

The Effect of Heat Treatment on the Structure of PEO Coating on Ti-6Al-4v Alloy

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Abstract

In order to increase the corrosion resistance and improve the biocompatibility of Ti-6Al-4V alloy used in medical applications such as implants, it has been modified with various methods including PEO. On the other hand, this alloy is also capable of heat treatment. In this study, firstly different structures were obtained by heat treatment of Ti-6Al-4V substrate and then different structures were coated with the same parameters, by PEO method. The scanning electron microscope equipped with EDS was used to investigate the morphology and cross-sectional of the coatings. X-ray diffraction was also applied to analyze the phases created in the coating. Additionally, investigation of surface topography was performed by atomic force microscopy. Results have represented that the martensitic structure has a lower porosity with more regular dispersion. The creation of coating with martensitic structure also shows good thickness with high quality smoothness. On the other hand, the coating of the α -plate and inter-grain β structure were included large and irregular porosities.

Keywords: Ti-6Al-4V, Heat Treatment, PEO, Porosity.

1. Introduction

Titanium and titanium alloys are used in various industries such as petrochemical, medical and aerospace industries due to different properties as good corrosion resistance, biocompatibility and high strength to weight ratio [1]. One of the applications of these alloys in the medical field is implants. Biocompatibility, corrosion resistance and abrasion resistance are the most important features of an implant [2]. Ti-6Al-4V is one of the most widely used titanium alloys in the α - β group [1]. This alloy is used as dental and orthopedic implants because of its corrosion resistance and desirable mechanical properties. On the other hand, due to the presence of aluminum and vanadium in this alloy, increment of biocompatibility for dental and orthopedic implant applications are required [3]. The titanium substrate, which has a TiO₂ oxide layer, increases corrosion resistance and helps the implant stabilization [4]. One of the methods to create an oxide layer on a metal substrate such as Ti, Al, Zr, and Mg is plasma electrolytic oxidation (PEO). The important feature of this method is the creation of thick and well-adhered coatings in order to improve corrosion and wear resistance [3]. A significant characteristic of the PEO process is the creation of a coating (oxide layer) with various elements on the substrate surface [4]. These include calcium and phosphorus, which can be incorporated into the coating of metals used as implants in the PEO process [4].

The presence of an oxide layer containing calcium and phosphorus associate with of Ti-OH can lead to the formation of a hydroxyapatite phase on the coating [5]. Various PEO process parameters such as process time, voltage, electrolyte composition, substrate chemical composition, electrolyte temperature and current density determine the coating quality [3, 4]. Montazeri et.al. [5] showed that with increment of the voltage in the PEO process, the porosity with increase as well as the absorption of calcium and phosphorus elements in the electrolyte will occur by the oxide layer created on Ti-6AL-4V Ying-liang Cheng et.al [6] showed that with increment of time in the PEO process, the porosity increase Jung-In Kang et.al [3] showed that the size porosities will be affected by changes of Mn percentage (available in electrolyte).

As the percentage of Mn in the electrolyte increased, the number of porosities increased, resulting in large porosities with irregular shapes [3]. Since one of the important properties of titanium alloys (α - β) such as Ti-6Al-4V is the microstructure control by heat treatment, the aim of this study is to investigate the effect of heat treatment of Ti-6Al-4V substrate on coating structure created by PEO method.

2. Materials and Methods

The Ti-6AL-4V alloy in accordance with the ASTM- grade 5 standard was used in this study as the substrate.

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Chemical analysis of this alloy was done by optical emission spectrometry (Table. 1).

