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Pure Commercial Titanium Color Anodizing and Corrosion Resistance

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In order to improve titanium corrosion behavior, we can increase the thickness of oxide layer on titanium surface during anodizing process and by electrochemistry. In this research, self-color anodizing of Ti in sulfuric acid was done, and anodizing layers were created in different colors. The highest value of chromaticity was 37.8 for the anodized sample in 10 V, and the lowest value was 8.6 at 15 V. The oxide layer thickness was calculated by optical method (light refraction). The anodic film thickness increased by increasing the anodizing voltage. The highest thickness of anodic film was 190 nm in sulfuric acid solution for the anodized sample in 80 V. Corrosion resistance of anodized Ti was studied by potentiodynamic polarization curves in biological solution of Ringer's at 37 °C. On increasing the anodizing voltage further, corrosion rate of the alloy increased from its lowest rate. The lowest rate of corrosion was for the sample anodized in 10 V, which was 0.96 × 10^{-3} mpy.

Keywords anodic film, polarization curve, refractive index, titanium

1. Introduction

Titanium and its alloys are extensively used in orthopedic and dental implants because of their excellent corrosion resistance, suitable bond making, and biological compatibility.

Pure commercial titanium with α structure is the most commonly used material for dental implants (Ref 1). Titanium lies within the neutral biomaterials which are not able to make a chemical bond with the bone. Anodizing is an electrolytic oxidation process for thickening the oxide layer on active titanium metals (Ref 2). Anodic oxidation is a surface improvement technique for implants which is very cheap, and also enables the formation of uniform coatings on the surface (Ref 3). Passive layers which are formed during anodic oxidation are more stable than oxide layers which are formed on the alloy surface in contact with air (Ref 4).

These metal surfaces are covered by a very thin oxide layer in contact with air. This very thin layer of high porosity and low mechanical strength cannot protect metal against corrosion (Ref 5). The oxide layer thickness is directly related to anodizing voltage so that by increasing the voltage the anodic film thickness increases (Ref 6). The colors formed on titanium surface after anodizing are known as interference colors. There is no pigment associated with the production of these colored surfaces (Ref 7).

Accordingly, two theories were stated to explain for the self-color formation during anodizing of titanium on its surface as follows:

1. Color formation can be due to stoichiometric defects in the oxide layer composition.
2. Color formation can be due to the interference of waves in crystalline layers (Ref 7).

Now it is specified that the main cause of formation of color is the interference of waves in transition oxide layer of titanium (Ref 8, 9). Colors formed on titanium parts after anodizing are known as interference colors (Ref 6). The anodic film thickness can be obtained from the light equations as shown in Eq 1.

$$t = \frac{\lambda_{\max}}{4n_0} \qquad \text{(Eq 1)}$$

In the above equation, t is the film thickness in nm, $\lambda_{\max}$ is the wave length of maximum film intensity absorption in nm, and n_0 is the film refractive index. Titanium oxide film refractive index varies with wavelength which can be obtained from Eq 2.

$$n_0^2 = 5.193 + \frac{2.441 \times 10^7}{\lambda_{\max}^2 - 0.803 \times 10^7} \qquad \text{(Eq 2)}$$

Using the interference method to calculate thickness of very thin films is not recommended because of their island nature (accumulation of thin anodic film island growth). Therefore, thicknesses less than 200 Å (anodizing in the voltage of 2 V) cannot be calculated using Eq 2 (Ref 6). Principles of chromaticity were introduced by an International Committee entitled CIE which were based on visual experiments. CIE Chromaticity system is the only internationally agreed metric system for measuring color. In order to detect the correct color of objects and their color differences, CIE has proposed uniform and three-dimensional color spaces, which are [CIE (L ab)] CIELAB and [CIE (L uv)] CIELUV color spaces and have similar structures. Three characteristics of colors in

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three-dimensional spaces are: (1) type of color (Hue); (2) saturation (Chroma); and (3) lightness which are shown in Fig. 1.

