

An Investigation on Corrosion Behaviour of Colour Anodized Ti6Al4V Alloys

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Abstract

In this study colourful anodic oxide films were obtained on Ti6Al4V by applying constant voltages 25-125 V for 1 min at room temperature. Electrolyte was 0.5 M phosphoric acid solution. Colours of the oxide layer varied with the applied voltage. As soon as the exposure of the samples in acidic solution, a rapid oxidation was observed. Different colours were obtained because of the light interferences through the oxide layers. Electrochemical properties of oxide layers were investigated by OCP, EIS and PDP techniques. The best corrosion properties were achieved with a voltage 50 V with a light yellow colour, while non-anodized sample shows the worst corrosion behaviour.

Keywords: Ti6Al4V alloy; Colour anodizing; Corrosion; Electrochemical impedance spectroscopy (EIS).

Introduction

Titanium (Ti) and its alloys have many applications, especially in aerospace, cryogenic and biomedical industry thanks to its high strength, elastic modulus and good biocompatibility [1–4]. It exhibits high fracture toughness compared to ceramic materials used for the same purpose [5]. Colour anodizing of Ti alloys are used in order to improve the success and accuracy of inserting the implants in the operating media. Ti6Al4V is the most widely used in biomedical industry, as the alloying elements increase mechanical properties [5,6]. However, its long term performance induces safety concerns because Ti6Al4V exhibit low wear resistance, it can cause to contamination of Al of V into human body which are toxic, can cause to diseases like Alzheimer [6,7]. Even though mechanical properties are related to bulk structure, biological properties depend on surface properties of the alloy [8]. Corrosion is well expected when metallic implants are concern. In this context, the inertness of the alloy in human body is related to oxide layer on the surface [7]. Passive layer produced by anodic oxidation produces a strong barrier between the alloy and its surrounding, without affecting the biocompatibility of the substrate [2,5].

Passive layers that induced with anodic oxidation in acid solutions are more stable and more homogenous than oxide layers which are formed on the alloy surface in contact with air [2,5,6].

The purpose of this study was to investigate corrosion properties of colour anodized Ti6Al4V alloy in 0.5 M phosphoric acid at voltages varies between 25-125 V by OCP, PDP and electrochemical impedance spectroscopy (EIS) since they are the most used techniques to understand corrosion behaviour of experimental systems.

Experimental

Materials – All samples of Ti6Al4V alloy were heat treated at 760 °C and air cooled. The samples used were machined to Ø4x20 mm dimensions. Chemical composition of the alloy used is given in Table.1. Sharp edges of the samples were grinded using SiC paper of 120 and 1000 respectively and followed by rinsing in ethanol before the anodizing process starts. The microstructure of tested material Ti6Al4V was given in Figure 1.

Table 1. Chemical analysis of the Ti6Al4V alloy.

Alloy	Ni	Si	Mn	Cr	Fe	Al	V	Ti + Other
Ti6Al4V	0.015	0.02	0.0048	0.015	0.098	5.877	3.919	Balance

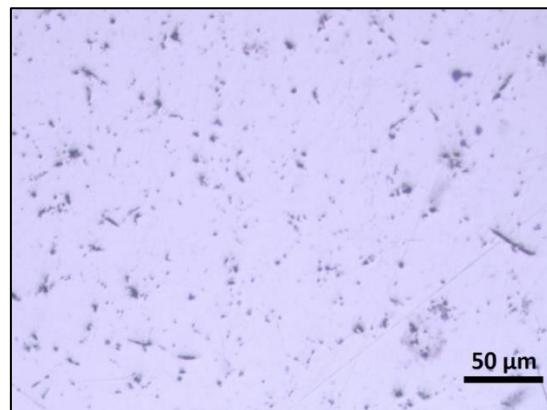
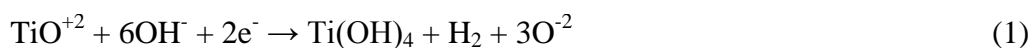


Figure 1. Optical image of Ti6Al4V samples.

Anodizing – Before the anodizing process all the samples were pickled in 30% nitric acid for 5 min. at room temperature to remove dirt and metal stains can be caused by cutting and then cleaned in distilled water. The anodizing process was conducted with two electrode cell. Each anodizing process was monitored and controlled during the experiment to have identical experimental conditions. For the anodizing process 0.5 M phosphoric acid solution was used and process was carried out at 21 ± 1 °C for 1 min. The process was conducted in a continuous stirring and after every operation the solution was renewed. Stainless steel was used as cathode and tested titanium alloy worked as anode. The coloured samples were cleaned in distilled water and dried after the anodizing process completed. As a constant voltage was applied between 25 V - 125 V, a colourful oxide layer were obtained according to following reactions [9]:



Electrochemical Experiments – Electrochemical experiments were carried out by open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) technique and potentiodynamic polarization (PDP) experiments in 0.1 M NaCl solution without stirring at room temperature. Standard three electrode system consisting of a working electrode (sample), a counter electrode (graphite rod), and a reference electrode (Ag/AgCl) was employed by using Gamry Interface 1010B Potentiostat/Galvanostat/ZRA. Open circuit potential is applied for 300 sec. The potentiodynamic polarization scan was started from the starting potential (-0.25 V vs. OCP) to ending potential (+1.5 V vs. OCP) with a scan rate of 1 mV/s. EIS measurements were performed applying a sinusoidal signal of 10 mV, of amplitude in a frequency range from 10 kHz to 10 mHz, and recording 5 points per decade.

