Influence of thermal and electrochemical oxidation on the mechanical and corrosion properties of titanium alloy

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Abstract

In this paper, thermal oxidation and electrochemical anodizing processes were used to produce titanium oxide films on titanium alloy and to examine the effects of oxidation on mechanical and corrosion properties. The surface morphology oxide films, thickness and chemical composition of the surfaces were evaluated using scanning electron microscopy and energy dispersive spectroscopy. The microhardness of titanium oxide films prepared at different experimental conditions is maintained between 8.2 GPa and 9.6 GPa, measured by ultra tester. The microhardness increased with temperature and voltage. The values of roughness parameters Rz, Rt and Ra indicate a somewhat less roughness of the anodized samples. The values of the roughness parameter Rk are nearly identical for both groups of samples. The cyclic polarization tests showed that none of the tested samples were susceptible to localized corrosion. The oxide films produced by anodic oxidation on titanium alloy showed a higher corrosion resistance than the ones produced by thermal oxidation.

K e y w o r d s: oxidation, titanium alloy, roughness, corrosion

1. Introduction

Titanium alloy is usually used in biomedical implantation for its excellent biocompatibility due to its extraordinary mechanical properties and corrosion resistance. Titanium began to be used in the late 1930s as its low density and good mechanochemical properties had proved as a salient feature for implant application. Extensive research on titanium alloy in early 1950s employed several types of alloys, but mostly Ti6Al4V. Titanium is a light metal with density of $4.505\,\mathrm{g\ cm^{-3}}$ at 25 °C. Since aluminium represents a lighter element and vanadium is barely heavier than titanium, the density of Ti6Al4V alloy is very close to pure titanium. The melting point of titanium is 1665 °C, having two allotropic forms. One is α-form as closepacked hexagonal crystal structure with c/a ratio 1.587 at room temperature. Second is β form as body centred cubic structure which is stable at above 882.5 °C. Therefore, the presence of V in Ti6Al4V alloy is likely to form α-β at room temperature. The Young's modulus of α-titanium at room temperature is 107 GN m^{-2}, the shear modulus 38 GN m^{-2}

and Poisson's ratio 0.34. Titanium oxide consists of a range of oxygen to titanium ratios, such are Ti_3O to Ti_2O, Ti_3O_2, TiO, Ti_2O_3, Ti_3O_5 and TiO_2 [1–7]. Titanium alloys consist of different oxidation stages. The stable oxidation stage of titanium is TiO_2 (IV). However, in their native form, TiO_2 films have poor mechanical properties [8–12]. Therefore, any surface treatment that will thicken and toughen the oxide film, will improve mechanical properties of surface. The corrosion behaviour of Ti6Al4V alloy has been investigated by many authors [13–18]. It has been observed that Ti6Al4V alloy is highly corrosion resistant. Corrosion resistance of implant metals needs to be good because specific metal ions released from the implant can induce inflammation reactions around the implant resulting in implant rejection. Moreover, long-term exposure can be harmful to the human body [19–21]. Thermal oxidation of Ti6Al4V alloy decreases corrosion resistance when it is treated at 500 °C and 700 °C. Thermal oxidation and electrochemical anodizing processes are surface treatments used to form oxide films on the surface of titanium. In this paper, morphology, chemical composition, thickness, hardness and rough-

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ness of the oxide film produced by thermal oxidation and electrochemical anodizing processes have been investigated.

2. Experiment

2.1. Materials and oxidation treatments

The material used in this research was Ti6Al4V (wt.%) alloy. Specimens of size ø 5 mm × 10 mm were prepared from titanium ingot. In this investigation samples were divided into two groups. The first, group A samples, were subjected to oxidative isothermal heat treatment at 450 °C, 550 °C and 650 °C at normal atmospheric pressure. In the second category B, samples were oxidized by electrochemical anodizing in (40 ± 2) V, (50 ± 2) V and (60 ± 2) V. Before oxidation, all the corresponding surfaces were abraded by successive fine silicon carbide papers. These specimens were pickled in an acid bath (HNO_3 400 g L^{-1} + HF 40 g L^{-1}) for 10 min to remove the oxide layer completely and make the surface free of any contaminants. Specimens were washed in running water, cleaned ultrasonically with alcohol and finally dried in hot air. Electrochemical anodizing was performed in 3 % wet H_3PO_4 at room temperature at potentials ranging from 40 to 60 V for 10 min. The anodized specimens were rinsed using distilled water and then ultrasonically cleaned using detergent solution to remove all traces of acid on the surface. Anodizing in different voltages produced different colours on the surface of Ti alloy, apparently due to the formation of oxide layers of different thicknesses. Titanium oxide thin films were characterized by using several techniques for their composition, structure and mechanical properties.