In CIELAB space, L^* represents the light intensity value of which varies from zero (black) to hundred (white). a^* and b^* are the coordinates of rainbow. a signifies the red (positive) axis to green (negative), and zero for gray. b signifies the yellow (positive) axis to blue (negative), and zero for gray. Moving away from the central point $(a, b) = (0, 0)$, the color saturation will increase. Figure 1 shows CIELAB color space.

Color saturation is measured using Eq 3 which shows the value of color (Ref 10).

$$\text{Chromaticity} = \sqrt{a^2 + b^2} \qquad \text{(Eq 3)}$$

In this method (anodizing by potentiostat method), there is no color creation on the surface at low voltages (less than 2-3 V), since the thickness of created oxide layer is low. Also during anodizing by galvanostat, there is no color creation on the surface at low current densities. However, since color creation is due to interference of waves, we can reach the natural color of titanium during self-color anodizing which is a result of interference of waves and not due to the low thickness of the anodizing layer (Ref 11).

2. Experimental

2.1 Materials and Equipments

The samples for anodizing were cut from a pure commercial titanium plate with the thickness of 2 mm. The chemical composition of titanium plate is given in Table 1.

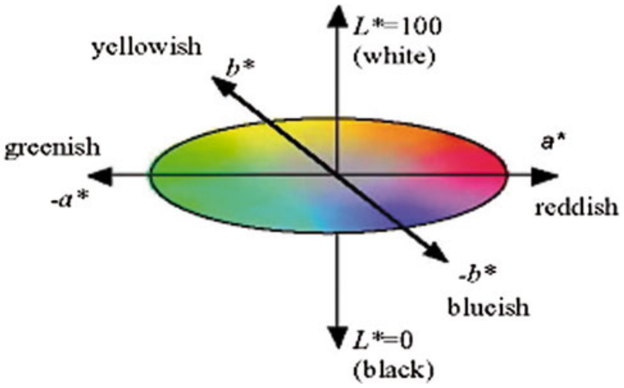


Fig. 1 3D CIELAB color space (Ref 10)

Table 1 Chemical composition of titanium plate

Element	Ti	Al	Zr	Mo	V	Fe	Mn
% Composition by weight	Base	0.28	<0.1	<0.5	<0.1	0.05	<0.1

Table 2 Ringer's solution chemical composition (Ref 12)

Composition	NaCl	$NaHCO_3$	KCl	$CaCl_2$
Concentration, g L^{-1}	9.00	0.20	0.43	0.24

The samples were cut in the dimensions of 30 × 20 mm^2 and then were grinded by emery-papers no. 400-2000. Afterward, the samples were degreased by acetone solution and were acid washed in the 20 vol.% HNO_3 (70%) + 2 vol.% HF (60%) solution for 20 s according to ASTM B600. The samples were then washed by twice-distilled water not to allow any trace of acid wash solution. The anodizing process was performed using a potentiostat (EG&G 273 MODEL) in this