Results and Discussion

As a result of anodizing at constant voltages of 25 V, 50 V, 75 V, 100 V and 125 V, titanium samples had different colour. The colour of the layer at 25 V was navy blue, at 50 V was light yellow, at 75 V was magenta, at 100 V was green and at 125 V was grayish yellow. Colour chart of the anodized samples were shown in Figure 2.

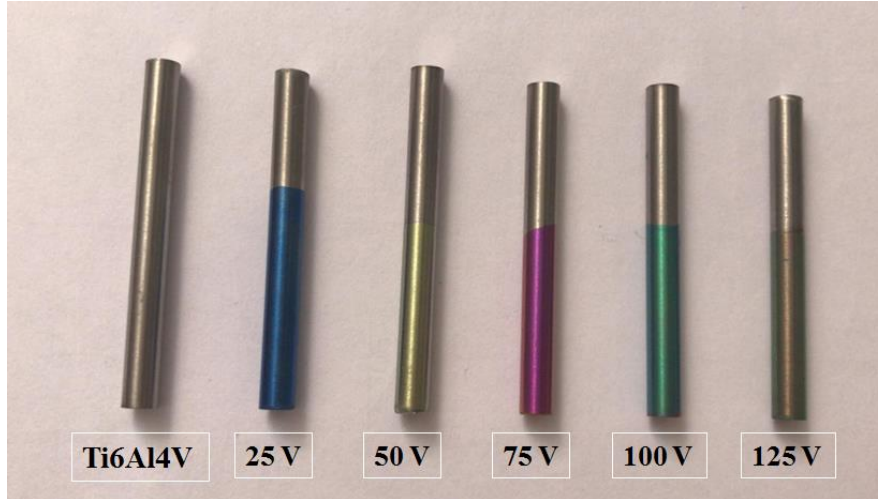


Figure 2. Colour chart of the anodized samples in phosphoric acid solution at different voltages

According to PDP results conducted in 0.1 M NaCl solution, best corrosion properties were obtained for 50 V voltage applied samples. Figure 3 shows Tafel curves for all applied voltages and Ti6Al4V itself. Table 2 shows best corrosion current was obtained for 50 V, followed by 75 V, 100 V, 25 V, 125 V and Ti6Al4V, respectively.

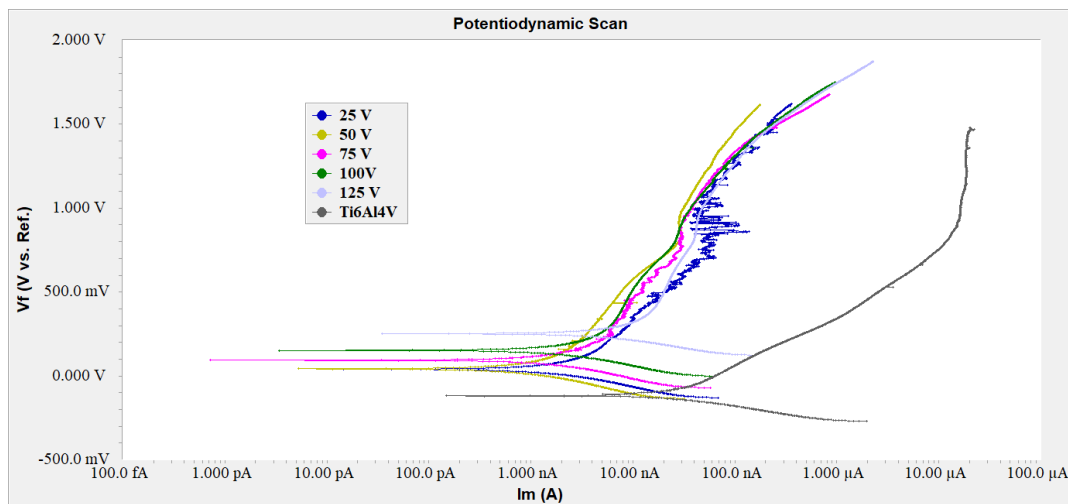


Figure 3. Comparison of polarization curves of anodized samples in different voltages and non-anodized sample

In the present study, the EIS data brought in Figure 5 as Bode plots show alteration after the formation of the oxide layer. For the Ti6Al4V substrate and colour anodized samples two equivalent circuits are proposed to explain the received responses, shown in Figure 4. The both equivalent circuit comprises a resistor, R_e (electrolyte resistance) and α is the CPE-power ($0 \leq \alpha \leq 1$). It is important to remark that the use of CPE is frequently employed to fit impedance data arising from a broad range of experimental systems [10]. Behaviours in high frequency regions give parallel results with PDP results.

