



# Effect of anodizing time on the hardness and tribological properties of Ti–6Al–4V

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## Abstract

Electrochemical anodization of the Ti–6Al–4V alloy was performed using two types of organic electrolytes, one of NH<sub>4</sub>F in ethylene glycol and the other of NH<sub>4</sub>F in glycerol. The anodization times and voltages were varied to observe changes in the hardness and friction coefficients. Hardness values of 4.14 GPa and 4.68 GPa were achieved for ethylene glycol and glycerol, respectively. Relative to the untreated alloy the friction coefficient decreased to a value of 0.45 for both electrolytes. These improvements are attributed to the formation of TiO<sub>2</sub> nanotubes with diameters ranging from 27 to 86 nm.

## Introduction

The Ti–6Al–4V alloy possesses characteristics such as good corrosion resistance, high hardness, low density, and high biocompatibility, making it an excellent material for applications in biomedicine, aerospace, among other areas [1, 2]. However, the alloy tends to have a low wear resistance [2]. To improve this property, various synthesis methods have been employed, one such method is electrochemical anodization, in contrast to other methods, is an economical and highly reproducible option [3]. It allows for the growth of nanostructures, which enhance hardness and reduce the coefficient of friction, both attributes are essential for applications in the fields. Therefore, this study involved the electrochemical anodization using two types of organic electrolytes while varying the time and voltage to evaluate their effects on the morphology, hardness, and tribological behavior of the Ti–6Al–4V alloy.

## Materials and methods

Grade 5 titanium sheets (2 × 1 cm) were polished using silicon carbide sandpaper with grain sizes ranging from 80 to 1200. The samples were then cleaned in an ultrasonic bath using acetone, ethanol, deionized water, and then dried with hot air. The anodization process was conducted at room temperature using two organic solutions, both composed of 0.15 M NH<sub>4</sub>F and 10% water. One solution contained 90% ethylene glycol, and the other contained 90% glycerol. The solution was prepared under magnetic stirring. The grade 5 titanium sheets served as the anode and a graphite plate as the cathode. The anodizing process was carried out in two stages with respect to the voltage used. The first stage involved the application of a constant voltage for a specific period. In the second stage, a constant voltage was initially applied, and after a certain interval, the voltage was doubled, using voltages in the range of 10–60 V, and anodizing times from 10 to 120 min were applied. Finally, the samples were removed from the solution, cleaned with ethanol, and dried with hot air. The samples anodization with ethylene glycol were identified with the letters A, B, C, and D, whereas the samples anodized using glycerol were designated with the letters E and F. The morphology and chemical composition of the samples were studied using a field emission scanning electron microscope (JEOL JSM-7600F) equipped with an energy-dispersive X-ray spectrometer (Bruker XFlash 6-10). Hardness tests on the anodized surfaces were conducted using a Vickers microhardness tester (Mitutoyo HM-125) with loads ranging from 0.05 to 2 kgf, a 15-s dwell time,

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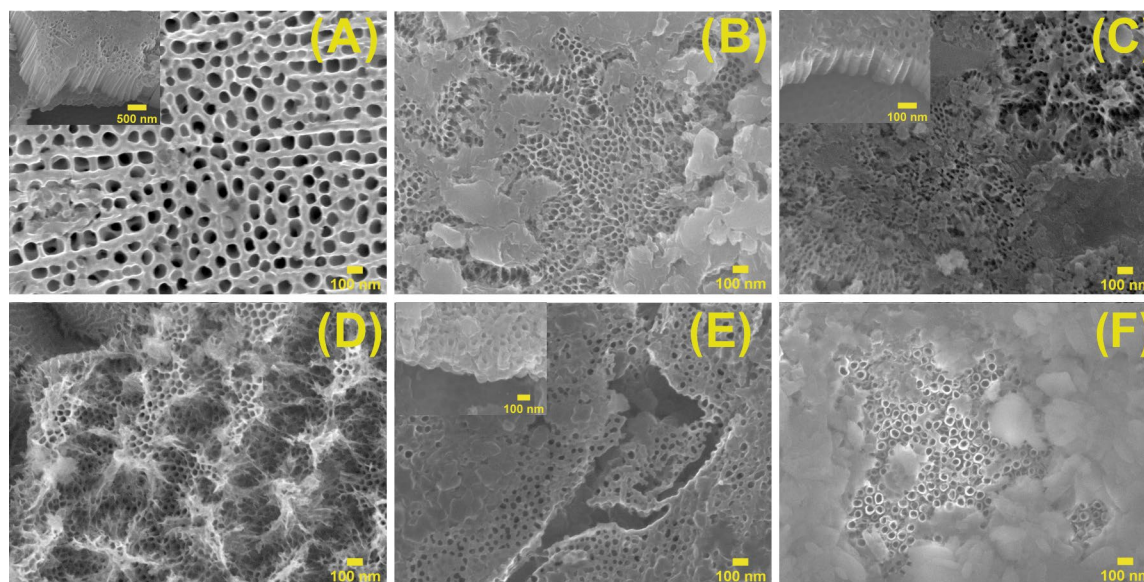
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and three repetitions per sample to determine the average microhardness values. The hardness values were adjusted using the Korsunsky equation [4]. To determine the coefficient of friction, tests were performed using the “Pin-on-Disk” technique according to ASTM G99 standards, at room temperature ( $25 \pm 1$  °C) and  $59 \pm 3\%$  relative humidity. The test parameters included a 6 mm diameter 100Cr6 steel pin, a workload of 5 N, a 3 mm test radius, a linear velocity of 0.5 cm/s, a test distance of 10 m, and a test time of 33.18 min. The test was conducted four times on each of the electrochemically anodized surfaces, and the results were averaged.

