

Anodizing of Titanium in NaOH Solution and its Corrosion Resistance in PBS Physiologic Solution

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Titanium is a highly reactive metal with an inclination to compose with oxygen. In order to increase its corrosion resistance and application, therefore, a thin layer of titanium oxide is produced on the surface by chemical and electrochemical methods. In the present research, titanium has been anodized in 20 M of NaOH solution under potentiostatic conditions at constant voltages of 25 and 35 V. The microstructure of the anodic layers has been studied by the use of a Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). The results indicated that the structure of the anodic layers is amorphous with low porosity and that thickness increases with an increase in anodizing voltage. The corrosion resistance of the anodized titanium in a Phosphate-Buffered Saline solution (PBS) is very low in comparison with non-anodized titanium, due to the compactive layers of the titanium oxide. Heat treatment of anodized titanium at 600°C for one hour had no effect on the corrosion resistance.

INTRODUCTION

Since titanium is a highly reactive metal, whenever it is exposed to air or other environments containing oxygen, a thin film of titanium oxide is formed on the surface. This layer causes an increase in the corrosion resistance of the titanium [1]. The quality and corrosion resistance of produced oxide layers depend on the type of area, the chemical composition of the titanium and its alloys, the amount of oxygen, the percentage of atmospheric humidity and the chemical composition of the environment. The corrosion resistance of an anodic film in a humid environment is higher than that in an oxidizing environment without humidity [2]. If the anodized layers were damaged due to an accident and exposed in a humid environment with a low level of oxygen (ppm), it would be remade [3]. Anodized layers with low porosity and high compactivity can be produced through chemical and electrochemical methods [4-6].

The structure and thickness of the anodic layer depend on the type of solution and the anodizing method (galvanostatic or potentiostatic). Thick anodic layers are produced in concentrated basic solutions (pH

> 13) [7]. These coatings are used for lubrication and anti-galling in the formation of titanium and its alloys at high temperature, freeting applications such as implants in knee and thigh bones [8,9] and, also, for increasing corrosion resistance [10-12]. In concentrated NaOH solutions, the oxide film is gray, homogeneous and compactive. The electrochemical properties and electrical conductivity of these layers are mainly different from the type of layers formed in H₂SO₄ and H₃PO₄ solutions. The glow discharge phenomena occurs, simultaneously, with the anodizing process and causes an increase in the surface temperature. The X-ray diffraction technique shows that anodized layers are made mainly from titanium dioxide [13].

The biocompatibility of metallic implant materials is closely related to their corrosion behavior. Corrosion and surface film dissolution are two mechanisms for introducing additional ions into the human body. It has been concluded that biocompatibility is determined, not only by corrosion products but, also, by the exchange currents and reaction products of different redox processes involving tissue compounds. It has been reported in some cases that, titanium implants (non-anodized), which have been inserted into the human body for a number of years, have shown high oxidation rates and relatively high amounts of titanium compounds have been found in tissue adjacent to the implant [14]. By anodizing titanium previous to its implantation in the body, the corrosion rate decreases and the rate of bone healing highly increases [15].

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EXPERIMENTAL

Commercially pure titanium specimens, with chemical composition given in Table 1, were prepared in the form of plates with $15 \times 15 \times 2$ mm dimensions. The specimens were degreased by acetone, rinsed and pickled using hydrofluoric acid (40 g/lit), ground with 320, 500, 800, 1000, 1200 emery paper and, finally, polished with 0.3 and 0.05 μm Al_2O_3 powder. After rinsing with distilled water, the specimens were dried using hot air.

For anodizing titanium, a concentrated NaOH solution (20 M) was used. Also, a PBS solution was used for study of the corrosion resistance of the specimens in the body's physiologic solution. The chemical composition of the PBS solution is given in Table 2.

Anodizing was performed in a cubic cell made of 316 stainless steel, with a dimension of $10 \times 10 \times 5$ cm (cathod), under potentiostatic conditions in potentials of 25 and 35 V at 25°C and over a period of 30, 70, 100 and 150 seconds. The variations of current versus anodizing time during the process were plotted. In order to reveal the effect of heat treatment on the structure of layers, a number of specimens were heated at 600°C for 1h under an argon gas atmosphere and then cooled in a furnace.