2.2. Characterization of titanium oxide films

The surface micromorphologies of the titanium oxide films formed by anodic and isothermal oxidation treatments were observed using field emission scanning electron microscopy (VEGA TESCAN TS 5136 MM equipped with Oxford Instruments INCA energy dispersive spectroscopy). The thickness of oxide film was evaluated by a cross-sectional view of the SEM micrograph. The chemical compositions of metal oxides formed by both treatments were analyzed using EDS energy dispersive spectroscopy.

The microhardness was studied by depth-sensing indentation techniques using a dynamic ultra microhardness tester DUH-211S Schimadzu. The hardness of the titanium oxide films were measured with a Berkovich, three sided pyramidal diamond indenter, with 8 complete cycles of loading/unloading and loads ranging from 0.5 mN to 10 mN. Scanning electron microscope was used to observe the morphology of the indentation. The length of diagonal line of the indentation was measured by means of the image processing system. The load used here was 10 mN, the loading rate was 0.2 mN s^{-1}, the load was kept for 12 s. For each sample, 10 points of data were performed to obtain an average value.

Roughness measurements were performed using a stylus instrument Perthometer S8P with Gauss filter, cut-off $\lambda_c = 0.8$ mm, evaluation length $ln = 4$ mm and tip radius $r = 2$ mm.

2.3. Corrosion test

The corrosion resistance of anodically and thermally oxidized sample groups was examined by measuring the open circuit potential (OCP) and cyclic polarization for all samples per group using a Potentiostat/Galvanostat (EG & G PAR 273 A). Corrosion tests were carried out in electrolyte of 0.9 % NaCl solution (normal saline solution) at (36 ± 1) °C. The potentials of the working electrode (titanium specimen) were measured against a saturated calomel electrode (SCE; reference electrode). A high-density graphite electrode was used as the counter electrode. Luggin capillary was placed close to the working electrode. The specimens were stabilized in the corrosion cell for 16 min before the anodic polarization test.

The OCP was measured as a function of time in order to understand the corrosion behaviour of the samples in the electrolyte. As soon as the samples were immersed into the electrolyte, the initial potentials of the samples were noted and monitored as a function of time up to 10 min. When samples attained a constant potential, cyclic polarization began from –400 mV. The samples were scanned up to 1700 mV in the positive direction, and the scan was then reversed to –300 mV in the negative direction. The sweep rate was 1 mV s^{-1}. All samples were used to evaluate the corrosion resistance.
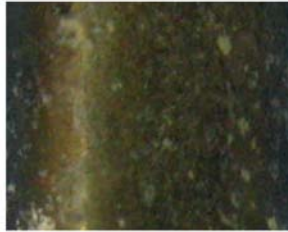
3. Results and discussion

3.1. SEM and EDS analysis

Table 1 shows different colours of oxide films on surface samples for A and B groups after thermal and electrochemical oxidations. Figure 1 shows SEM images of the isothermally and anodically oxidized sample surfaces. In addition, the density of the pores on the B group was higher than that on the A group.

Figure 1B shows the porous structures obtained with different anodizing voltages, 40, 50 and 60 V, in 3 % wet H_3PO_4 aqueous solution. At all anodizing voltage the morphology of the porous film is similar to that of porous (spongelike) alumina, with a typical

