

Investigation of Titanium Oxide Layer in Thermal-Electrochemical Anodizing of Ti6Al4V Alloy

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Abstract—In this paper the combination of thermal oxidation and electrochemical anodizing processes is used to produce titanium oxide layers. The response of titanium alloy Ti6Al4V to oxidation processes at various temperatures and electrochemical anodizing in various voltages are investigated. Scanning electron microscopy (SEM); X-Ray Diffraction (XRD) and porosity determination have been used to characterize the oxide layer thickness, surface morphology, oxide layer-substrate adhesion and porosity. In the first experiment, samples modified by thermal oxidation process then followed by electrochemical anodizing. Second experiment consists of surfaces modified by electrochemical anodizing process and then followed by thermal oxidation. The first method shows better properties than other one. In second experiment, Surfaces modified were achieved by thicker and more adherent thick oxide layers on titanium surface. The existence of an electrochemical anodized oxide layer did not improve the adhesion of thermal oxide layer. The high temperature, thermal formation of an oxide layer leads to a coarse oxide grain morphology and a complete oxidative particle. In addition, in high temperature oxidation porosity content is increased. The oxide layer of thermal oxidation and electrochemical anodizing processes; on Ti-6Al-4V substrate was covered with different colored oxide layers.

Keywords—Electrochemically anodizing, Porosity, Thermal oxidation, Ti6Al4 alloy.

I. INTRODUCTION

TITANIUM and its alloys are the most appropriate materials for industrial applications, such as aerospace, chemical and biomedical because of their high strength to weight ratio, well-established corrosion resistance and biocompatibility. Passive oxide film formation of these materials at room temperature lead to their excellent corrosion resistance. This film, which mainly consists of TiO₂, provides chemical inertness in many aqueous media and assures their biocompatibility as a biomaterial [1, 2 and 3]. However, in their native form, TiO₂ films have poor mechanical properties and they are easily fractured under fretting and sliding wear conditions [4, 5, 6 and 7]. Therefore, any surface treatment that will thicken and toughen the oxide film; will improve

mechanical properties of surface. Thermal oxidation and electrochemical anodizing processes are surface treatments used to form oxide layers on the surface of titanium. Thermal oxidation treatments aimed to obtain “in situ” ceramic coatings, mainly based on rutile, can offer thick, highly crystalline oxide films with very good protective performances [4 and 5]. Thermal oxidation treatment tends to improve surface characteristics of titanium and its alloys. Increasing temperature induces the formation of a thicker oxide layer, which is accompanied with dissolution of oxygen beneath it [8]. Previous reports have described the influence of the thermal oxidation and electrochemical anodizing processes, separately on Ti6Al4V surfaces. In this investigation, a number of structural and property characteristics of the oxide layer produced by combination of both thermal oxidation and electrochemical anodizing processes are discusses.

II. MATERIALS AND METHODS

The material used in this research was Ti6Al4V (wt %) alloy. specimens of size 10 mm × 20 mm × 2 mm are prepared from titanium sheet. In this investigation samples are divided into two groups. The first group A, samples, were anodized in 43±2 V, 60±2 V, 65±2V first, followed by thermal oxidation at various temperatures ranging from 500 °C to 950 °C at normal atmospheric. In the second category B, samples were oxidized at 500 °C, 600 °C, 750 °C, 850 °C and 950°C followed by electrochemical anodizing in 43±2 V, 60±2 V and 65±2V. Before oxidation, all the corresponding surfaces were abraded by successive fine silicon carbide papers, and then mechanically polished with 1 μm diamond paste to achieve a mirror-like finish. Specimens were washed in running water, and cleaned ultrasonically with alcohol and finally dried in hot air. After the oxidation treatment, the samples were allowed to cool either in the furnace itself or outside the furnace in an ambient air. Electrochemical anodizing was performed in 1 M H₂SO₄ at room temperature at potentials ranging from 43 to 65 V. Anodizing in different voltages produced different colors on the surface of Ti alloy, apparently due to the formation of oxide layers of different thicknesses.

