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Corrosion Resistance and Color Properties of Anodized Ti-6Al-4V

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In this research, color anodizing of Ti-6Al-4V alloy was performed in phosphoric acid solution of 0.4 M concentration and within 30 s in different voltages (10-120 V) of a DC power supply. The effect of anodizing voltages on the color and thickness of anodized layers on Ti-6Al-4V alloy surface was surveyed. Thickness and refractive index of layers were measured by spectrophotometery and reflectance curves. According to the results, thickness of layers increased with increasing anodizing voltage and was in the range of 38-167 nm. Also the refractive index of anodic film was approximately constant at about 2 and increased inconsiderably with increasing anodizing voltage. Corrosion resistance of the anodized samples in 20 and 50 V was surveyed in physiological solutions of Ringer's solution, Artificial Saliva solution, and Ringer's + 150 mM H_2O_2 solution at the temperature of 37 °C by potentiodynamic polarization method. The anodized sample in 50 V indicated lower corrosion rate than the non-anodized sample as well as the sample which was anodized in 20 V in all solutions. The non-anodized sample indicated the highest corrosion rate of about 0.25 μA cm^{-2}.

Keywords anodizing, implant, polarization curve, titanium alloy

1. Introduction

Titanium and its alloys are extensively used in orthopedic and dental implants because of their excellent corrosion resistance, suitable bond making, as well as biological compatibility. Titanium lies within the neutral biomaterials which are not able to make a chemical bond with the bone (Ref 1). Bone formation around a metallic implant is a complex process in the dimensions of nanometer and micrometer. A number of surface operations are carried out for the creation of a faster bond between the bone and implant, which include anodizing (Ref 2).

Anodic oxidation is a method of surface improvement for the implant which leads to the formation of uniform coating layers at the environment temperature (Ref 3).

The relationship between the nature of an electrolyte and electrochemical growth of titanium oxide layer is not yet known completely. The effect of electrolyte on anodic oxidation of titanium is a function of electrolyte activity which is related to dissolution of anodic products. The rate of anodic film formation is much higher than its dissolution rate in acidic electrolytes like sulfuric acid, acetic acid, and phosphoric acid (Ref 4).

None of the ceramics which is used in the body has a fracture toughness as high as titanium alloys. Especially, Ti-6Al-4V alloy has high mechanical properties due to its alloying elements. Anodic oxidation of this alloy in an electrolyte is preferred for the creation of a barrier layer between alloy and the surrounding environment (without influencing its biological compatibility) (Ref 5).

In the anodizing by potentiostat method, a constant voltage is applied during the process, which affects the process. Oxide layer thickness is directly related to the anodizing voltage so that by increasing the voltage, the layer thickness increases (Ref 6).

Two theories were expressed to describe colors created on anodized titanium surfaces:

(1) Color creation can be due to the stoichiometric defects in the oxide film composition.
(2) Creation of color can be due to the interference of waves in crystalline layers (Ref 7).

Now it is specified that the main cause of creation of color is the interference of waves in transition oxide layer of titanium (Ref 8, 9). Color changes during anodizing are dependent only on the anodic film thickness (Ref 10). Colors created on titanium parts after anodizing are known as interference colors (Ref 6). The oxide layer thickness is proportional to the applied voltage and by increasing the voltage, the surface oxide layer thickness increases.

Anodic film thickness can be calculated using the equations of light (Eq 1):

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

where the film thickness t is in nanometer, $\lambda_{\max}$ is the wavelength of maximum absorption intensity of the film in nanometer, and n_0 is the refractive index of the film. Refractive index of titanium oxide film changes with wavelength, which can be calculated from Eq 2:

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

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The use of interference method to calculate the thickness of very thin films is not correct. This is because of their island nature (Accumulation of the island growth of thin film); therefore, thicknesses below 200 Å (anodizing at the voltage of 2 V) cannot be calculated by the above equations (Ref 6).

