Journal of Modern Processes in Manufacturing and Production, Volume 9, No. 1, Winter 2020

DOR: 20.1001.1.27170314.2020.9.1.3.5

Research Paper

Effect of Coating Process Parameters on Corrosion Behavior of Ti-6Al-4V

Mohammad Hossein Majidi[1], Amin Rabiezadeh[2*], Ahmad Afsari[1]
[1]Department of Mechanical Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran
[2]Department of Materials Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran
[*]Email of Corresponding Author: rabieezadeh@shirazu.ac.ir
Received: January 2, 2020; Accepted: March 17, 2020

Abstract

Titanium and its alloys (Ti-6Al-4V) are considered to be among the most promising engineering materials due to a unique combination of high strength to weight ratio, melting temperature, corrosion resistance, and biocompatibility. Anodizing is one of the coating methods that increases corrosion resistance and wear resistance and provides better adhesion of paint primers mostly applied to protect Al, Ti, Mg, and their alloys. The novel Plasma Electrolytic Oxidation (PEO) technique is gaining increased attention for depositing thick, dense, corrosion resistant, and hard ceramic coating on valuable metals (Al, Ti, and Mg). The aim of this research is a comparison between the corrosion behavior of anodized and plasma electrolytic oxidized Ti-6Al-4V at different voltages. The surface morphology, thickness, and phase composition of coatings were investigated using a scanning electron microscope and X-ray diffraction. The potentiodynamic polarization test was used to determine the corrosion behavior of the specimens. Results indicated that increasing of corrosion resistance by tests anodized sample at 50 V at 15 minutes and PEO sample at 375 V at 10 minutes.

Keyword

Ti-6Al-4V, Anodizing, Plasma Electrolytic Oxidation (PEO), Thermal Oxidation, Corrosion resistance

1. Introduction

Titanium and its alloys have been widely used in many fields, due to their high strength, non-magnetism, corrosion resistance, and other characteristics. Due to a unique combination of high strength-to-weight ratio, melting temperatures and corrosion resistance, interest in the application of titanium alloys to mechanical and tribological components are growing rapidly in a wide range of industries, e. g. the aerospace, marine and biomedical fields. In such an application, components made from Ti-alloy are often in tribological contact with different metals and media, under stationary or dynamic loading and at various temperatures. These contact loads can cause damage to the thin native oxide film which passivates the titanium surface; and the metal, which has a strongly negative standard electrode potential (- 1.63 V), can undergo intensive interactions with the counterface material and/or the surrounding environment [1]. Moreover, by surface engineering, the application of titanium alloys can be increased further through the improvement of some inherent weaknesses, such as inadequate wear behavior and poor biocompatibility [2, 3]. Ti-6Al-4V has a poor wear resistance, which can cause significant release of Al and V [4]. The release of Al and V from the implant into the body is most undesirable due to the element's toxic effects [5].

The commonly adopted surface engineering techniques include physical vapor deposition (PVD)/chemical vapor deposition (CVD) [6-9], laser nitriding [10, 11], anodizing [12-14], sol-gel method [15-18], etc. Among these techniques, plasma electrolytic oxidation (PEO) [19-22], and emerging environmentally friendly technology for preparing ceramic coatings on valve metals (such as Ti, Al, Mg), has been widely studied in recent years.

Recently, there has been a great interest in the PEO technique because of the promising application prospects of this technique in the surface treatment of metals. The process of PEO treatment involves reactions caused by electric breakdown on the metal surface, and the coating material in crystalline or amorphous phases, forms at breakdown sites, usually contains constituent species derived from the substrate and electrolyte. This character reveals that PEO coatings have excellent bonding strength to the substrate due to its in-situ growth process. Moreover, by adjusting the composition of the applied electrolyte, various desired elements can be introduced into PEO coating.

Anodic oxidation, which is carried out in various solutions providing passivation of the titanium surface, generates thin films of amorphous hydrated oxide or crystalline TiO2 in the anatase form [23].