The thickness and surface morphology of the oxide layer were studied by scanning electron microscopy (SEM, LEO 1450 VP). The porosity of oxide layers was determined using

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an Archimedean Method. The Archimedean method for measuring porosity is reliable and time efficient for this study [9]. The samples are submersed in water. The samples act like a sponge, in that as air diffuses out of the samples, water will diffuse in it and increase the weight. The pores in the samples allow for the diffusion of water. The more pores, or the larger the pores, the more weight the samples gain. The weight gain of the sample can be directly related to the volume of the pores and, therefore, the apparent porosity of the sample [10]. Closed or sealed pores are not included in the apparent porosity value. The apparent porosity values are usually close to the total porosity as long as the closed porosity in the sample is low. The porosity is calculated by taking the wet mass in air and subtracting the dry mass. This number is then divided by the exterior volume and converted to the percent apparent porosity by using Equation 1; where P is the apparent percent porosity, M is the saturated mass or wet mass in air, D is the dry mass and V is the exterior volume, calculated as $V = \frac{M - S}{\rho}$, where S is the mass while suspended in water or the wet mass in water.

III. RESULTS AND DISCUSSION

Efforts were first made to produce a thick ($>100 \mu\text{m}$) and adherent oxide layer by combination of both thermal oxidation and electrochemical anodizing. It was observed that a combination process, including, first thermal oxidation and then electrochemical anodizing; leads to decrease in oxide layer thickness. It seems that the thermally oxidized layer is somewhat dissolved during subsequent electrochemical process. Fig. 1a shows the oxide layer of a sample anodized in $65 \pm 2 \text{ V}$ and then oxidized at $950 \text{ }^\circ\text{C}$. The thickness of this layer was about $153.4 \mu\text{m}$, whereas, Fig 1b shows the thickness of oxide layer that proceed oxidizing process at $950 \text{ }^\circ\text{C}$ was about $354 \mu\text{m}$. In thermal oxidation, increasing temperature lead to increase in the thickness. At temperatures above $850 \text{ }^\circ\text{C}$, samples showed a significant increase in growth rate of the oxide layer formation. The increase in thickness of the oxide layer as a function of oxidation temperature for the samples oxidized at 5 h is shown in Fig. 2. Thus the maximum thickness of oxide layer was obtained in thermal oxidation (more than $350 \mu\text{m}$).

The minimum oxide layer thickness (about nm) belongs to electrochemical anodized sample treated at $43 \pm 2 \text{ V}$.

When the samples first electrochemically anodized, and then thermally oxidized, the thickness of oxide layer was increased. For example, the variation of thickness of samples electrochemically anodized at $43 \pm 2 \text{ V}$, $60 \pm 2 \text{ V}$ and $65 \pm 2 \text{ V}$ and then thermally oxidized at 750°C is shown in Fig.3. Fig.4 shows the comparison of thickness of the oxide layer that thermal oxidized at 750°C and 950°C followed by anodized at $43 \pm 2 \text{ V}$, $60 \pm 2 \text{ V}$ and $65 \pm 2 \text{ V}$. It is obvious that the thickness value increases with increasing the voltage. This increase is more at higher temperatures.