The specimens with 30 mm in long and 20 mm in wide and 4 mm in thickness were prepared for heat treatment. Also, some of specimens were cut to 20 mm \times 20 mm \times 4 mm in dimension for microstructural investigation after heat treatment. Surface preparation of substrate prior to the coating was performed for some specimens. In order to heat treatment of specimens, they divided to three groups. The first one was put in the furnace for 30 minutes at 1050°C and then quenched in the water (the code for these specimens is one). The second one was put in the furnace for 30 minutes at 1050°C and then cooled in the furnace (the code for these specimens is two). The last one and was put in the furnace at 860°C for 30 minutes and then quenched in water (the code for these specimens is three). The induction furnace was used with ± 50 c accuracy for heat treatment. Plasma electrolytic oxidation process was used to perform the coating process after heat treatment. The electrolyte which used for the coating process was made of distilled water, hydrated calcium acetate and dehydrated sodium dihydrogen phosphate. The cathode and anode were stainless steel tank wall and work piece, respectively. The wall of the reservoir was water cooled and the maximum electrolyte temperature was about 35°C during the process. The coating process was carried out for 15 minutes using a constant voltage of 500 V from a DC source with 30% cycle and frequency of 1000 Hz. The specimens for microscopic observations were etched in HCl/ HF/ HNO (5:10:15 V/V/V). An optical microscope (B-500 tiph) was employed for the observations. Also, a scanning electron microscope (SERONAI S 2300) equipped with EDS detector was used to investigate the microstructure of surface and cross section of coated specimens. Images was prepared using a

secondary electron detector at 30 kv working voltage.

The XRD (PHILIPS Model) used with a copper target (Cu) for studies of the oxide layers on the atomic force microscopy (AFM-Dual scope/ Raster scope C 26, DME) with AC current were used for evaluating surface topography.

3. Results and Discussion

3.1. Heat Treatment

In order to investigate the effect of heat treatment on the substructure, thickness and roughness of the coating created by plasma electrolytic oxidation on the substrate of Ti-6Al-4V alloy, different heat treatment were performed on specimens. Optical microscope images of the specimens after heat treatment are shown in Fig. 1a. shows microstructure of heat treated at 1050 ° C for 30 minutes and then quenched in water. A martensitic transformation occurred in this specimen and α' phase was formed. The microstructure of specimen heat treated at 1050 ° C for 30 minutes and then cooled in the furnace is shown is Fig. 1b. α -plate and inter-grain β phases are obvious in this image. Microstructure of specimen which heat treated at 860 ° C for 30 minutes and then cooled in water containing initial α and residual β phases is presented in Fig. 1c.

Therefore, it can be written that the purpose of different cyclic heat treatment in this study is to create different microstructures including α , β and α' phases which have different distribution of aluminum and vanadium elements.

Coating parameters of the PEO process including electrical parameters, electrolytic specification, and process time were constant during coating. After beginning of the coating process, bubbling was observed around the surfaces of the specimens.

Table. 1. The chemical composition of the Ti-6Al-4V alloy (wt.%).

Al	V	Fe	C	N	O	H	Ti
6.011	4.020	0.101	0.011	0.004	0.101	0.010	Balance

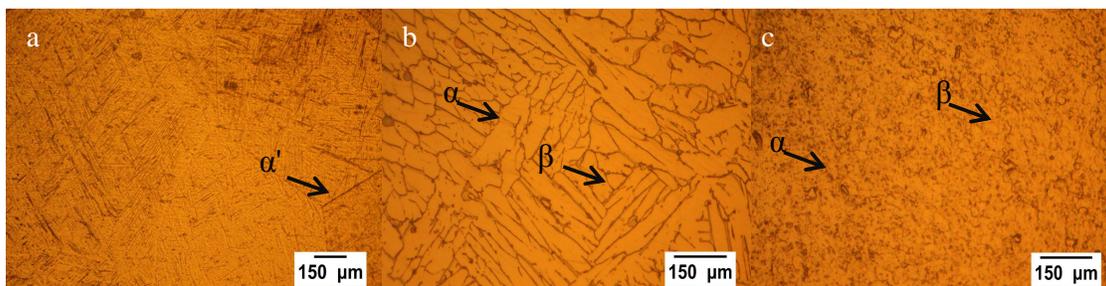


Fig. 1. Optical microscopic images of Ti-6Al-4V heat treated at, a) 1050 ° C for 30 min and then quenched in water, b) 1050 ° C for 30 min and then cooled in the furnace, c) 860 ° C for 30 min and then quenched in water.