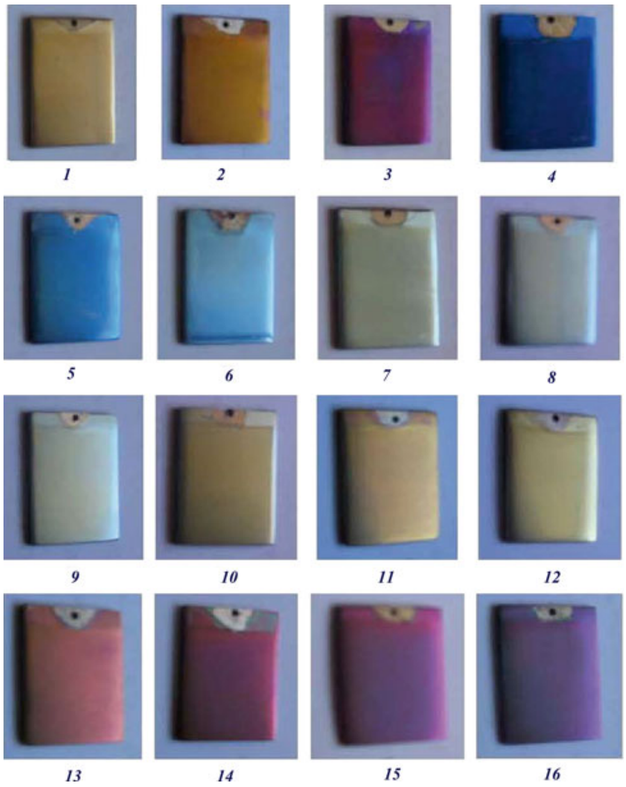
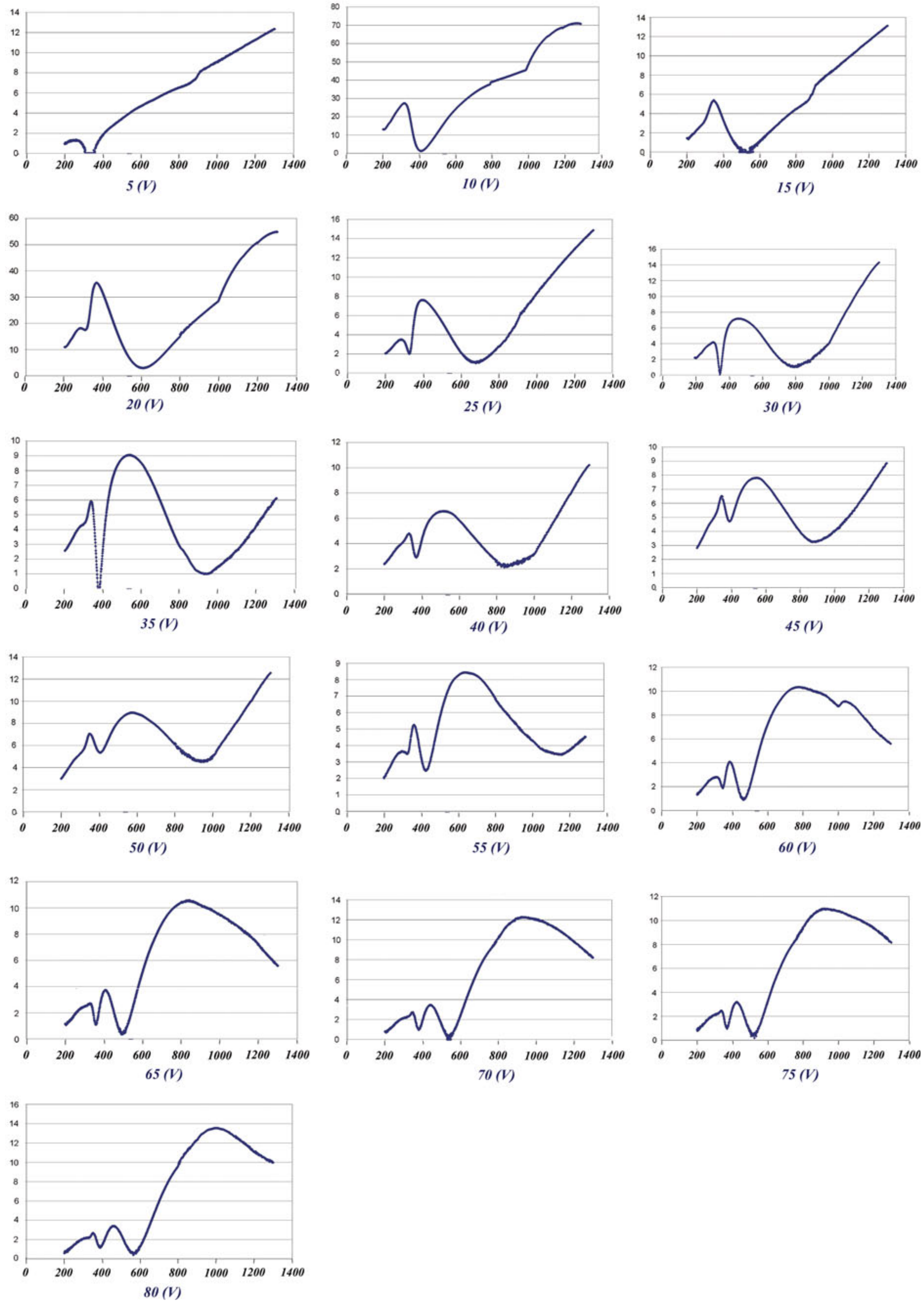