## Results

Figure 1 shows the images of the morphology of the samples obtained using the two electrolytics and at different anodizing voltages and times. Figure 1A–D corresponds to samples anodized with ethylene glycol and Fig. 1(E and F) with glycerol. For the sample shown in Fig. 1A a constant voltage of 60 V was used for 10 min, whilst for the case of Fig. 1B the same voltage was used for 30 min. Significant changes in morphology were observed, including a reduction in nanotube inner diameters from 86.80 to 27.38 nm with the increased anodization time. Additionally, the growth of tubes in Fig. 1A resembled a mesh, while in Fig. 1B, a honeycomb structure covered by a layer of titanium oxide residues [5–7]. This last structure was also observed by other

groups when  $\text{NH}_4\text{F}$  was used as the fluoride source [5, 8]. It has been reported that time and voltage primarily influence diameter and length of the nanostructure [9], with increased time causing a reduction in pore diameter at the bottom of the tube, giving a decreased diameter at the top [10, 11]. On the other hand, when the synthesis was carried out using a two-step voltage approach (Fig. 1C and D), this consisted of 10 V for 30 min and then increased to 20 V for 60 min, sample of Fig. 1C, while for Fig. 1D the same voltages were used, but with times of 60 and 120 min. A similar morphology was observed as with the single-step procedure, but with the two-step method, the nanotube diameters were seen to increase from 27.11 to 33.69 nm rather than decrease as observed with single-step process. This change is attributed to the second voltage, which, despite being lower than in the single-step procedure, was applied for a longer time, favoring the charge transport rate, and directly affecting oxide dissolution [12]. The sample shown in Fig. 1E corresponds to anodization using 30 V for 30 min, minimal growth on the surface can be seen due to the highly viscous nature of glycerol, which reduces the relative permittivity of the oxide and increases its dielectric breakdown voltage [13, 14]. Figure 1F shows the surface of the sample which was prepared using the two-step process of 10 and 20 V for times of 30 and 60 min, respectively. A similar result can be seen as for the sample anodized with ethylene glycol using the two-step voltage with the nanotubes being covered with oxide [15]. Likewise, when the times were increased (60 and 120 min) no nanostructure formation was observed. The

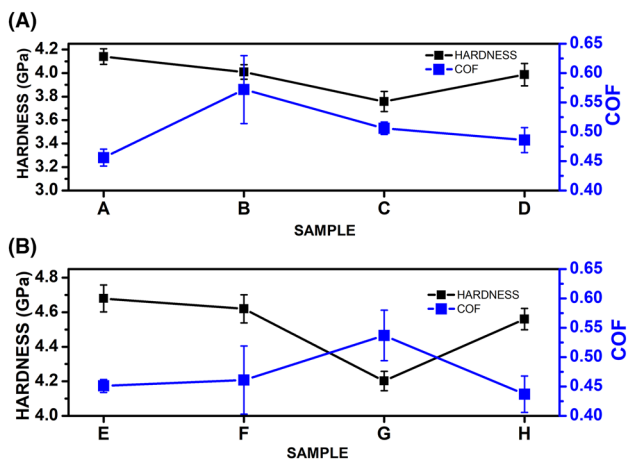


**Fig. 1** Top-view and cross-sectional view (inset) of samples obtained through electrochemical anodization using ethylene glycol-based electrolytes (A–D) and glycerol (E–F). Experimental conditions included **A** 60 V for 10 min, **B** 60 V for 30 min, **C** 10 V for 30 min and 20 V for 60 min, **D** 10 V for 60 min and 20 V for 120 min, **E**

30 V for 30 min, and **F** 10 V for 30 min and 20 V for 60 min. In the top view of each sample, the scale bar corresponds to 100 nm. In the cross-sectional view, the scale bar is shown at 500 nm for A and 100 nm for C and E

**Table 1** Chemical composition obtained through EDS analysis of the electrochemical anodization process using ethylene glycol and glycerol

Sample	Element (at.%)				
	O	F	Al	Ti	V
A	58.86	10.94	2.48	26.66	1.06
B	49.99	25.90	2.57	21.57	–
C	51.56	25.95	2.15	19.10	1.25
D	41.07	33.19	3.04	21.87	0.83
E	30.51	40.95	2.26	24.32	1.96
F	26.56	33.05	3.51	36.18	0.69

**Fig. 2** Microhardness and Tribology results graphs: **a** Sample anodized with ethylene glycol, and **b** Sample anodized with glycerol

chemical composition of the studied samples is presented in Table 1, with labels A, B, C, and D corresponding to

ethylene glycol samples and E and F to glycerol samples. It has been reported that after the electrochemical anodization process, an amorphous phase of titanium oxide is obtained [1, 13, 16]. Therefore, a technique such as EDS is employed to confirm the formation of  $\text{TiO}_2$ . However, factors such as the chemical composition of the substrate and the dissolution rate of the oxide layer can lead to the formation of a combination of oxides of the alloy's elemental constituents with varying stoichiometric ratios [7, 8].