It is understood from polarization curves of Ti-6Al-4V alloy that it shows stable passivity in physiological body solutions. In these curves, current density reaches a constant value (i_{pass}), and no transpassivity is observed (Ref 11). When titanium is placed inside the body as implant, some inflammatory reactions occur inside the body. These reactions lead to the formation of H_2O_2. Results of EIS corrosion tests show that in the presence of H_2O_2 in simulated body solutions, the corrosion resistance of titanium is highly decreased (Ref 12).

2. Method of Investigation

In this study, color anodizing of Ti-6Al-4V alloy was investigated. Samples intended for the test were prepared from a sheet of Ti-6Al-4V alloy with a thickness of 1 mm. The chemical composition of the test specimen is shown in Table 1.

The samples were cut using the cutter to the dimensions of 30×20 mm^2. The samples were then grinded using emery-papers no. 600-2500 to obtain a smooth surface. Afterward, the samples were cleaned by pure acetone solution. Then, the samples were washed twice using distilled water not allowing any trace of degreasing solution to remain on their surface.

The solution used for anodizing was phosphoric acid solution with concentration of 0.4 M. The cathode was stainless steel type 304. Anodizing process was performed within 30 s for all the samples, the variable parameter being the anodizing voltage. Anodizing was performed in the voltage range of 10-120 V and with the steps of 10 V.

Light reflectance method was used to measure the thickness of the anodizing layer. After determining the values of λ_{max} (nm) from spectrophotometry curves and putting the values into the Eq 2, the value of refractive index (n_0) for each sample was obtained. By substituting the values of λ_{max} (nm) and the corresponding values of refractive index (n_0) in Eq 1, the values of thickness of anodized layer were obtained in nanometer.

The anodizing process was done using a potentiostat (EG&G 273 MODEL) in this study applying constant voltages during each process.

In order to study the corrosion resistance of the samples, potentiodynamic polarization test was conducted, and corrosion rates of samples were measured using linear polarization method. Before conducting polarization tests, all the samples were immersed in physiological solutions and simulated solution of acid rain for to allow the open circuit potential to reach a stable value. Scanning rate was 1 mV s^{-1}, and the range of potentials for tests was from −800 to 2000 mV with respect to the reference electrode SCE (Ref 11). The chemical composition of acid rain is given in Table 2.

Table 1 Chemical composition of Ti-6Al-4V alloy

Alloy	%Cr	%Mo	%Mn	%Fe	%Al	%V	%Ti
Ti-6Al-4V	0.45	0.3	0.12	0.17	6.0	4.1	The remaining

3. Results and Discussion

3.1 Anodizing Voltage

There were different colors in different anodizing voltages which are shown in Fig. 1.

Table 2 Composition of simulated acid rain solution

Composition	$(NH_4)_2SO_4$	H_2SO_4	$NaNO_3$	NaCl
Concentration, μM	160	127	164	189