Fig. 2 Colors formed on titanium during anodizing in different voltages in sulfuric acid solution

Table 3 Color parameters of anodized samples in sulfuric acid solution at different voltages

Sample no.	Anodizing voltage	L_1	a_1	b_1	C (chromaticity)
1	5	72.1	−29.75	3.15	29.9
2	10	75.8	−35.4	13.55	37.8
3	15	62.7	−7.15	−4.8	8.6
4	20	62.95	−5.75	−18.65	19.4
5	25	68.9	−14.65	−18.75	23.7
6	30	62.1	−10.3	−5.95	11.8
7	35	77.6	−26.45	−4.55	26.7
8	40	78.65	−27.95	−7.85	28.9
9	45	81.2	−30.95	−2.1	30.9
10	50	82.9	−35.4	3.35	35.5
11	55	82.1	−34.3	10.45	35.8
12	60	78.2	−26.9	12.65	29.7
13	65	73.05	−14.45	3.2	14.7
14	70	70.05	−7.75	−4.3	8.8
15	75	69.05	−5.1	−9.1	10.4
16	80	69.45	−8.95	−9.1	12.7



5 (V)
10 (V)
15 (V)
20 (V)
25 (V)
30 (V)
35 (V)
40 (V)
45 (V)
50 (V)
55 (V)
60 (V)
65 (V)
70 (V)
75 (V)
80 (V)

Fig. 3 The curve of reflection percentage vs. wavelength for anodized samples at different voltages in sulfuric acid solution obtained by spectrophotometer device

Table 4 Values of λ_{max}, refractive index, and thickness of anodic film in sulfuric acid solution

Sample no.	Anodizing voltage, V	λ_{max}, nm	Anodic film refractive index	Anodic film thickness, nm
1	5	259	1.458	44
2	10	319	1.454	84
3	15	348	1.451	59
4	20	366	1.449	63
5	25	398	1.446	68
6	30	452	1.440	78
7	35	541	1.427	94
8	40	519	1.430	90
9	45	545	1.427	95
10	50	569	1.423	99
11	55	643	1.410	114
12	60	780	1.379	141
13	65	802	1.374	145
14	70	826	1.376	150
15	75	912	1.342	169
16	80	1000	1.311	190

study such that constant voltages were applied during each process. Anodizing was performed at 16 constant voltages in the range of 5-80 V, with incremental voltage of 5 V in each step. The anodizing time was 30 ± 1 s in all voltages. The sample was immersed in the solution in cell, and then anodizing process was done. The circuit was cut off after anodizing, and the sample was immediately pulled out of solution and was washed with twice-distilled water.

Chromaticity of anodized layers at different voltages was performed in CIE L*a*b 1976 color space, and different color parameters of each anodized sample (L_1, a_1, and b_1) were measured.

In order to measure thickness of anodizing layer, light reflectance method was used. For this purpose, a spectrophotometer device (Varian Model Cary 500) was used. The curve used by this method was the curve of wavelength versus reflectance percent or (λ-%R). In this curve, the maximum λ (λ_{max}) is important because the thickness of anodizing layer is obtained from the maximum in the "Wavelength-Reflectance percent" curve and by the use of the Eq 1 and 2.