On the other hand, Fig. 2 shows the results of hardness and friction coefficients obtained by anodizing grade 5 titanium surfaces using single-step and two-step voltage, as well as time increments. Figure 2A corresponds to samples anodized with ethylene glycol, while Fig. 2B corresponds to glycerol. In general, samples anodized with glycerol gave higher hardness values (4.68 GPa) compared to ethylene glycol (4.14 GPa). Both groups also exhibited improvements compared to the alloy, which had a hardness value of 3.45 GPa. Likewise, the influence of increased time, primarily related to thickness and length, was observed [17]. For single-step voltage, an increase in time did not result in an increase in hardness. However, for two-step voltage, an increase in time led to a hardness increase of approximately 0.3 GPa. The coefficient of friction (COF) also showed improvements compared to the substrate, which had a COF of 0.65. All COF values exhibited a similar trend, with an inverse relationship with hardness; as hardness values increased, COF decreased, and vice versa. This behavior was observed in another study [18]. Finally, Table 2 summarizes the results obtained in this study, describing anodizing conditions, nanotube diameters, hardness, and coefficients of friction, as previously discussed. It should be noted that the surfaces anodized with glycerol with increased time were included in the table, even though these surfaces did not

**Table 2** Electrochemical anodization conditions and results obtained for diameter, hardness, and friction coefficients

Sample	Time (s)	Voltage (V)	Diameter (nm)	Microhardness (GPa)	Coefficient of friction
NH <sub>4</sub> F + ethylene glycol					
A	10	60	86.80 ± 12.89	4.14 ± 0.66	0.456 ± 0.14
B	30	60	28.37 ± 3.50	4.01 ± 0.06	0.57 ± 0.06
C	T <sub>1</sub> = 30 T <sub>2</sub> = 60	10 20	27.11 ± 4.85	3.75 ± 0.09	0.50 ± 0.01
D	T <sub>1</sub> = 60 T <sub>2</sub> = 120	10 20	33.69 ± 3.29	3.98 ± 0.09	0.49 ± 0.02
NH <sub>4</sub> F + glycerol					
E	30	30	35.85 ± 7.03	4.68 ± 0.08	0.45 ± 0.01
F	60	30	–	4.62 ± 0.08	0.46 ± 0.06
G	T <sub>1</sub> = 30 T <sub>2</sub> = 60	10 20	38.35 ± 4.04	4.20 ± 0.05	0.54 ± 0.04
H	T <sub>1</sub> = 60 T <sub>2</sub> = 120	10 20	–	4.56 ± 0.06	0.44 ± 0.03

develop nanostructures. However, it was possible to measure their hardness and COF.

## Conclusions

TiO<sub>2</sub> nanotubes were obtained by anodizing the Ti–6Al–4V alloy using two types of organic electrolytes based on NH<sub>4</sub>F, one with ethylene glycol and the other with glycerol. It was observed that increasing the anodizing time resulted in a reduction of inner diameters for samples anodized with ethylene glycol using single-step voltage, a phenomenon observed in other studies. In the case of two-step voltage, an increase of 6.58 nm in diameter was observed with longer times. However, for glycerol samples, it was not possible to make diameter comparisons, as doubling the anodizing time in both groups did not lead to the development of nanostructures. Furthermore, the development of nanotubes with both electrolytes resulted in an improvement in Vickers microhardness values. However, glycerol-anodized samples exhibited higher hardness values. A decrease in hardness was also observed when two-step voltage was used for both groups. Regarding friction coefficients, samples anodized with single-step voltage exhibited a greater reduction compared to those anodized with two-step voltage. Furthermore, it was observed that an increase in time did not significantly improve the friction coefficient values. However, all surfaces studied exhibited lower COF values than the alloy, which had a COF of 0.64. Finally, the microhardness and tribological values showed a consistent relationship, where an increase in hardness resulted in a reduction of friction coefficients for all surfaces studied. This behavior was observed in both glycerol and ethylene glycol groups.

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**Authors contributions** RCR-J, SM, AL-V, and LZ-P synthesized and characterized the TiO<sub>2</sub> samples, while RCR-J, JH-T, JBS-G, and LG-G wrote and analyzed the results.

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**Data availability** The data reported in this study are available through corresponding author at reasonable request.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest in this work.

**Ethical approval** Not applicable.

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