Table 1. Colors of samples with oxide films

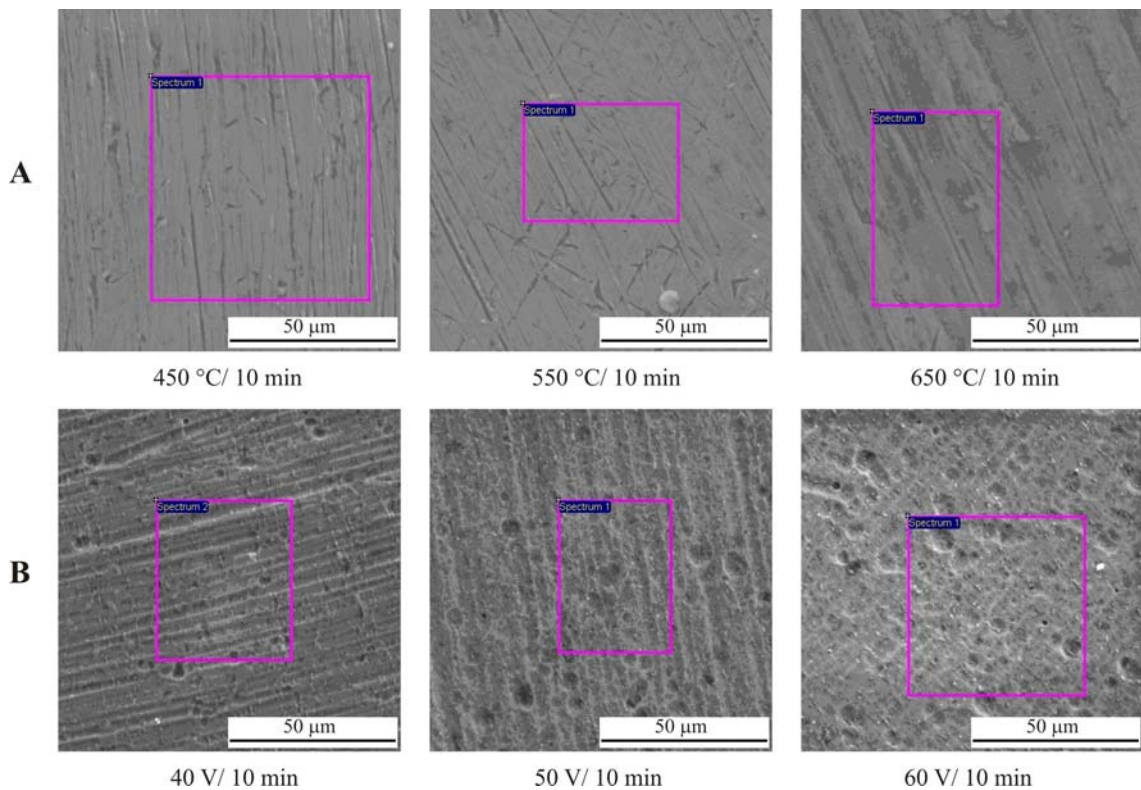| Process	450 °C/10′	550 °C/10′	650 °C/10′
Thermal oxidation	a) brown	b) blue	c) dark brown
Process	40 ± 2 V/10′	50 ± 2 V/10′	60 ± 2 V/10′
Electrochemical anodized	d) yellow	e) pink	f) purple

Fig. 1AB. SEM images of the sample surfaces.

pore size of 15 nm to 30 nm. The porousness of surface titanium alloys increased with voltage.

The thicknesses of oxide films on anodized Ti6Al4V, measured on cross-sectional images of the samples, were approximately 190 nm, 240 nm, 370 nm. The thickness value of electrochemical anodized oxide layer increased with increasing the voltage. The thickness of oxide films obtained by isothermal heating of
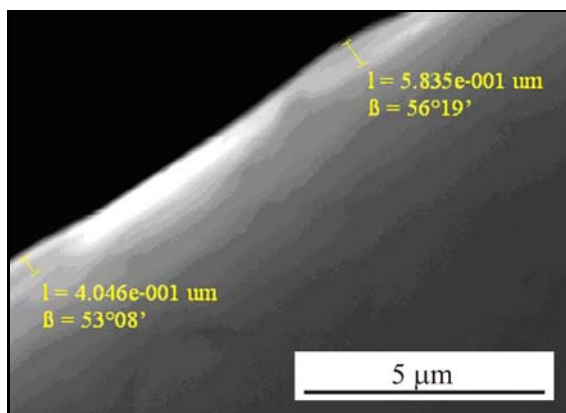
Fig. 2. SEM image showing cross-sectional view of the oxide film of sample group A oxidation at 550 °C.

Ti6Al4V was highest (450 nm to 680 nm) (Fig. 2). In thermal oxidation, increasing temperature led to the increase in the thickness.

Figure 3 shows the EDS spectra of metal oxides formed by thermal and anodizing treatments. Ti and O peaks were dominant for both sample groups.

3.2. Microhardness and roughness

For all samples, measurements of roughness parameters Rz, Rt, Ra and Rk were carried out at nine sampling lengths. For all roughness parameters expanded measurement uncertainty U, with extension factor $k = 2$, and probability $P = 95$ %, have been denoted. Results are presented in Table 2.