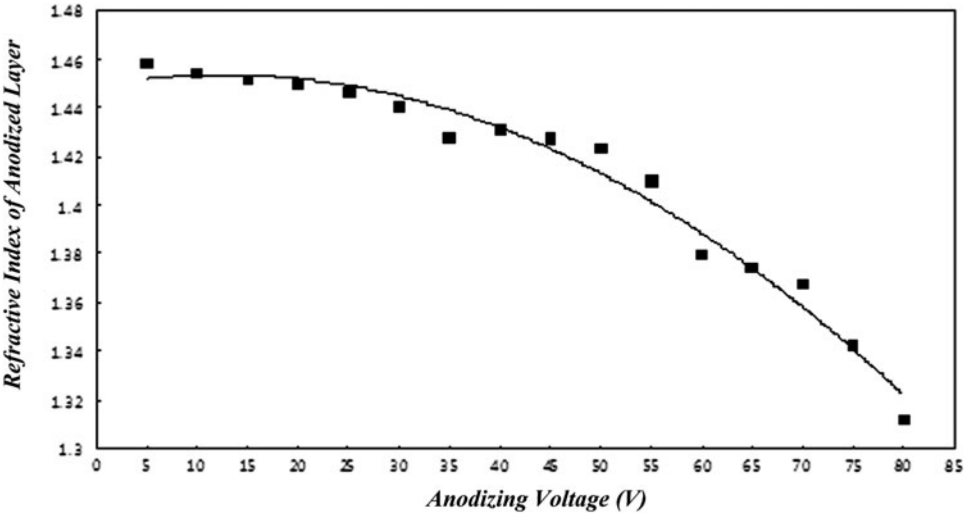


Fig. 4 Changes in refractive index of anodized samples in sulfuric acid solution vs. anodizing voltage

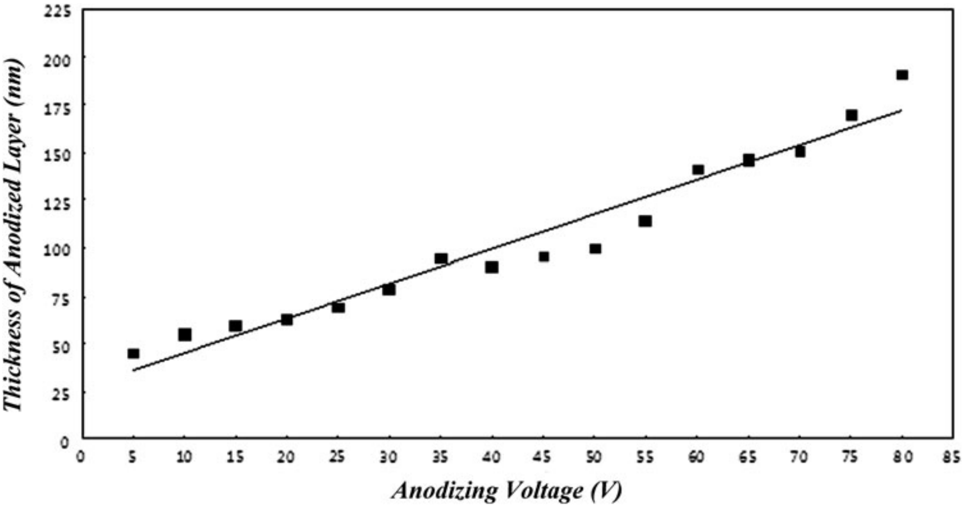


Fig. 5 Changes in thickness of anodic film of samples anodized in sulfuric acid solution vs. anodizing voltage

In order to study the corrosion resistance of samples, potentiodynamic polarization test was conducted, and corrosion rates of samples were measured using linear polarization method. The counter electrode was made of platinum, and the equipment used was potentiostat (EG&G 273 MODEL).

Before conducting polarization tests, all the samples were immersed for 30 min in physiological solution (Ringer's solution) for their open circuit potential to reach a stable value. Scanning rate was 1 mV s^{-1}, and the range of potential for tests was from −250 to 3000 mV with respect to the reference electrode SCE. The chemical composition of Ringer's solution is given in Table 2 (Ref 12).

This solution was prepared from pure compounds and twice-distilled water at the measured pH of 7.6. The polarization curves were drawn in the selected solution in 37 °C which was the normal body temperature.

3. Results and Discussion

Figure 2 shows the created colors on titanium during anodizing at different voltages in sulfuric acid solution.

The results of chromaticity are shown in Table 3. With the use of Eq 3, we could obtain chromaticity or color saturation.

