comparable to the research that was done by Macak *et al.* [8] which stated that there were two phases in ternary titanium alloy, such as Ti-6Al-47Nb and Ti-6Al-4V, but on the sample, that was anodized in ethylene glycol + NH₄F for 2 hours, those phases were not clearly visible. This could be caused by the viscosity differences. Ethylene glycol electrolyte solution was more viscous than HF. One of the factor that affected nanotube formation was the type and concentration of the electrolyte solution [13].

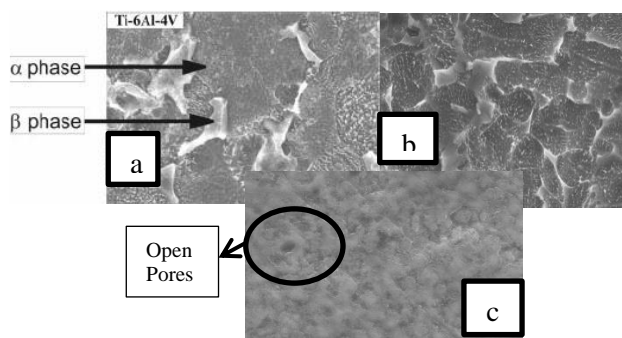


Figure 4. SEM characterization images of Ti-6Al-4 V metal alloy using electrolyte solution (a) HF for 30 minutes (Macak *et al.* 2005) (b) HF for 1 hour with magnification 5.00 x (c) ethylene glycol + NH₄F for 2 hours.

The result of sample characterization using SEM has not yet showed the formation of nanotube, but there was a possibility that the nanotube would form. Sample with HF electrolyte solution treatment which was anodized for 1 hour showed the presence of two phases (α and β) on the sample surface, but nanotube has not been formed. Meanwhile, the sample with ethylene glycol + NH₄F electrolyte solution treatment for two hours showed opening pore that formed nanotube on metal alloy surface (Figure 4).

On the metal with HF electrolyte solution treatment and anodization time of 1 hour, the nanotube has not been formed because F⁻ ion concentration in HF was too low. The concentration of HF that was used in this study was 5% wt. According to Roy *et al.* [2], the pore formation was the result of the competition between oxide formation through electrochemical process and chemical dissolution by F⁻ ion. The concentration of F⁻ ion in the solution influenced the nanotube morphology [12,13]. Without F⁻ ion, chemical dissolution which caused the formation of the pore would not happen, meanwhile high F⁻ concentration could produce inhomogeneous structure of nanotube [13]. The optimum concentration of F⁻ ion was needed in the formation of nanotube. The nanotube has not been formed in the HF electrolyte solution because HF which was used in this study was technical HF which was low in concentration although the anodization time was optimum. Bai [14] reported

that anodization using HF electrolyte solution needed to be done for 3 hours to achieve a perfect nanotube.

In the treatment using ethylene glycol +NH₄F electrolyte solution with anodization time of 2 hours, sample showed nanotube prospective nanotube was starting to show as can be seen in figure 5. The formed pores have not been formed perfectly on the sample surface because the anodization time was not optimum. Anodization time was also an affecting factor in the formation of nanotube. Purwanti [15] stated that the result of characterization using SEM showed that TiO₂ nanotube which was formed by anodization for 4 hours using ethylene glycol +NH₄F had high and uniform porosity. Figure 6 showed SEM characterization image of the sample with ethylene glycol + NH₄F and HF electrolyte solution that was anodized for 1 hour.

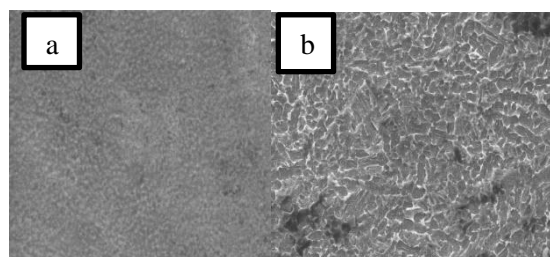
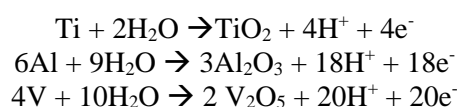


Figure 5. Result of SEM characterization of samples that was dipped in ethylene glycol +NH₄F (a) and HF (b) and anodized for 1 hour.