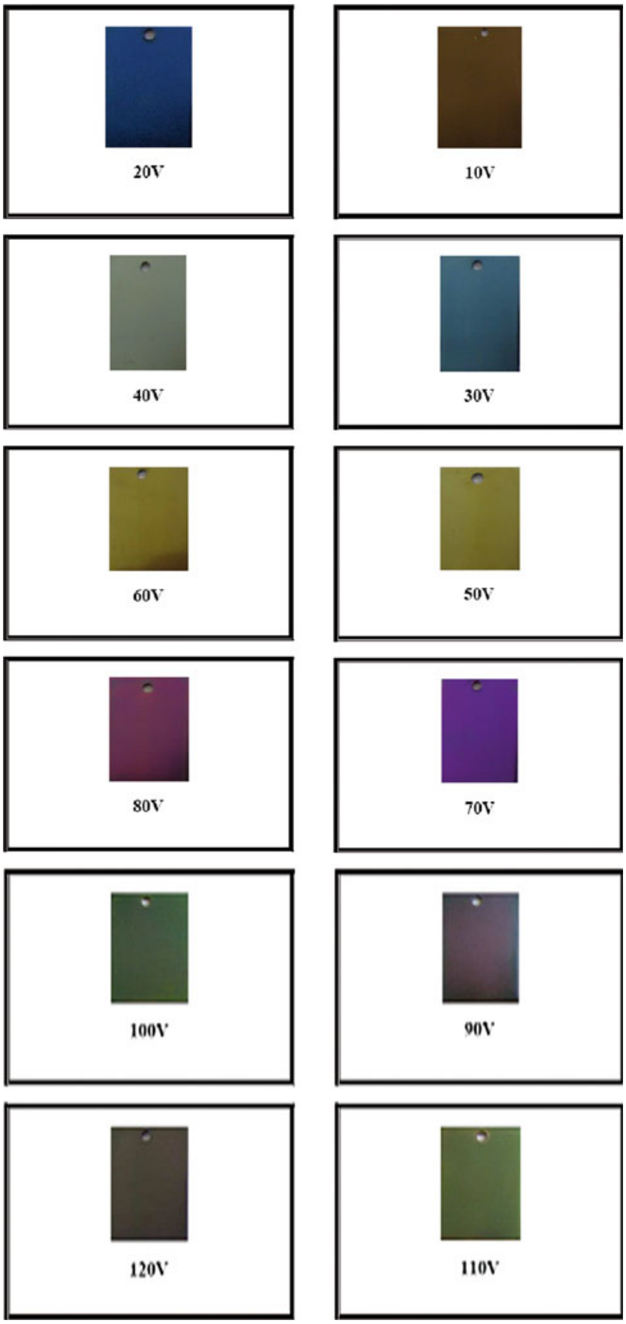

Fig. 1 Created colors during anodizing of Ti-6Al-4V alloy in the 0.4 M phosphoric acid solution during 30 s in different voltages

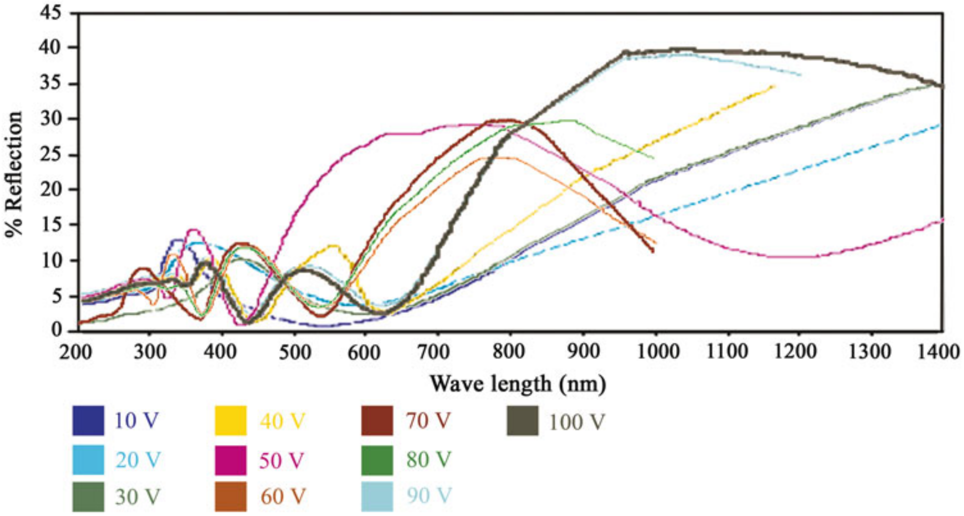

Fig. 2 Curves of changes in reflectance percentage vs. wavelength for anodized samples in phosphoric acid solution at voltages of 10-100 V for 30 s in the concentration of 0.4 M of phosphoric acid solution