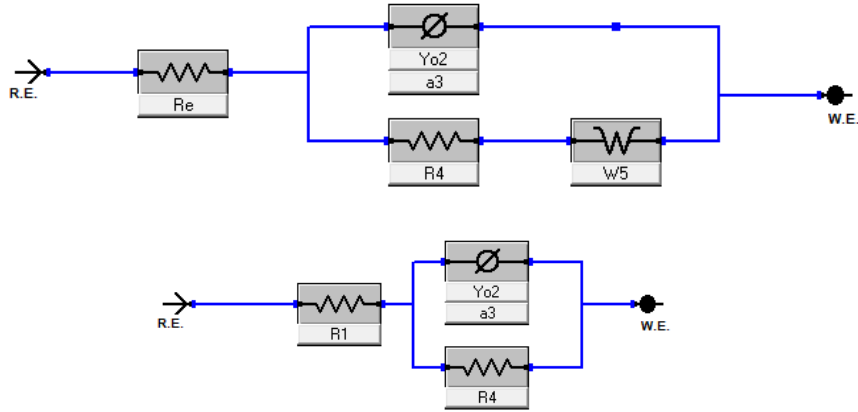


Figure 4. Equivalent circuit for colour anodized alloys (top) Ti6Al4V alloy (below).

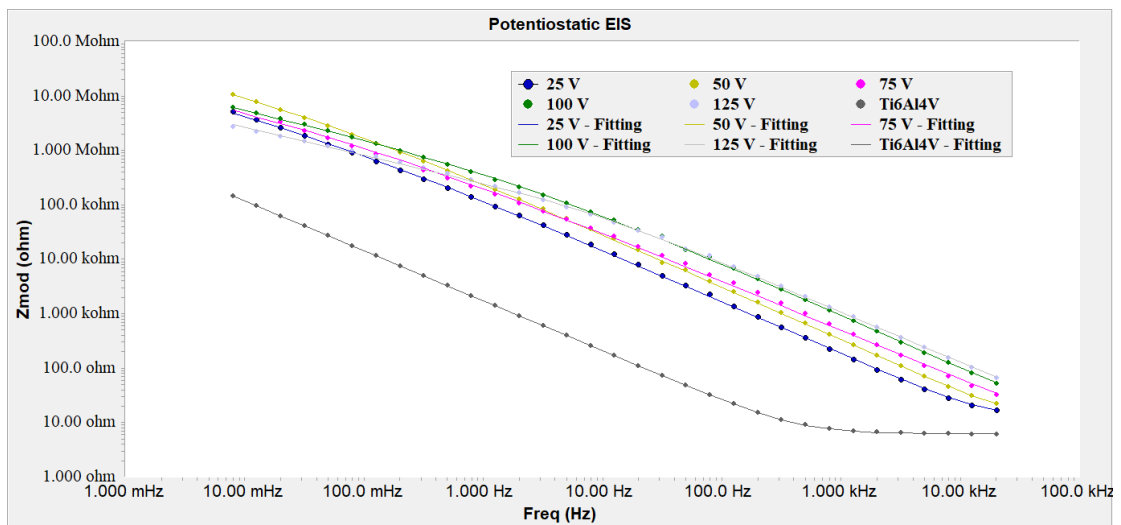


Figure 5. EIS spectra of the untreated Ti6Al4V alloy and anodic layers grown in phosphoric acid solution.

Table 2 shows the values of the electrical parameters obtained for the untreated Ti6Al4V alloy and anodized samples in the fittings using the described circuits.

Table 2. Results of electrochemical tests of samples anodized in phosphoric acid solution.

	Ti6Al4V	25V	50V	75V	100V	125V
OCP (mV)	-119.5	-48.1	113.4	140.5	246.7	371.8
E_{corr} (mV)	-118.9	39.1	42.89	93.5	152.3	251.5
i_{corr} (nA)	32.2	2.72	1.44	1.68	2.57	5.24
R_e (Ω)	6.195	11.93	10.81	8.05	12.51	26.56
CPE_{oxide} (μSs^α/cm²)	106.50	1.33	0.64	0.73	0.24	0.20
α	0.92	0.95	0.96	0.91	0.96	0.98
R_{ct} (MΩ)	1575	75.89	156.3	58.9	40.99	104.1

Conclusion

The results obtained in this study are summarized below:

1. Anodic oxidation at different constant voltage values led to different colours.
2. With introducing an anodizing layer, better corrosion properties were achieved than Ti6Al4V itself.
3. The worst corrosion properties were obtained with a voltage 125 V among anodized samples.

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