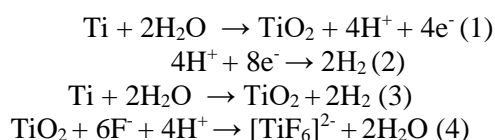
Nanotube on pure TiO₂ would only be formed on pure Ti has been reported as the main component of the nanotube that was formed on Ti-6Al-4V metal alloy, nanotube that was formed also contained vanadium, aluminum, and fluorine from the electrolyte solution such as HF/HNO₃/H₂O, which was used before anodization. During the process of nanotube TiO₂ nanotube formation not only Ti that was oxidized but also Al and V, forming Al₂O₃ and V₂O₅ [16]. The reaction as followed:



In this study, anodization was done at the voltage of 20 V for 3 hours using NH₄F 0.6% (b/v)

in ethylene glycol:distilled water (9:1) which was the best condition for oxide layered nanotube, as comparable with the research that has been done by Pawelska and Cydzik [17]. The addition of ethylene glycol in the electrolyte solution could decrease heat that was caused by reaction. The anodization on the Ti-6Al-4V metal would form TiO_2 , VO_2 , and Al_2O_3 oxide layers. According to Pawelska and Cydzik [17], most of the oxide layer was TiO_2 , because titanium was the dominant compound in Ti-6Al-4V metal alloy.

The mechanism of the oxide titanium formation through oxidation electrochemically on the surface of Ti-6Al-4V metal was showed in the reaction below:



Reaction (1) showed oxidation of titanium (anode) by H_2O producing TiO_2 . Water was the oxygen supply in anodization solution. During Anodization, H_2 gas was found around the cathode because of the reduction of H^+ into H_2 (2). The overall reaction of TiO_2 formation was showed in Reaction (3). The oxide layer of TiO_2 would react with fluorine ion (4) from the NH_4F which was the key of the nanotube formation. Nanotube formation was heavily affected by F^- ion. The detailed mechanism of nanotube formation by F^- ion has not been discovered.

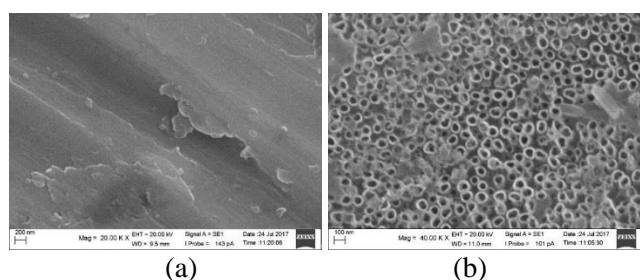


Figure 6. SEM characterization image of TiAl4V without anodization(a) and nanotube formed through anodization (b).

Oxide layered nanotube could be visualized as a layer with tube-liked pores with the diameter in nanometer scale formed in the surface of metal.

Figure 6 (a) was the image of SEM with magnification of 20.000 on the Ti-6Al-4V without anodization so that there was no nanotube formed. Oxide layered nanotube through anodization showed in Figure 7 (b) with the magnification of 40.000. Figure 7 showed the formed nanotube by the presence of pores. Tube-like pores were classified as nanotube because its average diameter size was 28.05 nm.

CONCLUSIONS

The result of this study showed that using HF electrolyte solution with anodization for 1 hour, α and β phases that composed Ti-6Al-4V metal alloy was formed, meanwhile using ethylene glycol+ NH_4F for 2 hours resulted in the opening pore on the surface of Ti-6Al-4V metal alloy. The nanotube morphology on the surface of Ti-6Al-4V metal alloy was formed when ethylene glycol + NH_4F electrolyte solution was used and anodized for 3 hours.

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