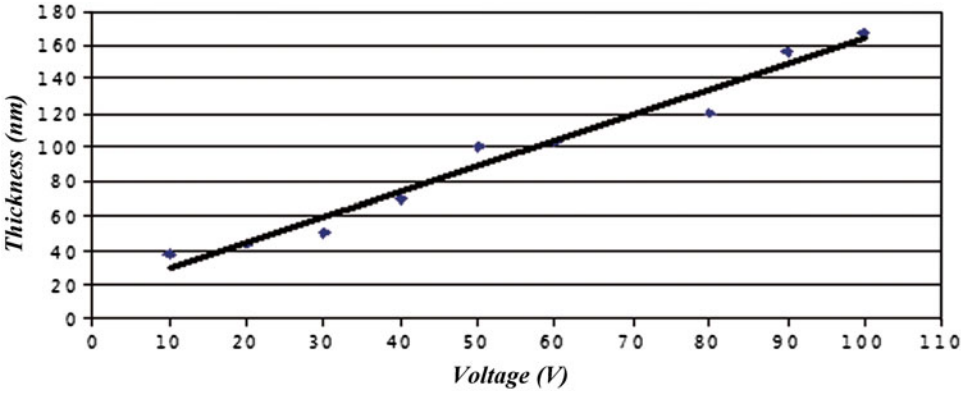

Fig. 3 Curve of the thickness changes vs. anodizing voltages of Ti-6Al-4V alloy during 30 s and in the phosphoric acid concentration of 0.4 M

In some voltages, similar colors were created, which only differ in their amounts of lightness and color saturation. The color of the samples remained gray at the voltages above 120 V.

3.1.1 The Effect of Anodizing Voltage on Anodizing Layer (Anodic Film) Thickness. Light reflectance method was used to measure the thickness of anodizing layer. Figure 2 shows changes in reflectance percent versus the wavelength of anodized samples in the range of voltages from 10 to 100 V.

As the results show, by increasing the anodizing voltage, the thickness of anodizing layer increased so that the range of thicknesses for voltages between 10 and 100 V was between 38 and 167 nm as shown in Fig. 3. Table 3 shows refractive index and anodizing layer thicknesses which were obtained by the above mentioned method. Also the refractive index of the anodic film was nearly constant at 2.0, which decreased insignificantly on increasing the voltage. Figure 3 shows the relationship between voltage and anodizing layer thickness. This relationship was almost a linear relationship which could be traced by Eq 3.

$$t = 1.4846V + 15.1 \qquad \text{(Eq 3)}$$

In the above equation, t is the thickness of anodizing layer in nm, and V is the anodizing voltage in volts. In this range of voltages, the lowest thickness was 38 nm for 10 V, and the highest thickness was 167 nm in 100 V. The oxide layer growth coefficient in the phosphoric acid electrolyte was 1.4 nm V^{-1}.

Table 3 Values of λ_{max}, refractive index (n_0), and anodizing layer thickness (t) at different voltages in the range of 10-100 V with the duration of 30 s and the phosphoric acid solution concentration of 0.4 M

Anodizing voltage, V	λ_{max}, nm	Refractive index	Thickness, nm
10	341.5	2.11	38
20	370	2.1	44.03
30	421	2.08	50.5
40	570	2.02	70.4
50	766	1.905	100
60	781	1.903	102.6
70	800	1.89	105
80	884	1.82	121
90	1048	1.67	156.7
100	1090	1.62	167