This work aimed to study the effect of voltage on the corrosion properties of plasma electrolyte oxidized and anodized Ti-6Al-4V under DC power. The surface morphology and the element phase compositions of the coatings were characterized by SEM, energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), respectively. The corrosion resistance of the PEO coating was evaluated by a potentiodynamic polarization technique in a 3.5% NaCl solution.

2. Material and methods

Disc samples made of the Ti-6Al-4V (6% aluminum, 4% vanadium, 0.25% (maximum) iron, 0.2% (maximum) oxygen, and the remainder titanium) alloy with a diameter of 20 mm and thickness of 6 mm were ground using SiC abrasive paper sequentially to #2000 and then were degreased with ethanol and dried in air. The samples were then anodically treated in 0.1 M H_2SO_4 at room temperature at a constant current density up to various maximum voltages of 10, 20, 30, 40, 50 and 55 V for 15 minutes. The PEO treatment was carried out at constant voltages of 325, 375, 425 and 475 V for 5 minutes. The working electrolyte was 0.04 M calcium acetate hydrate ($(CH_3COO)_2Ca.H_2O$) with the addition of 0.1 M sodium dihydrogen phosphate hydrate ($NaH_2PO_4.H_2O$). During the PEO process, the electrolyte was mixed and cooled to prevent heating over 35 ºC. Coated samples were rinsed with water after the treatment and dried in warm air.

A qualitative study of oxide film appearance was carried out visually. The scanning electron microscopy technique (by CamScan MV2300) was employed to observe the surface morphology of samples. The semi-quantitative chemical composition of coatings was analyzed by an energy-dispersive X-ray spectrometry (Oxford) incorporated into scanning electron microscopy. Film Phase Composition was estimated using a Phillips X'pert Pro X-ray diffractometer (Cu Kα radiation) by scanning in the $2\theta=20^{\circ}-100^{\circ}$ range with 0.02 steps at a grazing angle of 5º.

Linear polarization measurements were performed in a standard three-electrode cell with silver/silver chloride reference electrode and platinum counter electrode by µ AUTO LAB type III instrument. The electrodes were sealed in epoxy resin (exposed surface area 1 cm^2). The Electrochemical measurement was performed at the open circuit potential in 3.5% sodium chloride, aerated test solution at room temperature (25 ^oC). Corrosion measurements consisted of stabilizing the working electrode in the corrosion test electrolyte at open circuit potential (OCP) for 1 hr with a scan rate of 0.2 $mV.S^{-1}$.

3. Results and Discussion

The effect of anodizing voltage on the coating color is shows Figure 1. As shown in Figure 1(a), the Ti-6Al-4V alloy is a gray shiny metallic after polishing and cleaning. Anodizing at different voltages produced different colors on the sample surfaces (Figure 1), containing yellow, blue, and gold. Different color of anodized surfaces is apparently due to the formation of oxide layers with different thickness caused by anodizing conditions**.**

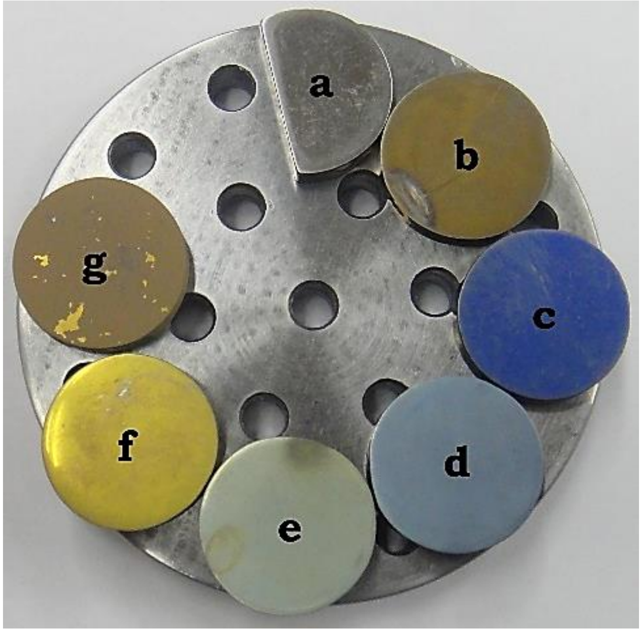

Figure1. Optical micrograph of anodized samples: (a) polished sample prior to anodizing; anodized sample at (b) 10 V, (c) 20 V, (d) 30 V, (e) 40 V, (f) 50 V and (g) 55V.