The thickness of the anodized layers was measured using a microscope. Scanning electron microscopy and X-ray diffraction techniques were used to study the morphology, structure and porosity of the layers. Evaluation of the corrosion resistance of anodized and non-anodized titanium in a PBS physiologic solution (simulated solution of body) at 37°C , was carried out using the potentiodynamic polarization method by AMEL potentiostat instrument model 5000. The scan rate of potential in these tests was 1 mV/sec. The corrosion rate was calculated using the linear polarization method and was derived via the following equation [16]:

$$\text{C.R.} = 0.129 (I_{\text{corr}}/D)(M/n),$$

Table 1. Chemical composition of titanium used in this research.

Element	C	O	Fe	Ti
Wt%	0.06	0.22	0.37	rest

Table 2. Chemical composition of PBS solution.

Chemical Composition	NaCl	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	KH_2PO_4
Concentration (g/L)	8.77	3.58	1.36

where:

C.R. (mpy)	corrosion rate
I_{corr}	current density of corrosion ($\mu\text{A}/\text{cm}^2$)
M	atomic weight $(M/n)_{\text{TiO}_2} = 13.585$ gr
D	density (gr/cm^3) $(M/n)_{\text{Ti}} = 11.97$ gr
n	valency
D_{TiO_2}	$3.84 \text{ gr}/\text{cm}^3$
D_{Ti}	$4.5 \text{ gr}/\text{cm}^3$

RESULTS AND DISCUSSION

Anodizing

Figure 1 shows the variation of current versus anodizing time at constant voltages of 25 and 35 V. It is evident that the current required for nucleation of the oxide layer in the processes under potentiostatic conditions were 1 and 2 A at 25 and 35 V, respectively. Also, an increase in anodizing voltage caused an increase in this current. With an increase in anodizing time, the thickness of the layer increased and, as a result, current flow decreased. This case has been verified by Kelly [17]. The formation of an oxide layer on titanium in a NaOH solution involves nucleation, formation, growth and breakdown steps. At the nucleation stage, the variations of current versus time at the voltages of 25 V and 35 V are constant. Then, the current decreases to a certain minimum value (formation stage). After decreasing the current to a minimum, it stabilizes further in proportion to the time (growth stage) and the thickness of the layer, also, increases slightly with time. In the course of such treatment, a stable, non-porous and compactive layer is produced

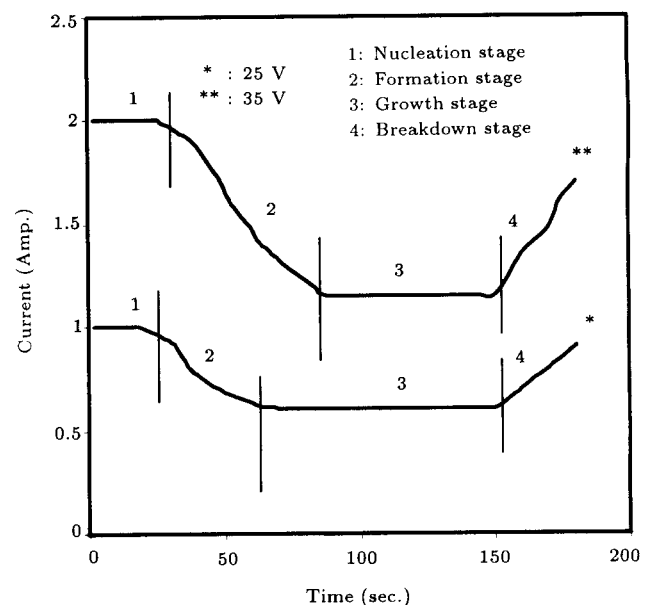


Figure 1. The variation of current vs anodizing time in 20M NaOH solution at constant voltages of 25 and 35 V.

Table 3. Thickness of anodized layers in NaOH solution.

