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Effects of pH on the electrochemical behaviour of titanium alloys for implant applications

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Abstract The electrochemical behaviour of two commercial titanium alloys Ti-6Al-4 V (ASTM F136) and Ti-13Nb-13Zr (ASTM F1713) was investigated in Ringer physiological solution at two pH values (5.5 and 7.0). The corrosion properties were examined by using electrochemical techniques: Potentiodynamic anodic polarization, cyclic polarization and electrochemical impedance spectroscopy (EIS). The electrochemical corrosion properties of both alloys at different conditions were measured in terms of corrosion potential (E_{corr}), corrosion current density (i_{corr}) and passivation current density (i_{pass}). Equivalent electrical circuits were used to modulate EIS data, in order to characterize alloys surface and better understanding the pH effect on the interface alloy/solution.

1 Introduction

The biocompability of a material can be associated with its corrosion tendency, once corrosion is responsible for gradual degradation of materials by release of metal ions into the body environments [1]. The titanium alloys, because of properties such as low Young's modulus and biocompatibility has been used as permanent implants in the human body. In spite of these properties, these passivating alloys can generate metal ions, which react with the human fluid, especially with chloride ions forming complexes and precipitates. They also can form hydroxides or oxides with water and produce the local change of the pH [2–4]. These pH changes can generate potential and current gradients; hence the possibility of the local acceleration of the corrosion on some areas of the implant exists. Moreover, at inflammatory process, the pH can vary from 5.4 until 7.8 [5].

This way, the aim of this study is to investigate the effect of pH on the electrochemical corrosion behaviour of two titanium alloys: Ti-6Al-4 V (ASTM F136) and Ti-13Nb-13Zr (ASTM F1713). The influence of pH on oxide formation after polarization was studied by electrochemical impedance spectroscopy (EIS) analysis, and equivalent electrical circuits were used to verify possible modification on the surface alloys. Ringer's solution of two different pH values (5.5 and 7.0) was used to simulate extra-cellular fluids.

2 Experimental

The materials used for the investigations were Ti-6Al-4 V (ASTM F136—UNSR 56401) and Ti-13Nb-13Zr (ASTM F1713—UNSR 58130). Before electrochemical tests, samples were ground by using silicon carbide papers up to 1200 mesh and ultrasonically cleaned. All measurements were performed in Ringer's solution (8.6 g NaCl—0.3 g KCl—0.33 g $CaCl_2 \cdot 2H_2O$ dissolved in 1 l of boiled distilled water) of different pH values 5.5 and 7.0 (the acid pH was obtained with addition of hydrochloric acid). An electrochemical glass cell with three electrodes was used owning standard calomel electrode (SCE) as reference and a platinum electrode as a counter electrode. The open circuit potential (OCP) and the electrochemical polarization were measured in a Potentiostat EG&G 273A (Princeton

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Applied Research-PAR) controlled by the PowerCorr software. The OCP was registered during 60 min and the potentiodynamic polarization was determined in a range of −0.25 V from E_{OCP} to 3 V (vs. SCE) at a scan rate of 1 mV/s. EIS experiments were conduct in a Potentiostat EG&G 273A coupled to a Lock-in PAR 5210, commanded by software PowerSine. The impedance spectra were ranged from 10^{-2} to 10^{4} Hz. The amplitude of a.c. signal imposed was 10 mV. Measurements were made before and after polarization tests at E_{OCP}. The impedance spectra were analyzed using ZView software and equivalent electrical circuits model had been used to evaluation the behavior alloys surface.

3 Results

From the results of OCP versus time (Fig. 1a) it was observed that both alloys show a little increment on values of E_{OCP} in the acidified medium, suggesting that the alloys present a tendency to form a passive layer when in contact with the electrolyte. Similar polarization curves were obtained for both alloys in the two environments studied (Fig. 1b). The corrosion current density (i_{Corr}) and corrosion potential were obtained by Tafel analysis using both cathodic and anodic branches at the range of ±250 mV from E_{OCP} of the polarization curves (Fig. 1c). Also, the passivity current density (i_{pass}) and passivity potential (E_{pass}) are obtained from polarization curve at the point where the current density starts to present a stable behaviour (Fig. 1d). The values found for these parameters are presented in Table 1 and they suggest that the effect of pH on the corrosion resistance of alloys was more significant for Ti-13Ti-13Zy alloy in the Ringer's solution. The value of i_{corr} for this alloy shows an increase of almost three time when in acid solution for the other hand Ti-6Al-4 V alloy did not show significant alterations with change in pH solution. The passivation process in acid solution seems to be more difficult, once the value of E_{pass}, for both alloys, in this medium is higher. Higher values of i_{pass} is also observed, this behaviour can indicate that defects in the oxide film can be formed, i.e., there is a tendency of more irregular or porous oxide layer formation [6].