Figure 2 shows the formation of coating surfaces with increasing anodizing voltage from 10 to 50 V. Small and discrete pores exist in coating surfaces. It can be seen that with increasing anodizing voltage, the number and size of surface pores decreased. Anodizing voltage in 50V was an increased density of the surface coating. Coating surface formation in the anodizing process is an interaction between oxide formation and oxide solution in Sulfuric acid electrolyte. The rate of oxide formation increases with increasing anodizing voltage and caused more stable and uniform oxide coating. This phenomenon will cause the oxide layer to form a stable and uniform coating.

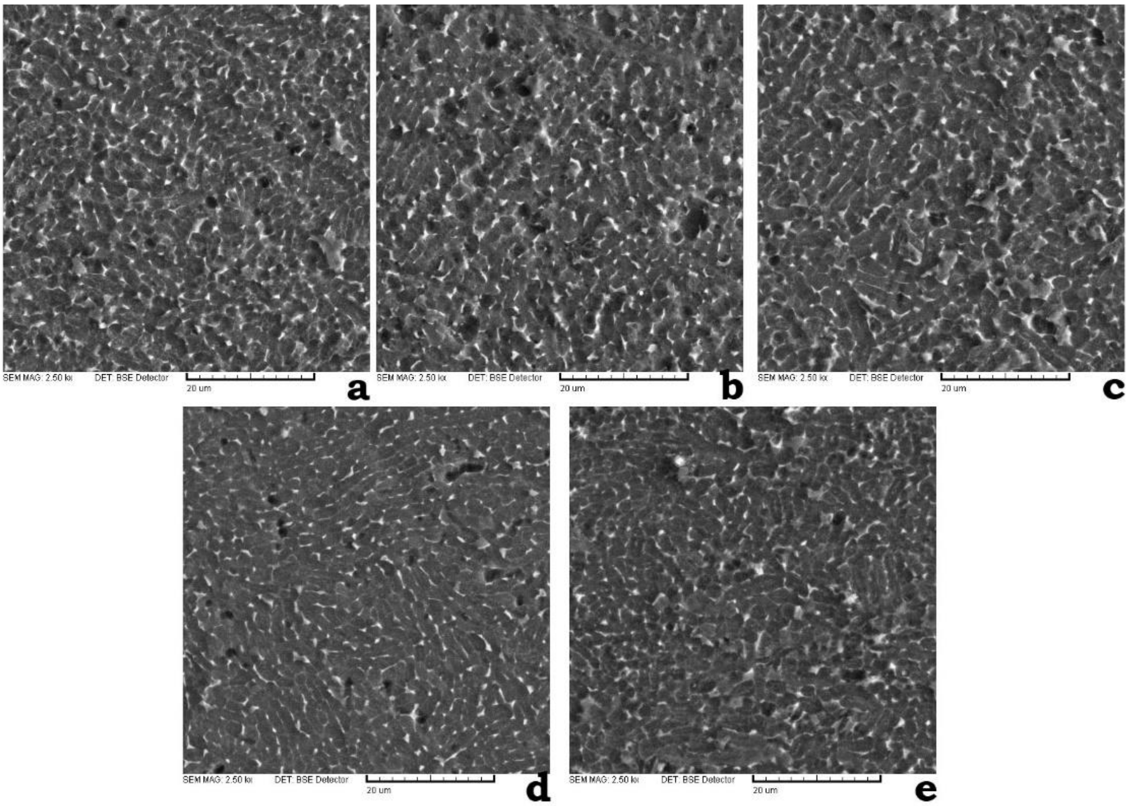

Figure2. Formation of oxide surface on anodized samples at different voltages of (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V and (e) 50 V.