Expanded measurement uncertainty for obtained results of parameter Ra is equal to

$$U = 0.08 \cdot Ra \ (\mu m); \ k = 2; \ P = 95 \ \%. \tag{1}$$

Expanded measurement uncertainty for obtained results of parameters Rz, Rt and Rk are equal to:

$$U = 0.1 \cdot Rz \ (\mu m); \ k = 2; \ P = 95 \ \%, \tag{2}$$

$$U = 0.1 \cdot Rt \ (\mu m); \ k = 2; \ P = 95 \ \%, \tag{3}$$

$$U = 0.1 \cdot Rk \ (\mu m); \ k = 2; \ P = 95 \ \%, \tag{4}$$

where Rz is maximum height of the profile, Rt is total height of the profile, Ra is aritmetic mean deviation of the assessed profile and Rk is core roughness depth.

The values of roughness parameters Rz, Rt and Ra indicate a somewhat lesser roughness of the samples from the B group (40 V/10 min, 50 V/10 min, 60 V/10 min). The close values shown by the Rz and Rt parameters indicate the consistency of surface finishing, and therefore the consistency of the surface itself. The values of the roughness parameter Rk are nearly identical for both groups of
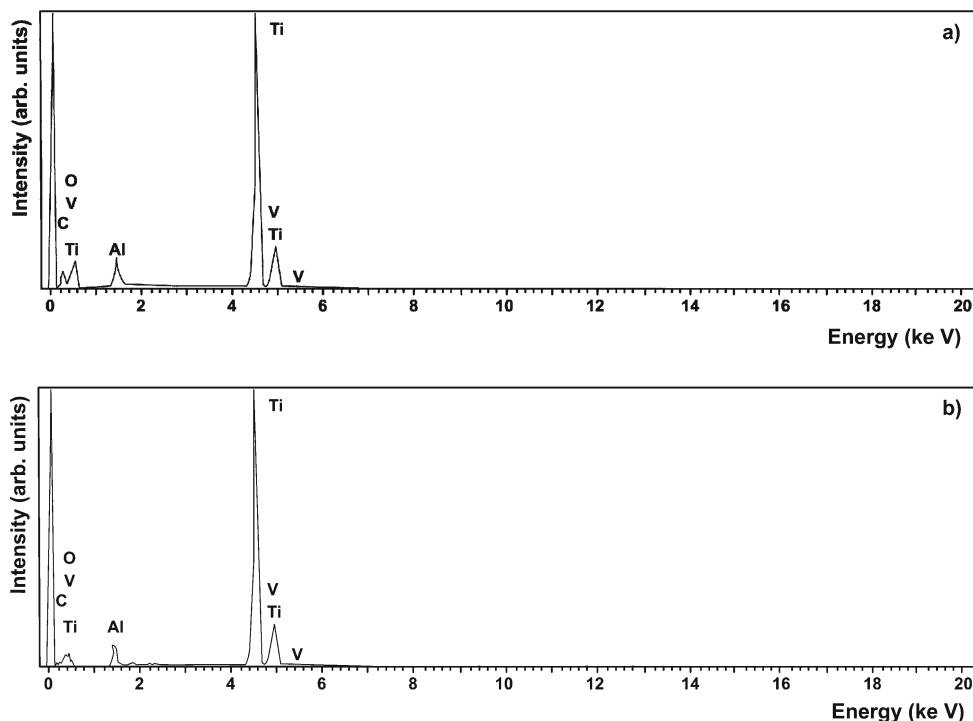

Fig. 3. EDS spectra of metal oxides formed on a) thermally (isothermal oxidation at 650 °C) and b) anodicaly oxidized (electrochemicaly anodized at 60 V) sample surfaces.