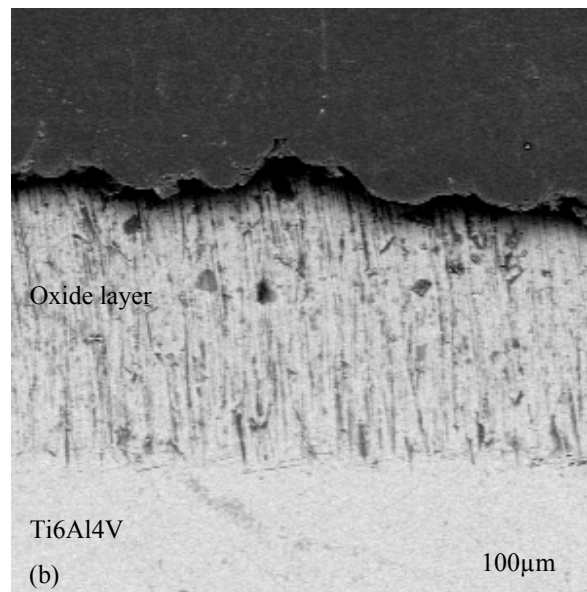
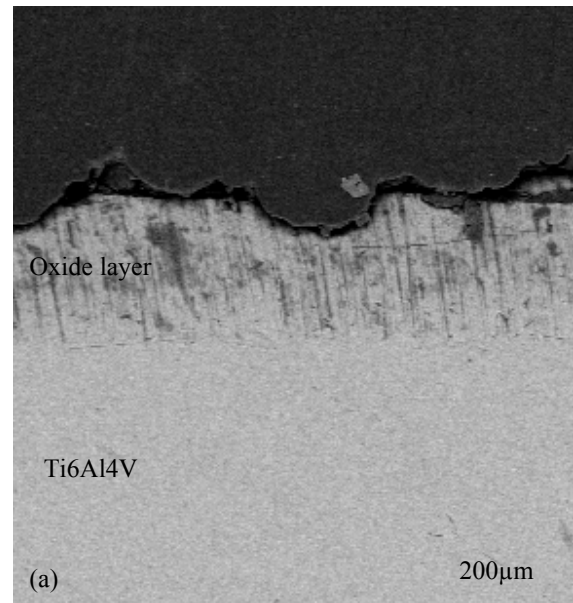


Fig. 1 SEM images showing cross-sectional view of the oxide layers: (a) anodized in $65 \pm 2 \text{ V}$ and then oxidized at $950 \text{ }^\circ\text{C}$ for 5 h, (b) only thermally oxidized at $950 \text{ }^\circ\text{C}$ for 5h

In all samples cooled in air, the oxide layer had poor adhesion to substrate, whereas the samples cooled in the furnace had an adherent oxide layer. Fig. 5 shows the cross-sections of the oxide layers formed on both air cooled and furnace cooled samples oxidized at $950 \text{ }^\circ\text{C}$ for 5 h. The furnace cooled sample showed very good adhesion between the oxide layer and the substrate (Fig. 5a). The poor adhesion of the oxide layer with substrate for the air cooled specimen (Fig. 5b) is due to the fast cooling. This lead to a large thermal residual stress arising from the difference in the coefficient

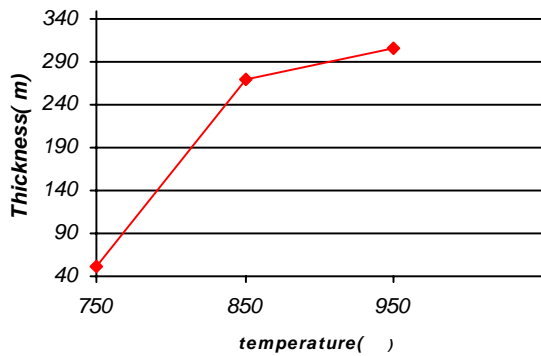


Fig. 2 Variation of oxide layer thickness as a function of temperature for 5h

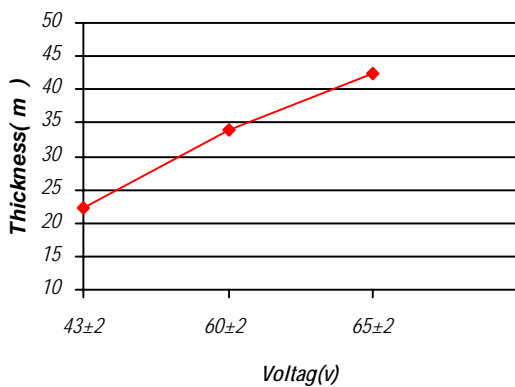


Fig. 3 Variation of the oxide layer thickness as a function of voltage, of a sample that anodized in 43±2 V, 60±2 V and 65±2V and then oxidized at 750°C