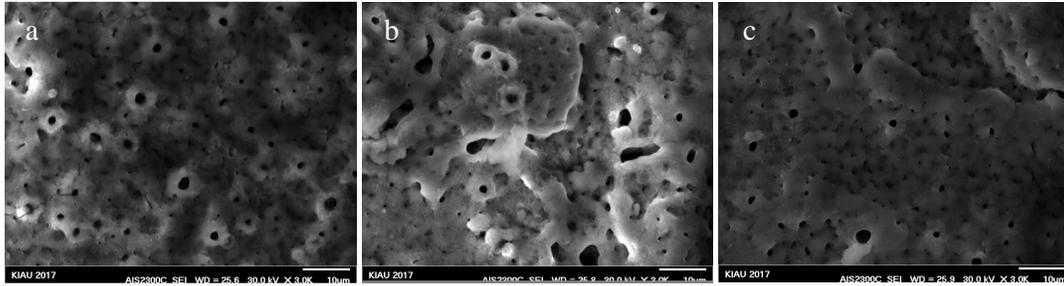


Fig. 2. Scanning electron microscope images of the coating surface of Ti-6Al-4V heat treated at, a) 1050 ° C for 30 min and then quenched in water, b) 1050 ° C for 30 min and then cooled in the furnace, c) 860 ° C for 30 min and then quenched in water.

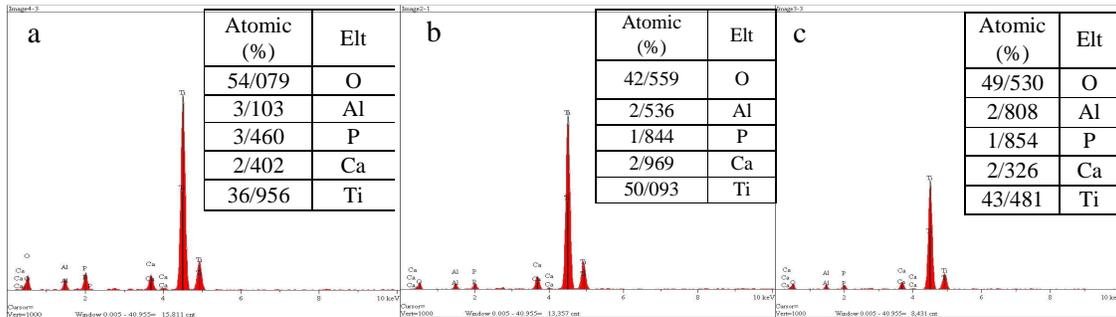


Fig. 3. Results of EDS analysis of the coating surface of Ti-6Al-4V heat treated at, a) 1050°C for 30min and then quenched in water, b) 1050°C for 30min and then cooled in the furnace, c) 860°C for 30min and then quenched in water

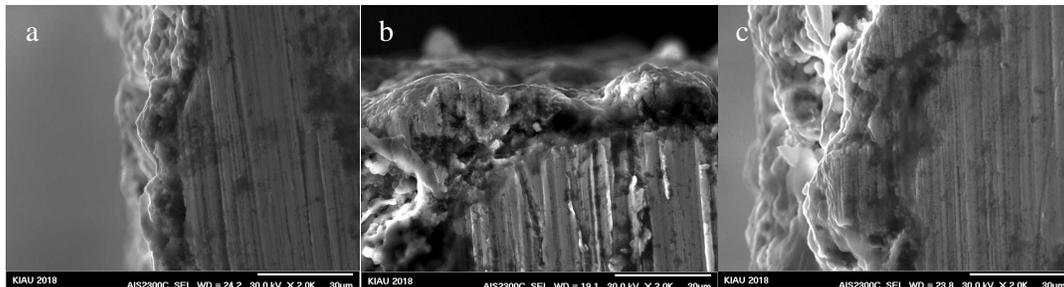


Fig. 4. Cross sectional of scanning electron microscope images, a) first specimen with martensitic structure, b) second specimen with α -plate and inter-grain β phases, c) third specimen with initial α and residual β phases.