The anodized oxide layer on the sample surface was broken by increasing anodizing voltage to 55 V, (Figure 3). The anodized oxide layer has consisted of coating islands about 50µm apart. This leaves uncoated Ti base alloy exposed to the outer atmosphere. If the anodizing process is carried out at voltages above the breakdown limit, the oxide will no longer be resistive enough to prevent corrosion by corrosive media [24].

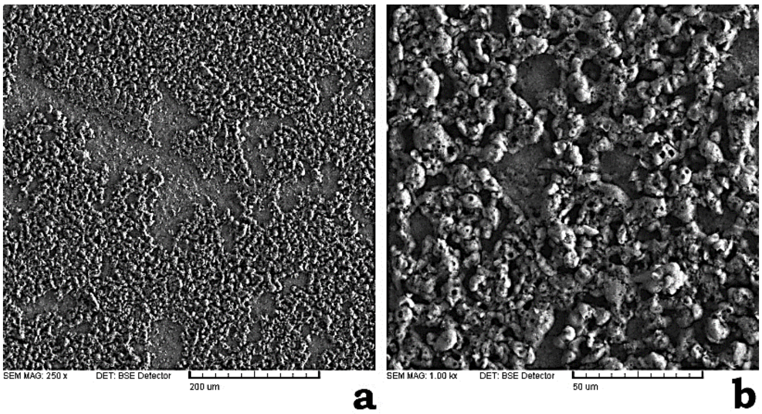

Figure3. SEM micrograph of the anodized sample at 55 V into magnifications of (a) 250 x and (b) 1000 x.

The polarization curves show that corrosion resistance will be increased by increasing below the breakdown limit (Figure 4). Likewise open circuit potential is nobler for high anodizing voltage samples with respect to other samples. The corrosion resistance of the samples is mainly the result of oxide coating uniformity and lack of uncoated base Ti alloy, beside corrosion resistance nature of oxide structures.

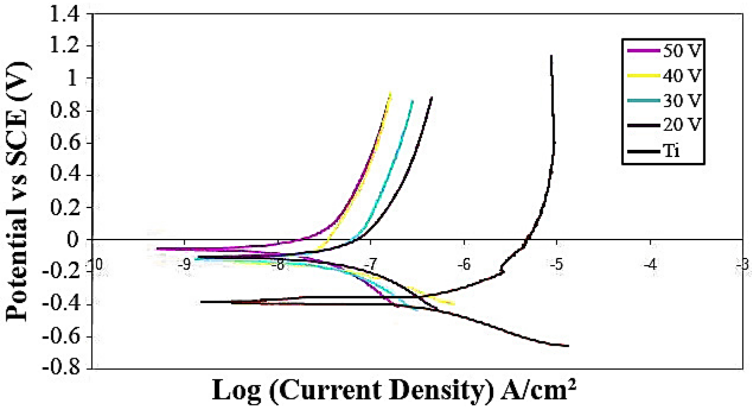

Figure4. Potentiodynamic polarization curves conducted in a 3.5% NaCl solution for the anodized samples prepared at different voltages.

Figure 5 demonstrates the evolution of surface morphologies of PEO coatings at different voltages. PEO is based on the modification of the growing anodic film by spark/arc micro discharges, which are initiated at potentials above the breakdown voltage of the growing oxide film and move rapidly across the anode surface. Since they rapidly develop and extinguish (within 10^{-4}-10^{-5} s), the discharges heat the metal substrate to less than 100-150ºC. At the same time, the local temperature and pressure inside the discharge channel can reach 10^{3}-10^{4} K and 102-103 MPa, respectively, which is high enough to give rise to plasma thermochemical interactions between the substrate and the electrolyte. These interactions result in the formation of melt-quenched high-temperature oxides and complex compounds on the surface, composed of oxides of both the substrate material and electrolyte-borne modifying elements [25].