Figure. 2 presents the EIE diagrams obtained before (B.P) and after (A.P) polarization for both alloys in the different pH solution. The formation of a passive film is confirmed by the increase of |Z| observed for Ti-13Nb-13Zr alloy which also presented a displacement at phase angle in both pH values (Fig. 2a, b). This displacement is more effective for pH 7 at low frequency range of (10^{-1} to 10^{0} Hz), for pH 5.5 this fact occurs at high frequency (10^{2} to 10^{3} Hz). For Ti-6Al-4 V the polarization process did not show significant alterations on pH 5.5 (Fig. 2d), two time constant are observed before and after polarization process.

Table 1 Electrochemical parameters for Ti-13Nb-13Zr and Ti-6Al-4 V alloys at different values of pH solution

Samples	PH	Parameters			
		I_{corr} (μA/cm^2)	E_{corr} (V)	I_{pass} (μA/cm^2)	E_{pass} (V)
Ti-13Zr-13Nb	7.0	0.054	−0.542	7.15	−0.08
	5.5	0.188	−0.485	9.44	−0.02
Ti-6Al-4 V	7.0	0.065	−0.573	7.79	−0.09
	5.5	0.059	−0.547	7.84	0.21

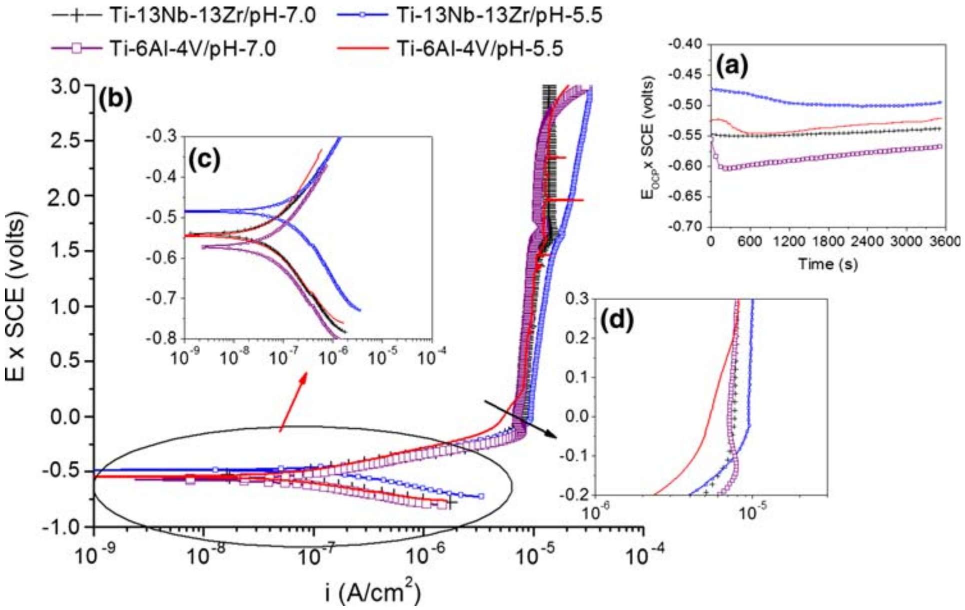

Fig. 1 Open circuit potential and potentiodynamic polarization curves of alloys at different pH conditions. **a** Open circuit potential versus Time; **b** potentiodynamic polarization curve; **c** Tafel region of polarization; **d** passivation region

Fig. 2 Bode diagrams from EIS results for both alloys at different values of pH solution