3.2. Coating Structure

Fig. 2. shows scanning electron microscopy images which taken from the surface of the specimens.

Fig. 2a. presents the surface of specimen heat treated at 1050 ° C for 30 min and quenched in water which had a martensitic structure prior to the coating process with same porosities in size and shape. Also, the average size of porosity by using the software of imagej was obtained 1.51 μm . Fig. 2b. displays the surface of specimens heat treated at 1050 ° C for 30 min and cooled in furnace, which contains a α -plate and inter-grain β structure prior to the coating process. As can be seen, the shape and size of the porosities are varied. The average size of porosity in this specimen was obtained 2.66 μm . Fig. 2c. shows the surface of specimen heat treated

at 860 ° C for 30 min and then quenched in water, which had a initial α and residual β structure prior to the coating process with tiny porosities and a few large porosities. Also the average size of porosity in this specimen was obtained 1.41 μm . Fig. 3. also presents the results of the EDS analysis. Due to the presence of calcium and phosphorus in the electrolyte, the atomic percentages of these elements are also specify.

3.3. Cross Section Coating

In order to investigate the coating thickness, cross-sectional of coated specimens were analyzed by scanning electron microscope, Fig. 4. shows the obtained images from the mentioned specimens. The thickness of first specimen, which has a martensitic structure, is greater than the other ones.

On the other hand, the least thickness is observed in the third specimen with initial α and residual β phases. The results showed that the thickness of first, second and third specimens were 25.65 μm , 15.90 μm and 11.15 μm , respectively.

3.4. XRD Analysis

Fig. 5. shows the XRD results of the specimens. The XRD results show that the coating layer consists of two layers including the anatase and rutile phases. Additionally, the presence of adhesive phase on the surface is obvious, which has the role of protecting the substrate against corrosion and is a kind of surface protective layer, it is the anatase phase and the porous layer on the outer portions the rutile phase coating.

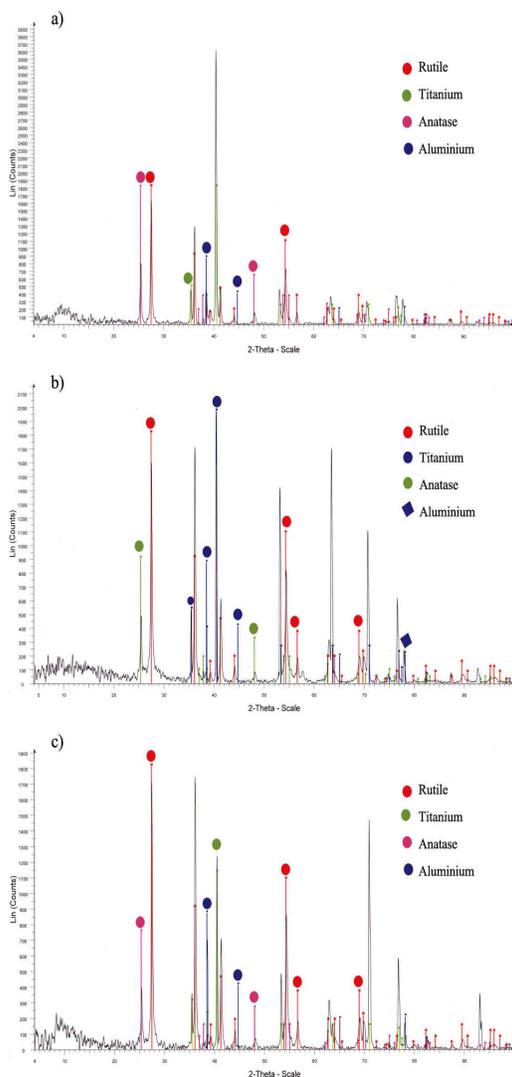


Fig. 5. Results of XRD analysis, a) first specimen with martensitic structure, b) second specimen with α -plate and inter-grain β phases, c) third specimen with initial α and residual β phases.