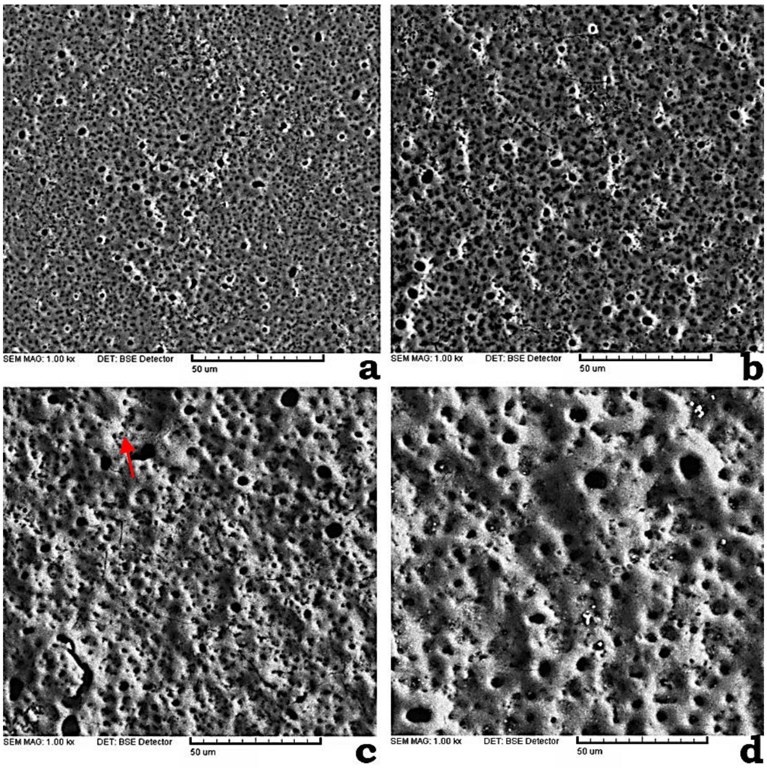

Figure5. Morphologies of the oxide coatings prepared for 5 min at (a) 325 V, (b) 375 V, (c) 425 V and (d) 475 V.

The effect of increasing PEO voltage on oxide coating formation for 5 min in different voltages from 325V to 475V is shown in Figure 5. All samples contain round discreet pores distributed on the coating surface. By increasing PEO voltage, pore size increased and the number of pores per surface area decreased. By increasing PEO voltage, the spark/arc micro discharge energy increased. These results show that in more material melting on the anode surface lead to large pores formation on the oxide surface. Increasing pore size was caused by interconnected pores that show by the arrows in Figure 5–c. shows PEO treated surface at 375 V (Figure 5-b) higher coating formation with no large or interconnected pores.

Variation of PEO coating morphology by increasing the PEO treating time from 1 to 20 min was examined at 375 V (Figure 6). By increasing PEO treating time, the number of pores per surface area decreased. The pores formed at higher treating time (10 and 20 min) were about twice bigger than pores at less treating times of 1 and 5 min. PEO treated sample for 10 min, contains more inform oxide film than 20 min treated sample. Increasing pore size is caused by the necessity of higher energy arcs for the destruction of thicker films formed on the surface. Studying oxide film on 20 min treated sample at higher magnification (4000X) shows the formation of microcracks in PEO coating which connects adjacent pores (Figure 7). Film cracking in this sample is caused by local high energy arcs and the release of a high amount of energy near existing arcs. This effect leads to high local mechanical stresses and the beginning of oxide file destruction by PEO treatment.