Potential (V)	Time (sec)	Thickness (μm)
25	30	0.40
	70	0.46
	100	0.52
	150	0.62
35	30	0.83
	70	0.99
	100	1.23
	150	1.50

on the titanium surface. The current passed through the layer causes it to heat and increases its resistivity, thus, a breakdown of the oxide layer occurs. Therefore, current flow increases versus time (breakdown stage).

The thickness of the anodized layers is given in Table 3. With regard to results, the thickness of the anodized layers at 35 V is higher than at 25 V. Also, an increase in anodizing time at each of the applied voltages, caused an increase in thickness. The color of these layers was dark gray.

Variation of the thickness of the layers versus anodizing time is shown in Figure 2. As evident, this variation is linear and follows the following equations:

$$y = 0.0018 t + 0.3414 \quad (\text{in } 25 \text{ V}),$$

$$y = 0.0058 t + 0.6317 \quad (\text{in } 35 \text{ V}),$$

where t is the anodizing time and y is the thickness of the layer.

In the process of layer growth, diffusion is not the determining factor in the kinetics of treatment. Chemical reaction is the controlling factor in the kinetics of anodizing titanium in the NaOH solution.

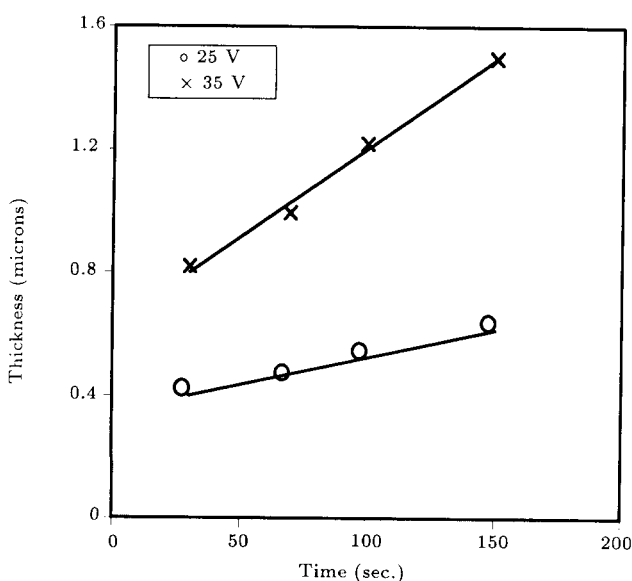


Figure 2. The variation of thickness of layer vs anodizing time in NaOH solution.

The scanning electron microscope images of the anodized layers cross section in an NaOH solution with thickness of 0.62 and 0.83 micron are shown in Figures 3 and 4.

An X-ray diffractogram of a specimen anodized for 150 seconds at a constant voltage of 35 V, has been shown in Figure 5. As shown in the figure, no TiO_2 peaks were observed. This situation could be due to one of the two following reasons: (i) The oxide layer is composed of amorphous titanium dioxide; (ii) The TiO_2 layer does not really exist and there is a continuous variation of the composition of the oxide film along the whole thickness. A heat treatment process was performed for 1 hour on a sample at 600°C in a furnace containing an argon atmosphere. After that treatment, the characteristic peaks of anatase and rutile at $2\theta = 29.5^\circ$ and $2\theta = 32.1^\circ$, respectively, were observed (see Figure 6). A comparison between Figures 5 and 6 shows that crystallization has occurred,

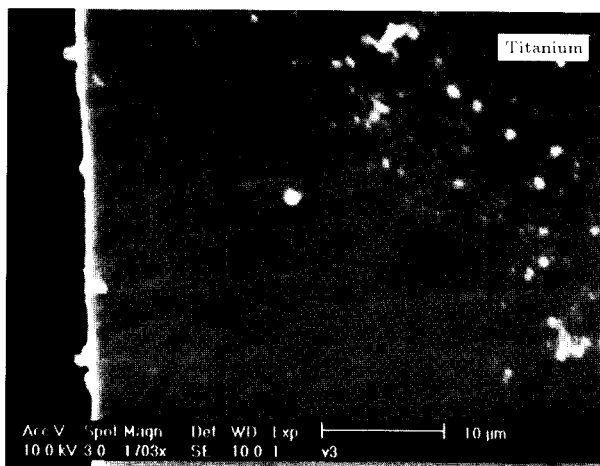


Figure 3. The SEM micrograph of anodic layer cross section (at 150 sec and 25 V).