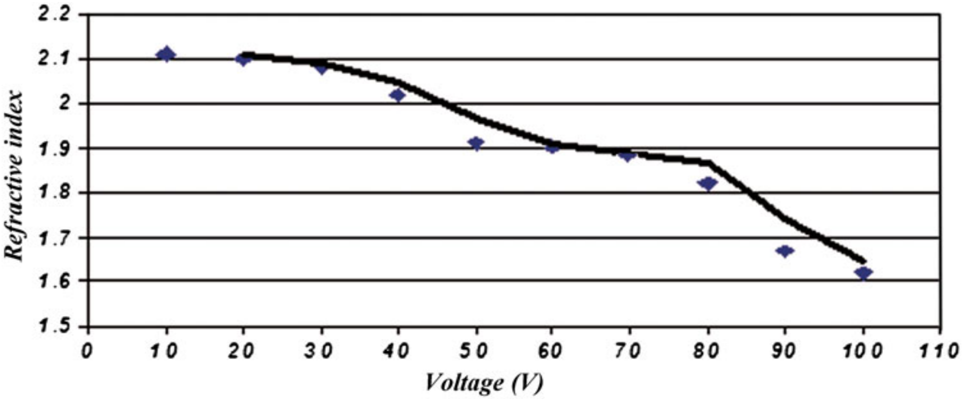

Fig. 4 Changes in refractive index of anodizing layer vs. anodizing voltage of Ti-6Al-4V alloy in phosphoric acid solution of 0.4 M

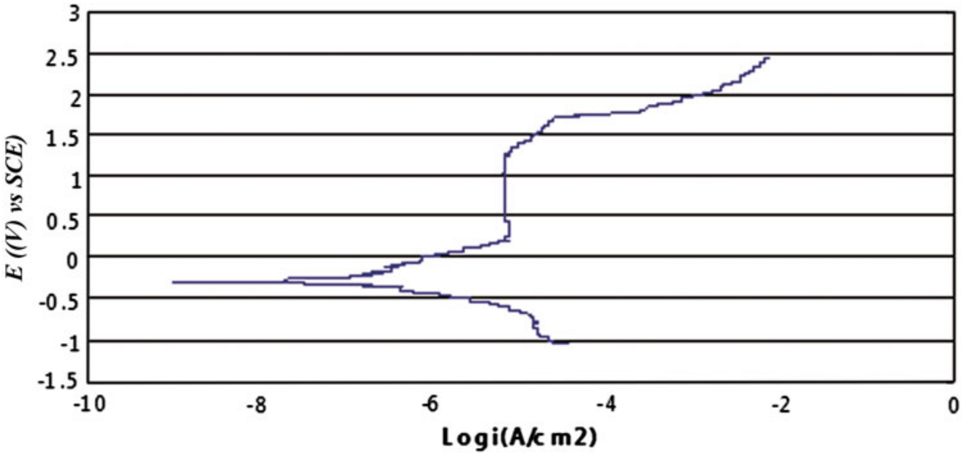

Fig. 5 Polarization curve for non-anodized sample (reference) in the Ringer's solution

Figure 4 is the curve of changes in anodizing layer refractive index versus the anodizing voltage. As can be seen, by increasing the voltage and thus increasing anodizing layer thickness, refractive index of the anodizing layer decreased.

Equation 4 shows that by increasing the anodizing voltage, the refractive index of the anodizing layer was decreased.

$$n_0 = -3E - 5V^2 - 0.0022V + 2.1481 \qquad \text{(Eq 4)}$$

In the above equation, n_0 is the refractive index of the layer, and V is the anodizing voltage in volts. The highest value of the refractive index was 2.11 which was obtained from the anodized sample in 10 V. Also the lowest value for refractive index was 1.62 which was obtained from the anodized sample in 100 V.