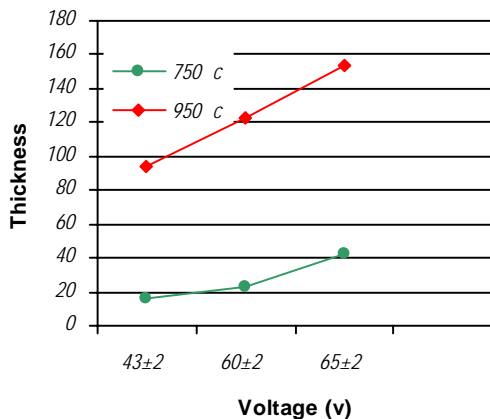


Fig. 4 Comparison of the oxide layer thickness samples oxidized at 750°C and 950°C and then anodized at 43±2 V, 60±2 V and 65±2V

of thermal expansion Ti substrate and the oxide layer. Slow furnace cooling obviously reduced the thermal residual stresses to maintain the integrity of the thick layer with the substrate. Thus furnace cooling has a key role in the production of a thick of surface of the Ti-6Al-4V alloy lead to different colors because of temperature variation. samples after thermal oxidation at 500 °C for 5 h, was characterized by

a dark purple surface; at 600 °C for 5 h was blue colored; at 750 °C and up ward appear in brown. Samples that anodized in 43±2 V, showed gold surface; in 60±2 V showed purple and in 65±2V had blue color. The sample that anodized in 43±2 V, oxide at 500 °C for 5 h would be purple, at 600 °C would be blue and up to 750 °C would be brown. When a sample that anodized in 60±2 V, oxide at 500 °C for 5 h it would be blue, at 600 °C it would be blue and up to 750 °C it would be brown. Colors are due to interference phenomena that establish at the metal-oxide interface. This indicates that the two colored surfaces are covered by homogeneous oxide films, a few hundred nanometer thick.

In this work also porosity in oxide layer is obtained. Studies showed that, an increase in the temperature led to an increase the porosity, therefore. Maximum porosity obtained in thermal oxidation at 950 °C. Porosity influences the physical and mechanical characteristics of the oxide layer. Porosity levels are established by using various methods, which can be tedious or unreliable, such as mercury intrusion porosimetry (MIP) or image analysis (IA) techniques.

The Archimedeian method for measuring porosity is reliable, inexpensive, uncomplicated, and safe technique. Results showed that an increase in temperature in thermally oxidation process lead to increase in the porosity of the oxide layer. The porosity of the oxide layer in thermal oxidation at 750 °C was % 9.66, but by increasing the temperature to 950 °C, it raised to %17.45. In the combination treatment, the porosity decreased. The reduction in an electrochemical anodizing-thermally oxidation combined process was more than in a thermally oxidation- electrochemical anodizing. For example in electrochemically anodized samples in 65±2V followed by thermally oxidation at 750 °C, the porosity of the oxide layer was %5, but in a thermally oxidation at 750 °C followed by the electrochemical anodizing at 65±2V; the porosity of the oxide layer was %6.04.

IV. CONCLUSION

A conclusion section is increasing temperature and oxidation period promoted formation of thick oxide layers and deeper penetration of oxygen into the substrate. The change in weight dose not appears until the temperature arises above 750 °C. In an electrochemical anodize-thermal oxidation process at constant voltage, the increase in temperature of thermal oxidation lead to an increase in thickness, this increase would be higher at high voltages. In all of the oxidizing or anodizing processes, the adhesion of oxide layer to substrate in furnace cooled samples was better than the air cooled samples. The thickness of oxide layer in a thermal oxidation- electrochemically anodizing process is similar to the thickness of oxide layer in an electrochemically anodizing-thermal oxidation process. Increasing temperature in thermal oxidation lead to an increase in the porosity of the oxide layer. In a combined treatment, porosity decreased and the reduction of electrochemical anodizing-thermally oxidation process was more than in a thermally oxidation- electrochemical anodizing process. After thermal oxidation and also after

electrochemically anodizing; the surface of the Ti-6Al-4V alloy was covered with oxide layers of different colors.