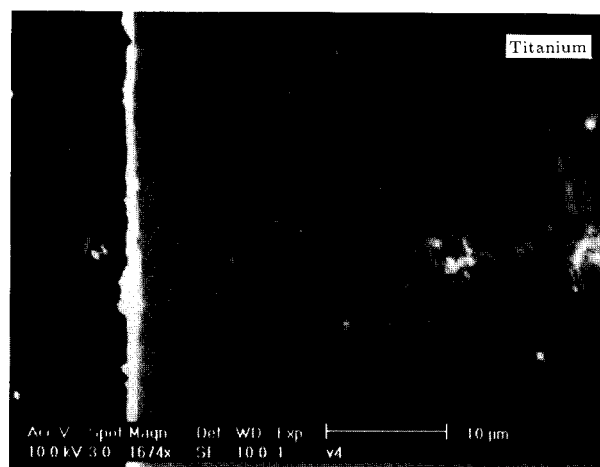


Figure 4. The SEM micrograph of anodic layer cross section (at 30 sec and 35 V).

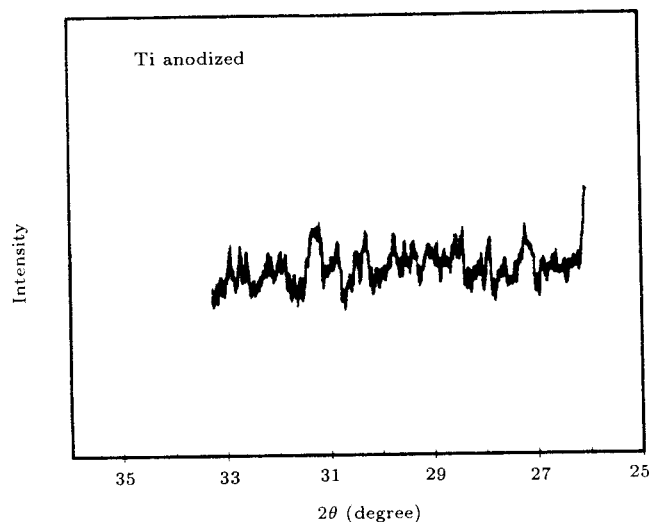


Figure 5. The diffractogram of anodized titanium surface for 150 sec.

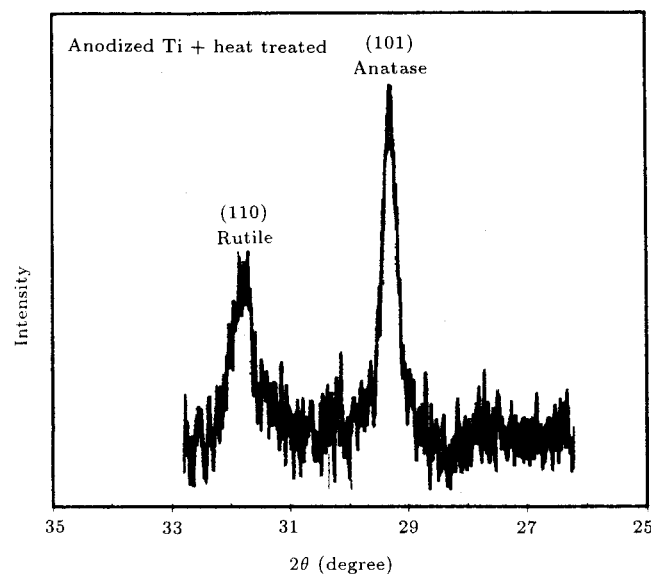


Figure 6. The diffractogram of anodized titanium surface for 150 sec after heat treatment at 600°C under an argon atmosphere.

therefore, it can be concluded that the oxide layer is composed of amorphous TiO_2 .

The scanning electron microscope image from the anodized layer's surface, formed after 150 seconds at a constant voltage of 35 V, is shown in Figure 7. It can be seen that the structure of the anodized layer is amorphous and contains very low porosity.