3.2 Corrosion Resistance of Anodized Samples in the Voltages of 20 and 50 V

In order to compare the corrosion rate of the anodized samples with the non-anodized sample, the non-anodized sample (reference sample) was tested by potentiodynamic polarization in Ringer's solution, and Fig. 5 shows the polarization curve. Then, this polarization curve was compared to those of the anodized samples. Polarization curve of Ti-6Al-4V alloy (without coating) in Ringer's solution showed that when the mentioned alloy was immersed in the solution, a passive layer was formed on its surface. Figures 6 and 7 are the polarization curves of the anodized samples in 20 and 50 V in different environments. Table 4 shows the results of polarization tests on the anodized samples in voltages of 20 and 50 V in different solutions. Table 4 shows that corrosion current densities were approximately equal, but passivation current densities were reduced. Comparing the results of Table 4 and polarization curves of anodized samples in 20 and 50 V in different physiological body solutions revealed that the anodized sample in 50 V had a lower corrosion current density than that in 20 V in all environments. In general, the anodized samples had a wider passive region in simulated acid rain solutions than in other environments. This showed that the anodized samples were suitable and stable in atmospheric environment for architectural applications. Figure 8 compares corrosion current densities of samples in different solutions, and Fig. 9 shows corrosion open circuit potentials of the samples in different solutions.

The open circuit potential of samples in different solutions were in the range of −550 mV to +50 mV. The values for open circuit potential of the anodized samples in 20 V and 50 V were more positive in Ringer's +150 mM H_2O_2 than other solutions. There was no passive layer on the alloy surface because of the presence of H_2O_2 as was mentioned previously. Also the most negative value of open circuit potential was for the samples in Saliva solution.

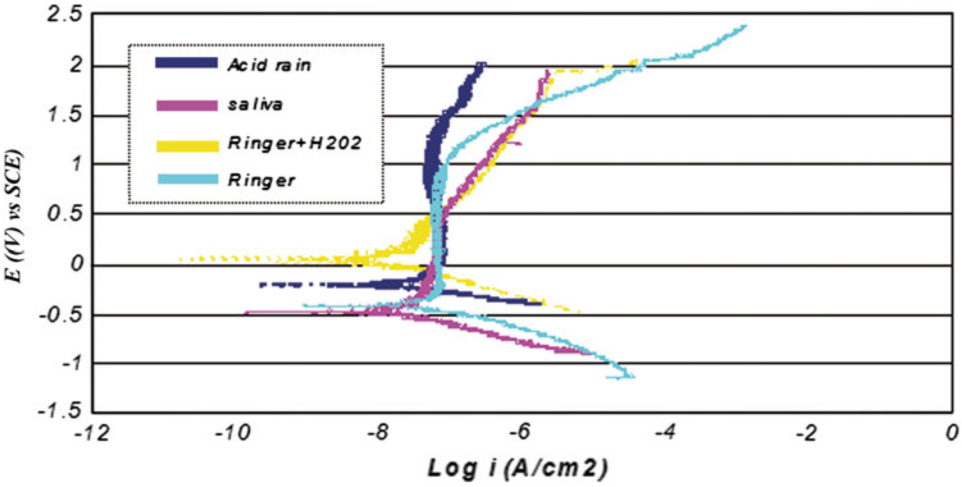

Fig. 6 Comparison of polarization curves in different environments for the sample anodized in 20 V

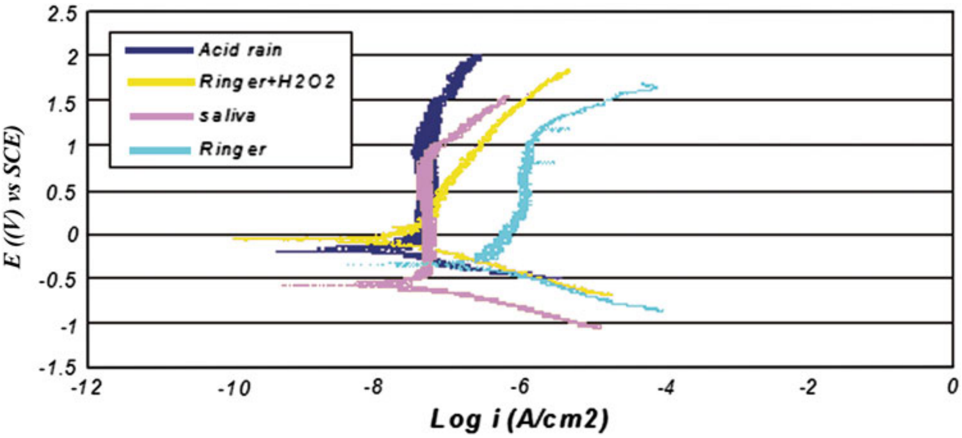

Fig. 7 Comparison of polarization curves in different environments for sample anodized in the voltage of 50 V