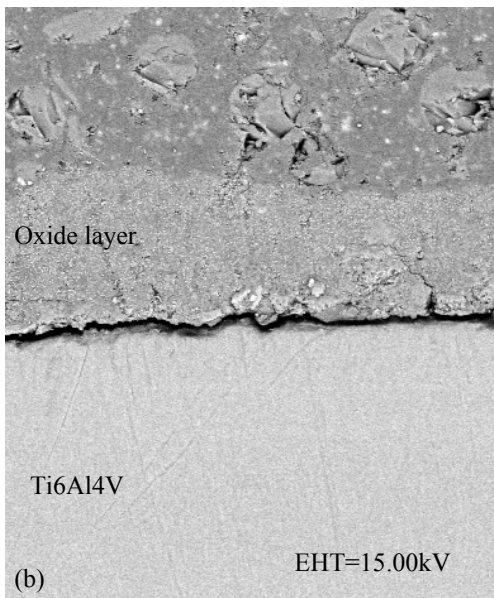
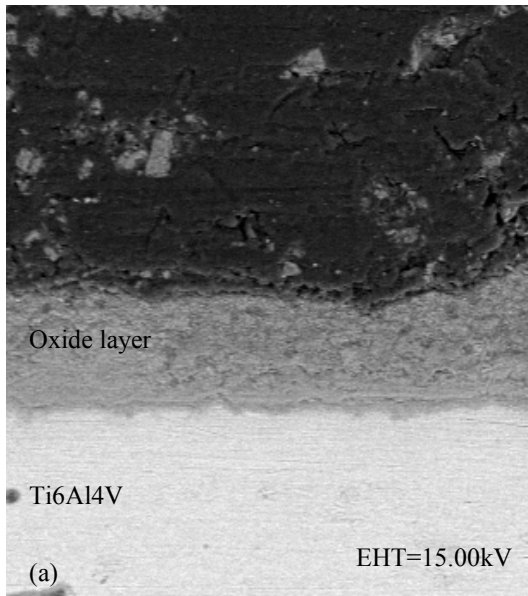


Fig. 5 SEM images showing cross-sectional view of the oxide layers oxides at 850 °C for 5h: (a) furnace cooled, (b) air cooled

- [5] J. Komotori, B.J. Lee, H. Dong and P.A. Dearnley, Corrosion response of surface engineered titanium alloys damaged by prior abrasion. *Wear* 88–98 (2001), pp. 1–11.
- [6] F. Galliano, E. Galvanetto, S. Mischler and D. Landolt, Tribocorrosion behavior of plasma nitrided Ti-6Al-4V alloy in neutral NaCl solution. *Surf Coat Technol* 145 (2001), pp. 121–131.
- [7] M. Long and H.J. Rack, Titanium alloys in total joint replacement—a materials science perspective. *Biomaterials* 19 (1998), pp. 1621–1639.
- [8] P. Kofstad. *High temperature corrosion*, Elsevier Applied Science, Essex (1988).

REFERENCES

- [1] D.M. Brunette, P. Tengvall, M. Textor and P. Thomsen. *Titanium in medicine*, Springer, Heidelberg (2001).
- [2] R. Boyer, G. Welsch and E.W. Collings. *Materials properties handbook: titanium alloys*, ASM International, Materials Park, OH (1994).
- [3] M.J. Donachie. *Titanium: a technical guide*, ASM International, Materials Park, OH (1989).
- [4] J.L. Gilbert, C.A. Buckley and E.P. Lautenschlager, Titanium oxide film fracture and repassivation: The effect of potential, pH and aeration. In: S.A. Brown and J.E. Lemons, Editors, *Medical applications of titanium and its alloys: the material and biological issues*, ASTM STP 1272, ASTM, Philadelphia (1996), pp. 199–214.