Corrosion Resistance

The polarization curve of the non-anodized titanium in a PBS solution at 37°C is given in Figure 8, the pure data for which is given in Table 4.

The polarization curves of the non-anodized and

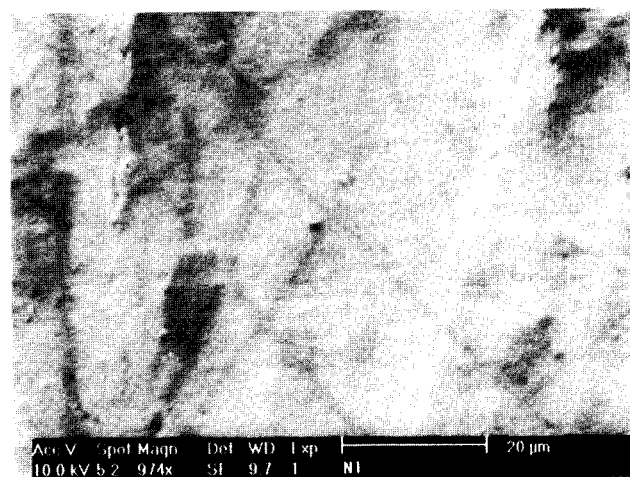


Figure 7. The scanning electron microscopy image of surface of anodic layer for 150 sec at 35 V.

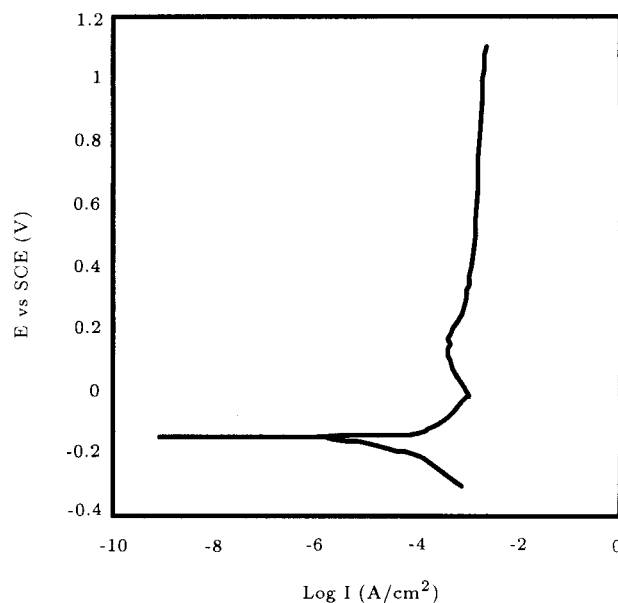


Figure 8. The polarization curve of non-anodized titanium in PBS solution.

anodized titanium (at 25 and 35 V for 150 sec) in a PBS solution at 37°C, are shown in Figure 9.

Table 5 gives the obtained data from Figure 9. With regard to the obtained results, it could be mentioned that the anodizing treatment has an effective role in decreasing the corrosion rate. The corrosion rate in the PBS solution is very low due to the compactivity and thickness of the anodized layers.

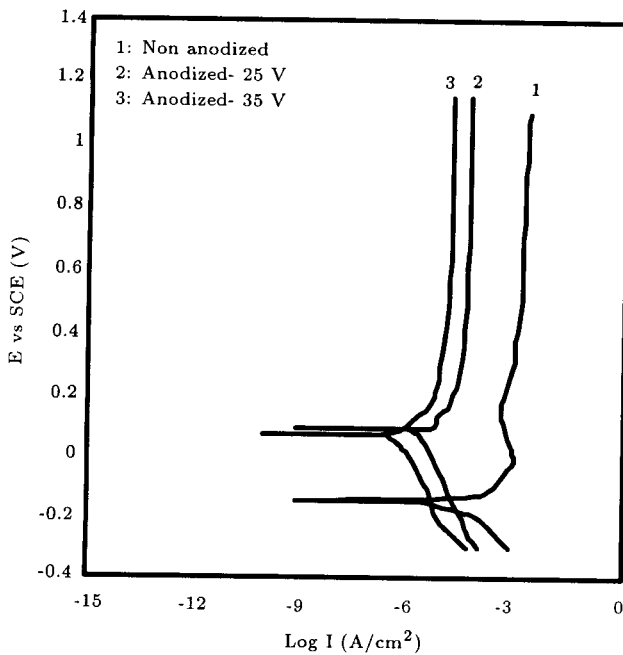
The polarization curves of the anodized and non-anodized titanium for 150 seconds at 35 V and anodized plus heat treated titanium are shown in Figure 10. As shown, the anodic and cathodic curve branches of the anodized titanium, with and without heat treatment, superimpose on each other. Thus, heat treatment has not affected the corrosion behavior of the anodized