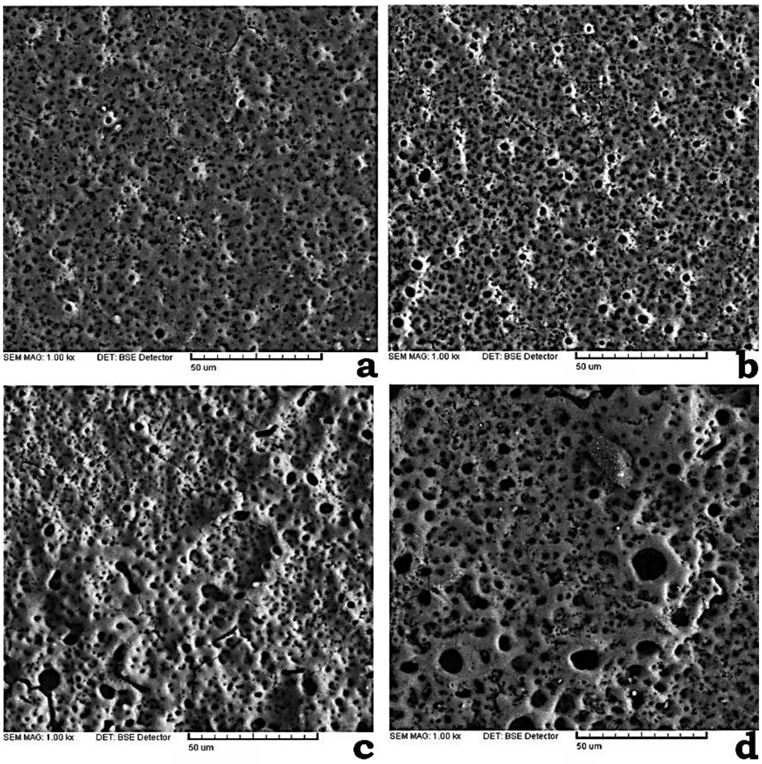

Figure6. Morphologies of the coatings prepared at 375 V for (a) 1 min, (b) 5 min, (c) 10 min and (d) 20 min.

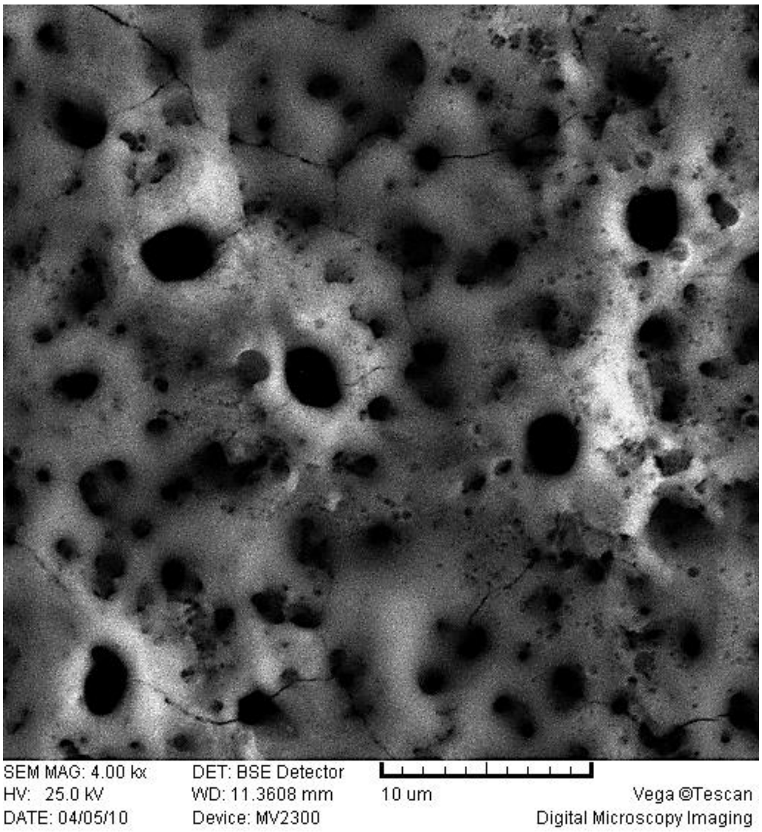

Figure7. Surface morphology of PEO coating at 375 V for 20 min.

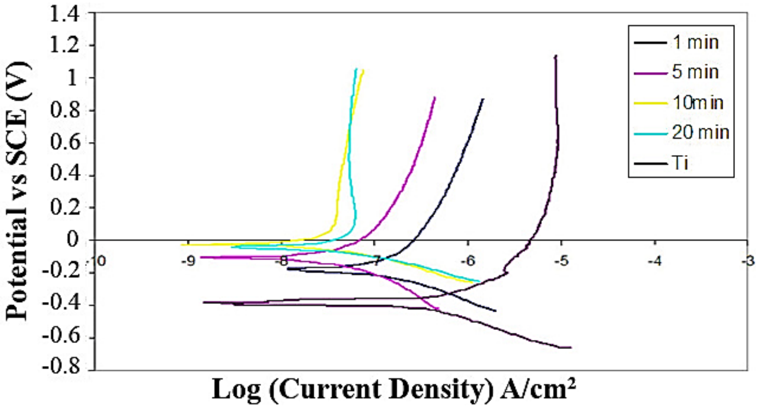

Figure8. Potentiodynamic polarization curves conducted in 3.5% NaCl solution for the PEO samples prepared at 375 V for different times.