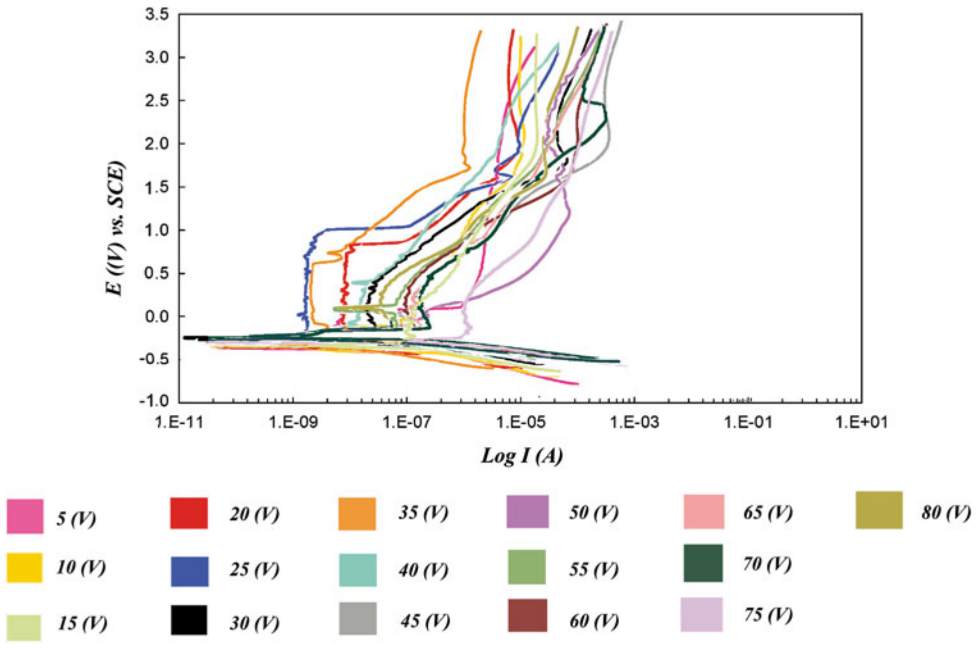


Fig. 6 Polarization curves of anodized samples in sulfuric acid solution vs. anodizing voltage in Ringer's solution

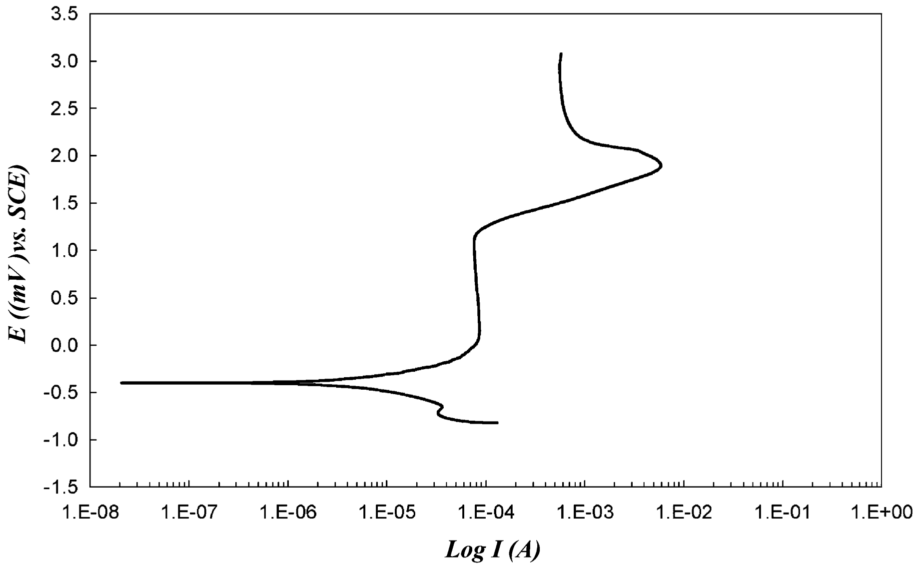


Fig. 7 Polarization curve of the non-anodized sample in Ringer's solution

3.1 Thickness of Anodized Layer

Curves in Fig. 3 which show the wavelength versus reflection percentage for each sample are obtained by spectrophotometer device.

To calculate the layer thickness, we needed $\lambda_{\max}$ (Eq 1, 2) which could be determined from Fig. 3. Table 4 shows $\lambda_{\max}$, refractive index and thickness of anodic film obtained from Eq 1 and 2.