3.5. Survey Topography

Fig. 6. shows three-dimensional AFM images of the top and bottom surface of the samples. The surface roughness of the three specimens differs greatly from each other. The cause of this phenomenon may be related to the uneven distribution of alloying elements in different phases after heat treatment. The presence of different phases in the base alloy will create the α , β , and α' phases, which have different oxidation rates, to change the surface topography. Fig. 6a. shows image topography of the first specimen. it is obvious that surface area of this specimen is higher than the other ones. Fig. 6b. indicates surface topography of second specimen. Fig. 6c. is the surface topography of third specimen with the highest surface roughness. The reason of the creation of the roughness in the PEO process is the porosity.

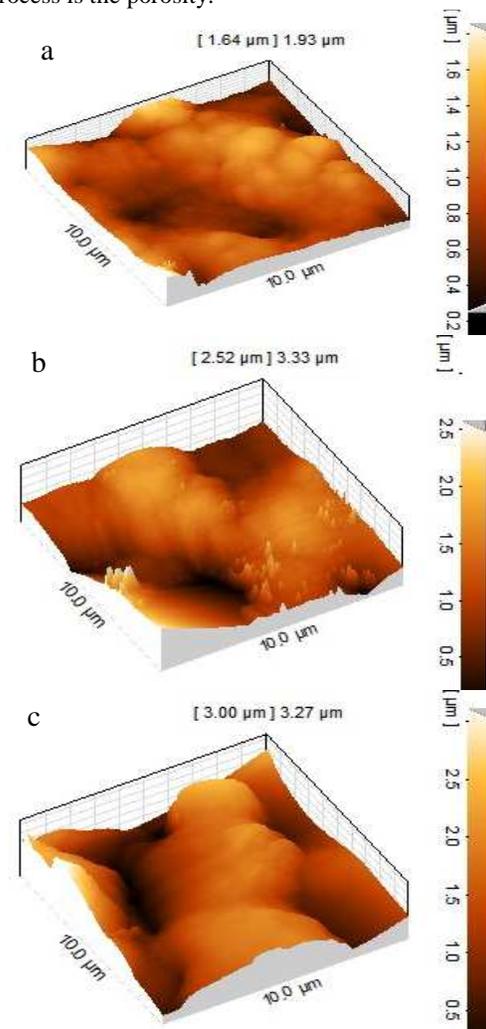


Fig. 6. Three-dimensional AFM images of the surface of the specimens, a) first specimen with martensitic structure, b) second specimen with α -plate and inter-grain β phases, c) third specimen with initial α and residual β phases.

4. Conclusions

1. The shape and size of the pores of coating created by the PEO will be affected by different structures of the Ti-6Al-4V substrate which obtained from different heat treatment. Among the three different heat treatment structures investigated in this study, the α -plate and β -intergranular structures had the highest porosity and the coatings on this structure had irregular porosities. The coating on the specimen with residual β and initial α structure had the lowest porosity and also the shape of the porosity was spherical. The specimen with martensitic structure had a porosity with same size in the residual β and α structure, but the porosities were volcanic and had a more regular distribution.
2. Heat treatment affects the Ti-6Al-4V substrate thickness due to the formation of different structures on the thickness of the PEO coating. The thickness of martensitic structure was higher than the others. Also, the specimen with initial α and residual β phases, had the lowest coating thickness among the three different structures.
3. Surveying the topography of the surface, revealed various structures that were affected by the heat treatment on the Ti-6Al-4V substrate they have specimen effect on the roughness of the PEO coating. The sample with martensitic structure has the highest surface smoothness. The specimen containing the initial α structure and the β residual phases has the highest surface roughness.

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