Investigating the effect of PEO treating time on corrosion resistance behavior of samples treated at 375V at different treating time is shown in Figure 8. Increasing treating time from 1 to 10 min has a distinctive effect on increasing the corrosion resistance of samples. Increasing film thickness by increasing PEO treating time improves the corrosion of samples. Less improvement in corrosion resistance of 20 min treated sample can be the result of large pores with interconnected cracks (shown in Figure 7).

4. Conclusions:

Effect of anodizing and PEO voltage and time on the corrosion properties of Ti-6Al-4V was examined and compared with the corrosion resistance of thermally oxidized Ti-6Al-4V. Evaluation of corrosion properties of the specimens by potentiodynamic polarization tests indicated that anodized sample at 50 V at 15 minutes and PEO sample at 375 V at 10 minutes shows the best corrosion resistance. Also from the comparison of the oxidized sample, it is concluded that increasing the time and temperature of oxidation thickness and hardness of the oxidized layer increased. Formation of the oxide layer increased the corrosion resistance and 600°C is the appropriate oxidation temperature for improvement of corrosion resistance of titanium alloy. By comparison of results, the best corrosion resistance is for thermally oxidize samples.

5. Reference

[1] Liu, Z. J., Zhong, X., Liu, H., Tsai, I. L., Donatus, U. and Thompson, G. E. 2015. Characterization of anodic oxide film growth on Ti6Al4V in NaTESi electrolyte with associated adhesive bonding behaviour. Electrochimica Acta. 182: 482-492.

[2] He, D., Zheng, S., Pu, J., Zhang, G. and Hu, L. 2015. Improving tribological properties of titanium alloys by combining laser surface texturing and diamond-like carbon film. Tribology International. 82: 20-27.

[3] Frauchiger, V. M., Schlottig, F., Gasser, B. and Textor, M. 2004. Anodic plasma-chemical treatment of CP titanium surfaces for biomedical applications. Biomaterials. 25(4): 593-606.

[4] Jiang, P., He, X. L., Li, X. X., Yu, L. G. and Wang, H. M. 2000. Wear resistance of a laser surface alloyed Ti–6Al–4V alloy. Surface and Coatings Technology. 130(1): 24-28.

[5] Okazaki, Y. and Gotoh, E. 2005. Comparison of metal release from various metallic biomaterials in vitro. Biomaterials. 26(1): 11-21.

[6] Vadiraj, A. and Kamaraj, M. 2006. Characterization of fretting fatigue damage of PVD TiN coated biomedical titanium alloys. Surface and Coatings Technology. 200(14-15): 4538-4542.

[7] Dobrzański, L. A. and Mikuła, J. 2005. The structure and functional properties of PVD and CVD coated Al2O3+ZrO2 oxide tool ceramics. Journal of Materials Processing Technology. 167(2-3): 438-446.

[8] Mkaddem, A., Ben Soussia, A. and El Mansori, M. 2013. Wear resistance of CVD and PVD multilayer coatings when dry cutting fiber reinforced polymers (FRP). Wear. 302(1-2): 946-954.

[9] Matykina, E., Arrabal, R., Mingo, B., Mohedano, M., Pardo, A. and Merino, M. C. 2016. In vitro corrosion performance of PEO coated Ti and Ti6Al4V used for dental and orthopaedic implants. Surface and Coatings Technology. 307: 1255-1264.

[10] Razavi, R. S., Salehi, M., Ramazani, M. and Man, H. C. 2009. Corrosion behaviour of laser gas nitrided Ti–6Al–4V in HCl solution. Corrosion Science. 51(10): 2324-2329.