Figure 4 shows changes in refractive index versus anodizing voltage. Equation 5 also shows the relation between refractive index and anodizing voltage obtained by interpolation in Fig. 4.

$$n_0 = -3 \times 10^{-5} V^2 + 0.0007V + 1.4488 \qquad \text{(Eq 5)}$$

It could be seen that by increasing the anodizing voltage and consequently increasing the anodic film thickness, the refractive index of the layer decreased.

Table 5 Changes in potential and corrosion rate of samples

Sample no.	Anodizing voltage, V	Corrosion potential, mV vs. SCE	Corrosion rate, $\times 10^3$ mpy
1	…	−399.7	391
2	5	−365.1	2.3
3	10	−339.9	0.96
4	15	−336.9	2.35
5	20	−355.2	1.01
6	25	−293.1	4.38
7	30	−287	5.41
8	35	−338.5	3.51
9	40	−260.3	2.87
10	45	−251.4	7.78
11	50	−236.9	3.16
12	55	−247.2	7.3
13	60	−264.9	12.21
14	65	−261.9	8.67
15	70	−256.2	4.95
16	75	−295.6	11.48
17	80	−260	7.6

This showed that by increasing anodizing voltage, density and compression of the anodic film decreased (Ref 13).

In the above equation, n_0 is the anodic film refractive index, and V is the anodizing voltage in volts. The highest refractive index which was obtained during anodizing in sulfuric acid solution was 1.458 for the sample in 5 V. Also, the lowest refractive index which was obtained during anodizing in sulfuric acid solution was 1.311 for the sample in 80 V.

Figure 5 shows changes in thickness of anodic film versus anodizing voltage. The relationship between anodic film thickness and anodizing voltage is as per Eq 6. The thickness of anodic film was directly related to the anodizing voltage. In the range of voltages applied in this study, the lowest thickness of anodic film was 44 nm for sample anodized in 5 V, and the thickest anodic film was 190 nm for anodized sample in 80 V.

$$t = 1/8059V + 27/188 \qquad \text{(Eq 6)}$$

3.2 Studying the Corrosion Resistance of Anodized Layer (Anodic Film)

In addition to the anodized samples, polarization curve was drawn for a non-anodized sample as the reference sample. Corrosion potential and corrosion current density of each sample were obtained in Ringer's solution. Figure 6 shows polarization curves of anodized samples in sulfuric acid solution in Ringer's solution environment, corresponding to the anodizing voltages.

Figure 7 shows the polarization curve of the non-anodized sample in Ringer's solution environment. Table 5 shows changes in corrosion potential and corrosion rate of samples.

According to Table 5, Fig. 8 shows changes in corrosion potential versus anodizing voltage. As shown in Fig. 8, by increasing the anodizing voltage, the metal corrosion potential increased which showed the positive effect of anodizing on titanium corrosion potential. This increase in potential did not continue forever and, at higher voltages, the potential reached a nearly constant value.

Figure 9 shows the corrosion rate with respect to the anodizing voltage in semi-logarithmic coordinate. As can be