Table 4. The obtained results of polarization curve of non-anodized titanium in PBS solution.

β_a (V/decade)	β_c (V/decade)	ΔI (A/cm ²)	ΔE (V)	I_{crit} (A/cm ²)	E_{crit} (V)	I_{pass} (A/cm ²)	I_{corr} (A/cm ²)	E_{corr} (V)	Corr. Rate (mpy)
0.05	0.05	3.6E-5	0.01	0.001	-0.02	0.001	3.91E-5	-0.15	13.432

Table 5. The results of polarization curve of anodized titanium in PBS solution.

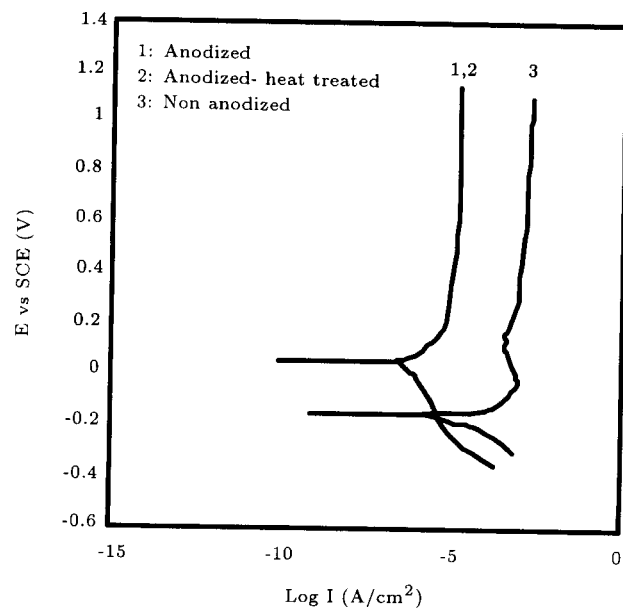
Voltage (V)	Thickness (μm)	β_a (V/decade)	β_c (V/decade)	ΔI (A/cm ²)	ΔE (V)	I_{crit} (A/cm ²)	E_{crit} (V)	I_{pass} (A/cm ²)	I_{corr} (A/cm ²)	E_{corr} (V)	Corr. Rate (mpy)
25	0.62	0.04	0.05	1.7E-7	0.01	-	-	5E-5	1.4E-7	0.08	0.066
35	1.5	0.03	0.05	1.7E-7	0.01	-	-	1.6E-5	9.2E-8	0.06	0.042

**Figure 9.** The polarization curves of non-anodized and anodized titanium (at 25 and 35 V, for 150 sec) in PBS solution.

titanium and only crystallized the structure of the layer.

CONCLUSION

1. Anodized layers in a NaOH solution (20 M) were compact and amorphous, so that by heat treatment at 600°C they became crystallized;
2. The thickness of the anodized layers produced at 25 and 35 V, versus time, increased on a linear basis;
3. Increasing the anodizing potential caused an increase in layer thickness produced by anodizing;
4. The corrosion rate of anodized titanium in a PBS solution is 200-300 times lower compared to non-anodized titanium;

**Figure 10.** The polarization curves of non-anodized and anodized titanium for 150 sec at 35 V with and without heat treatment in PBS solution.

5. Increasing the thickness of the anodized layer, decreases the corrosion rate;
6. Heat treatment at 600°C has no effect on the corrosion rate of the anodized titanium.

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