[11] Sun, F., Liu, J., Yang, Y. and Yu, H. 2005. Nitridation of iron by CW-CO2 laser nitriding technologies. Materials Science and Engineering: B. 122(1): 29-33.

[12] Narayanan, R. and Seshadri, S. K. 2007. Phosphoric acid anodization of Ti–6Al–4V – Structural and corrosion aspects. Corrosion Science. 49(2): 542-558.

[13] Mizukoshi, Y., Okajima, T. and Masahashi, N. 2015. Local structure of vanadium in Ti-6Al-4V alloy anodized in acetic acid aqueous solution and its contribution to visible light response in photocatalysis. Applied Catalysis B: Environmental. 162: 180-186.

[14] Diamanti, M. V., Sebastiani, M., Mangione, V., Del Curto, B., Pedeferri, M. P., Bemporad, E., Cigada, A. and Carassiti, F. 2013. Multi-step anodizing on Ti6Al4V components to improve tribomechanical performances. Surface and Coatings Technology. 227: 19-27.

[15] Stoch, A., Jastrze¸bski, W., Długoń, E., Lejda, W., Trybalska, B., Stoch, G. J. and Adamczyk, A. 2005. Sol–gel derived hydroxyapatite coatings on titanium and its alloy Ti6Al4V. Journal of Molecular Structure. 744-747: 633-640.

[16] Wu, C., Ramaswamy, Y., Gale, D., Yang, W., Xiao, K., Zhang, L., Yin, Y. and Zreiqat, H. 2008. Novel sphene coatings on Ti-6Al-4V for orthopedic implants using sol-gel method. Acta biomaterialia. 4(3): 569-76.

[17] Qi, G., Zhang, S., Khor, K. A., Weng, W., Zeng, X. and Liu, C. 2008. An interfacial study of sol–gel-derived magnesium apatite coatings on Ti6Al4V substrates. Thin Solid Films. 516(16): 5172-5175.

[18] Abrishamchian, A., Hooshmand, T., Mohammadi, M. and Najafi, F. 2013. Preparation and characterization of multi-walled carbon nanotube/hydroxyapatite nanocomposite film dip coated on Ti-6Al-4V by sol-gel method for biomedical applications: an in vitro study. Materials science & engineering. C, Materials for biological applications. 33(4): 2002-10.

[19] Snizhko, L. O., Yerokhin, A. L., Pilkington, A., Gurevina, N. L., Misnyankin, D. O., Leyland, A. and Matthews, A. 2004. Anodic processes in plasma electrolytic oxidation of aluminium in alkaline solutions. Electrochimica Acta. 49(13): 2085-2095.

[20] Stojadinovic, S., Vasilic, R., Belca, I., Petkovic, M., Kasalica, B., Nedic, Z. and Zekovic, L. 2010. Characterization of the plasma electrolytic oxidation of aluminium in sodium tungstate. Corrosion Science. 52(10): 3258-3265.

[21] Sarbishei, S., Faghihi Sani, M. A. and Mohammadi, M. R. 2014. Study plasma electrolytic oxidation process and characterization of coatings formed in an alumina nanoparticle suspension. Vacuum. 108: 12-19.

[22] Aliasghari, S., Skeldon, P. and Thompson, G. E. 2014. Plasma electrolytic oxidation of titanium in a phosphate/silicate electrolyte and tribological performance of the coatings. Applied Surface Science. 316: 463-476.

[23] Nakajima, M., Miura, Y., Fushimi, K. and Habazaki, H. 2009. Spark anodizing behaviour of titanium and its alloys in alkaline aluminate electrolyte. Corrosion Science. 51(7): 1534-1539.

[24] Liu, X., Chu, P. and Ding, C. 2004. Surface modification of titanium, titanium alloys, and related materials for biomedical applications. Materials Science and Engineering: R: Reports. 47(3-4): 49-121.

[25] Yerokhin, A. L., Nie, X., Leyland, A., Matthews, A. and Dowey, S. J. 1999. Plasma electrolysis for surface engineering. Surface and Coatings Technology. 122(2): 73-93.