Table 4 Results of polarization tests of samples anodized in 20 and 50 V in different solutions

Nomination	Sample	i_{corr}, μA cm^{-2}	i_{pass}, μA cm^{-2}
R20	Ringer's, 20 V	0.031	0.069
R50	Ringer's, 50 V	0.012	1.25
H20	Ringer's + 150 mM H_2O_2, 20 V	0.025	No passivation
H50	Ringer's + 150 mM H_2O_2, 50 V	0.019	No passivation
S20	Saliva, 20 V	0.019	0.067
S50	Saliva, 50 V	0.015	0.053
A20	Simulated acid rain, 20 V	0.019	0.06
A50	Simulated acid rain, 50 V	0.015	0.06
W	Uncoated sample	0.251	7.9

4. Conclusion

(1) By changing the anodizing voltage, color and thickness of the anodizing layer changed so that when the anodizing voltage increased, the anodizing layer thickness was increased consequently. The thicknesses of anodized layer in the range of voltages from 10 to 100 V were in the range of 38-167 nm, and their rate of changes were approximately linear.

(2) By increasing the anodizing voltage, and consequently increasing the anodizing layer thickness, the refractive index of film is decreased.

(3) After applying the anodizing layer, corrosion rate of Ti-6Al-4V alloy has decreased. The corrosion rate of the uncoated sample was 0.25 μA cm^{-2}, while after applying the anodizing coating (anodic film), the corrosion rates were in the range of 0.01-0.03 μA cm^{-2}.

(4) Ti-6Al-4V alloy showed passivity in physiological body solutions, and after anodizing, its corrosion current density was decreased. Polarization tests of anodized samples in 20 and 50 V showed that the anodized sample in 50 V had a lower corrosion rate than that in 20 V. The non-anodized sample had the highest passivation current density and highest corrosion current density.

(5) After immersion of the polarized samples in 20 and 50 V in Ringer's + 150 mM H_2O_2 solution, their