T a b l e 2. Measurement results of surface roughness parameters

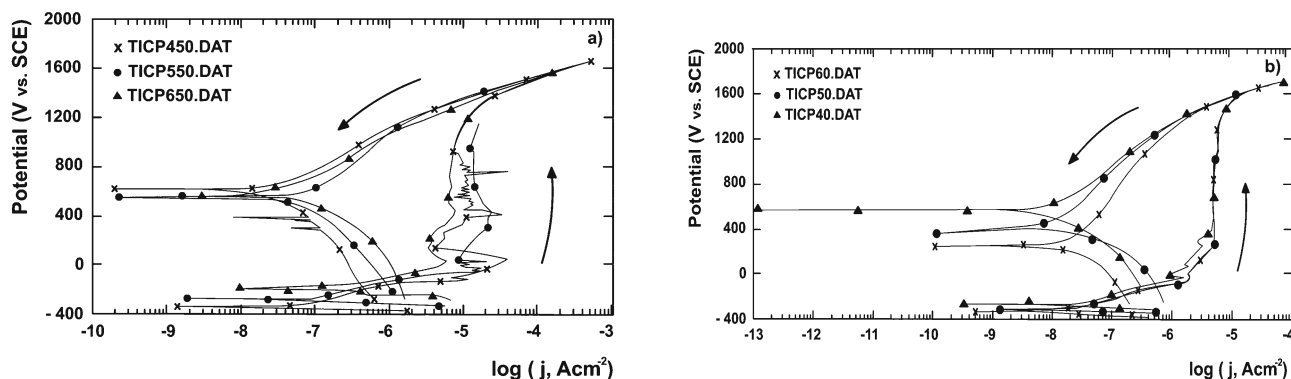| Sample	Process	Rz (µm)	Rt (µm)	Ra (µm)	Rk (µm)
A	450 °C/10 min	2.426	2.430	0.164	0.386
	550 °C/10 min	1.548	1.548	0.160	0.343
	650 °C/10 min	2.207	2.207	0.179	0.473
B	40 V/10 min	1.407	1.440	0.156	0.415
	50 V/10 min	1.319	1.351	0.118	0.374
	60 V/10 min	1.328	1.328	0.140	0.399

Fig. 4ab. Cyclic polarization curves of the tested groups A and B.

samples. The parameter Rk is defined as the depth of the roughness core profile or as a part of the profile with increased bearing capability, which then assumes basic load and as such has an important impact on the characteristics and longevity of the surface. The Rk roughness parameter is based on the material ratio curve or the Abbot Firestone curve.

The microhardness measurement results showed that the microhardnesses of titanium oxide films prepared under different experimental conditions have no significant differences, which are maintained between 8.2 GPa and 9.6 GPa, and showed a very marked hardness gradient across it, indicating an oxygen concentration gradient and suggesting that the rate of growth of the films is controlled by the inward diffusion of interstitial oxygen.

3.3. Corrosion properties

The corrosion potential E_{corr} values measured from the anodic polarization curves is shown in Table 3. This study showed that the E_{corr} values of the anodized samples were relatively lower than those of the thermal oxidized samples. Thermal oxidation of Ti6Al4V alloy decreases corrosion resistance when it is treated at 450 °C and 650 °C. Figure 4 shows cyclic polarization curves for both groups A and B. Wide passive regions were observed for the anodically oxidized sample group B, but the group A did not show distinct

T a b l e 3. Mean corrosion potential (E_{corr}) values

Sample	Process	E_{corr} vs SCE (mV)
A	450 °C/10 min	−300
	550 °C/10 min	−342
	650 °C/10 min	−398
B	40 V/10 min	−218
	50 V/10 min	−236
	60 V/10 min	−293

passivation regions. For both groups we could identify that the corrosion potential values measured at reverse scanning curves were higher than those measured at the forward scanning curves, which implies that none of the samples are susceptible to a localized corrosion.

4. Conclusion

The effect of thermal and electrochemical oxidation treatment on mechanical and corrosion properties of Ti6Al4V alloy were investigated. After thermal oxidation and after electrochemical anodizing treatment the surface of the Ti6Al4V alloy was covered with oxide films of different colours.

– The microhardness of the prepared titanium ox-

ide films by thermal oxidation are maintained between 9.2 GPa and 9.6 GPa and by electrochemical anodizing treatment between 8.2 GPa and 9.2 GPa.

– Samples morphology is greatly affected by high anodizing potential.

– For all specimens, thickness of oxide layers increases with increasing temperature and voltage. The thickness of oxide film in thermal oxidation is similar to the thickness of oxide film in an electrochemical anodizing process.

– The values of roughness parameters Rz, Rt and Ra indicate a somewhat less roughness of the anodized samples than thermally oxidized samples. The values of the roughness parameter Rk are nearly identical for both groups of samples.

– The electrochemical anodized samples had highest corrosion resistance compared with thermaly oxidized samples, but none of the samples were susceptible to a localized corrosion.

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