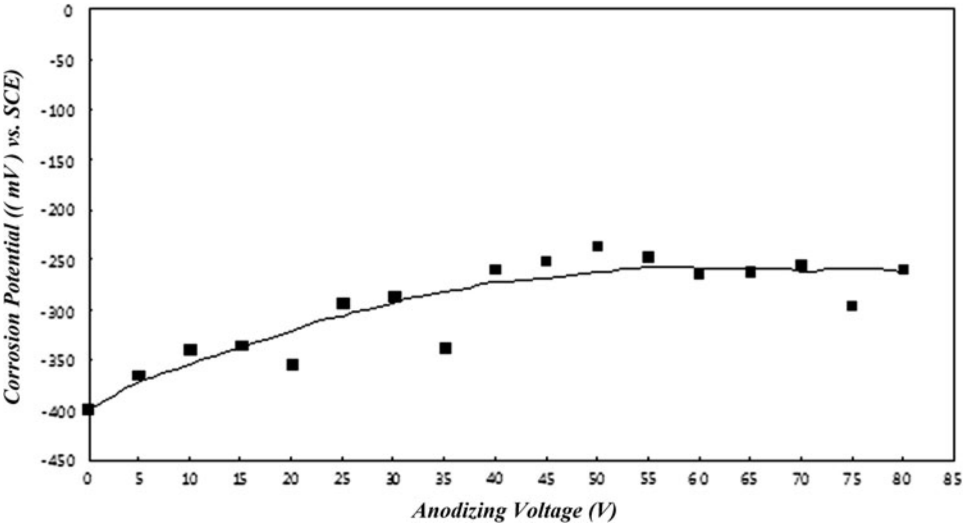


Fig. 8 Changes in corrosion potential of anodized samples in sulfuric acid solution vs. anodizing voltage in Ringer's solution

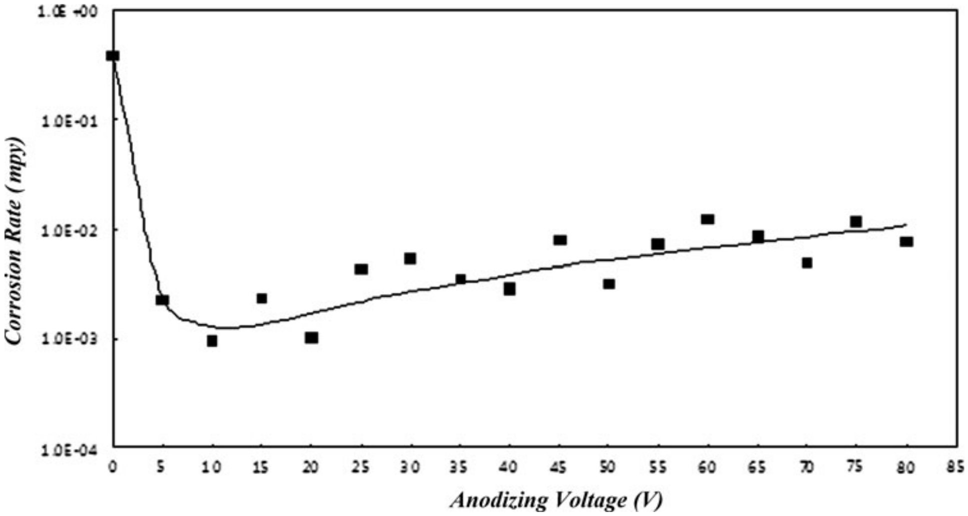


Fig. 9 Changes in corrosion rate of anodized samples in sulfuric acid solution vs. anodizing voltage in Ringer's solution

seen, the corrosion rate in non-anodized state is much higher than that in anodized one which was due to the resistant anodic film. Also by increasing anodizing voltage, the corrosion rate increased. It seemed that this increase was due to increase in porosity of anodized layer (Ref 14), such that anodizing in higher voltages resulted in more porous layers. From Fig. 9, we could conclude that anodizing at either high or low voltages decreased the corrosion rate with respect to the non-anodized sample such that the highest corrosion rate in anodized state was much lower than corrosion rate in the non-anodized state. Among the anodized samples in sulfuric acid, the lowest corrosion rate was in 10 V measured as 0.96×10^{-3} mpy.

4. Conclusion

1. The highest value for chromaticity (color saturation) was 37.8 for the anodized sample in 10 V, and the lowest chromaticity value was 8.6 for the anodized sample in 15 V.
2. By increasing anodizing voltage, the refractive index of anodic film decreased which showed that the density of anodic film has decreased. At voltages greater than 55 V, the slope of decrease in refractive index of anodic film has increased.
3. The thickness of anodic film increased by increasing the anodizing voltage (except in 10 V).
4. Anodizing in sulfuric acid solution has greatly decreased the corrosion rate of sample with respect to its non-anodized sample which was due to the formation of resistant anodic film. Increasing the anodizing voltage to higher voltages has increased the corrosion rate from its minimum value. This could be due to the increase in porosity of layers formed in higher voltages which was attributed to the decrease in refractive index of anodic film caused by increasing the anodizing voltages. Among the anodized samples in sulfuric acid solution, the lowest corrosion rate was for the sample anodized in 10 V measured as 0.96×10^{-3} mpy.

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