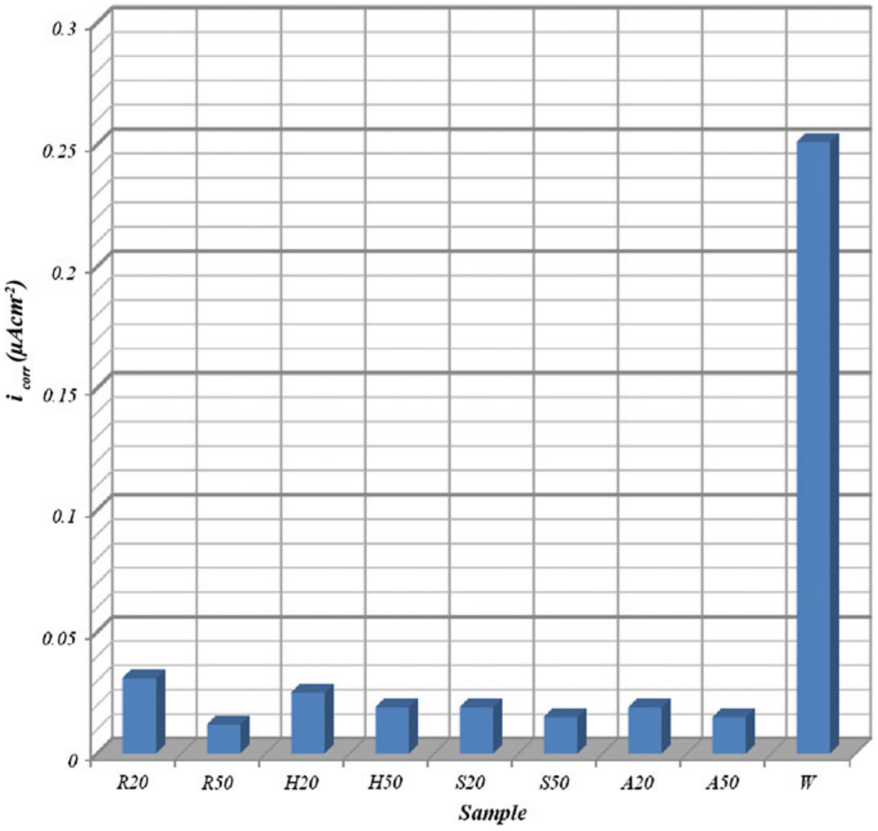

Fig. 8 Comparison of corrosion current densities of anodized samples in 20 and 50 V in different solutions

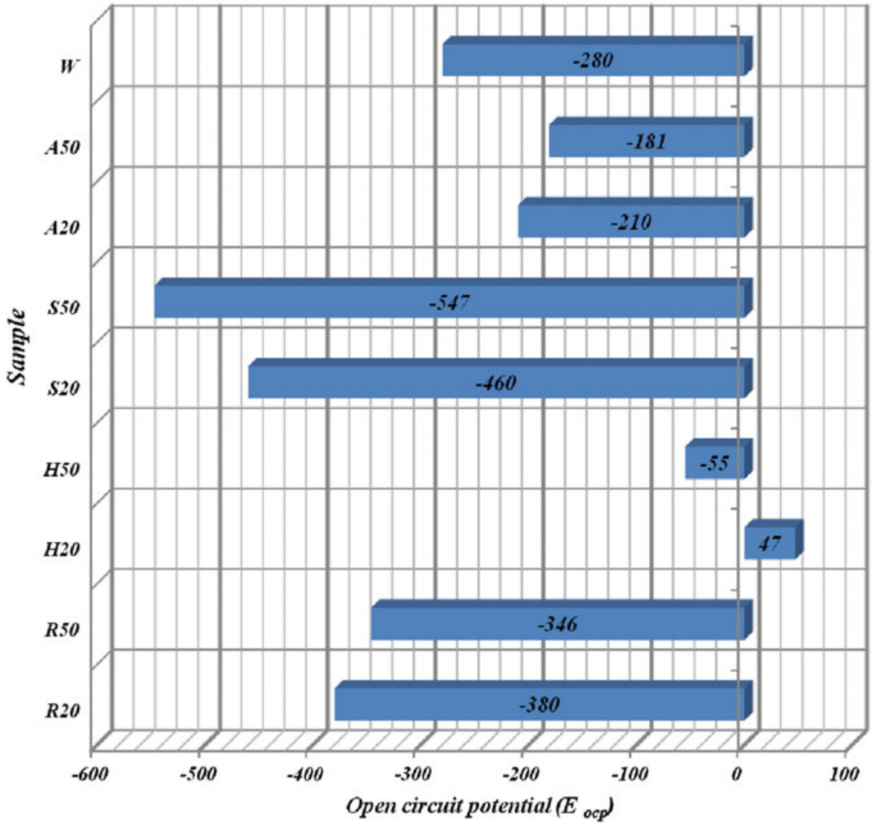

Fig. 9 Comparison of open circuit potentials of 20 and 50 V anodized samples in different physiological environments

polarization curves did not show any passive region. This was because of the existence of H_2O_2 in the solution.

(6) Also it was understood from the polarization test of the samples that the range of open circuit potential of the samples was from −550 mV to +50 mV and that this value of open circuit potential was more positive in Ringer's + 150 mM solution and was more negative in Saliva solution than other solutions.

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