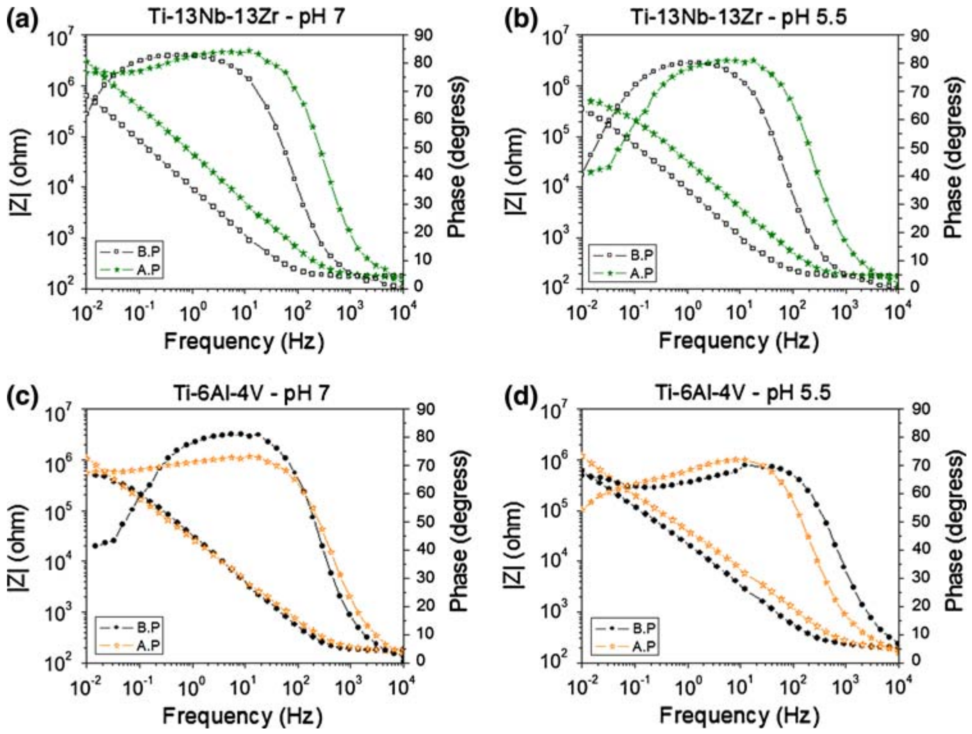

Table 2 Impedance parameters for Ti-13Nb-13Zr and Ti-6Al-4 V alloys at different values of pH solution

PH	Ti-13Nb-13Zr				Ti-6Al-4 V			
	7.0		5.5		7.0		5.5	
Parameters	A.P.	D.P.	A.P.	D.P.	A.P.	D.P.	A.P.	D.P.
R_s (Ω cm^2)	65.7	66.0	66.3	65.3	65.1	64.1	68.9	69.5
CPE$_1$ (F cm^{-2})	4.8e–5	9.6e–6	5.7e–5	1.4e–5	3.7e–5	1.8e–5	2.2e–5	2.1e–5
R_1 (Ω cm^2)	6.3e5	6.2e5	1.7e5	1.81e5	5.4e5	8.7e4	3.1e4	8.1e4
CPE$_2$ (F cm^{-2})	–	3.1e–6	–	7.3e–5	–	6.0e–6	1.4e–5	9.8e–6
R_2 (Ω cm^2)	–	5.9e6	–	4.03e5	–	2.1e6	8.7e5	1.7e6
χ^2	1.2e–3	2.4e–3	3.0e–3	2.0e–3	2.1e–3	1.0e–3	9.1e–4	3.4e–3

The impedance results were adjust by the ZView® software by adopting the well known equivalent circuit proposed by some researchers [7–10], as shown in Fig. 3. Circuit 1 assumes that the oxide layer consist of a compact layer with a polarization resistance (R_1) and a capacitance (CPE$_1$). Circuit 2 is a model which the oxide layer consists of a barrier-like inner layer and a porous outer layer. In this model, R_1 and R_2 are the resistances of porous and barrier layers [7, 9] which are associated to the charge transfer resistance through the porous layer and the participation of adsorbed intermediates. CPE$_1$ corresponds to the capacitance of the porous layer and CPE$_2$ to the capacitance of the barrier layer which seems to be associated to the double layer formation. A constant-phase element (CPE) representing a shift from an ideal capacitor was used instead of the capacitance itself. For both circuits R_S corresponds to the resistance of the electrolyte.

On Table 2 are presented the parameters obtained from adjust, the agreement between experimental and simulated results was evaluated by chi-squared (χ^2) and values next to 10^{-3} indicated a good fitting. All results of EIS obtained before polarization were adjust with circuit 1, except the

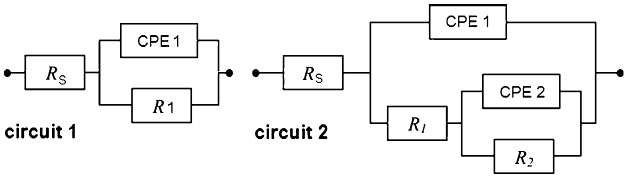

Fig. 3 Equivalent electrical circuits used to adjust EIS results

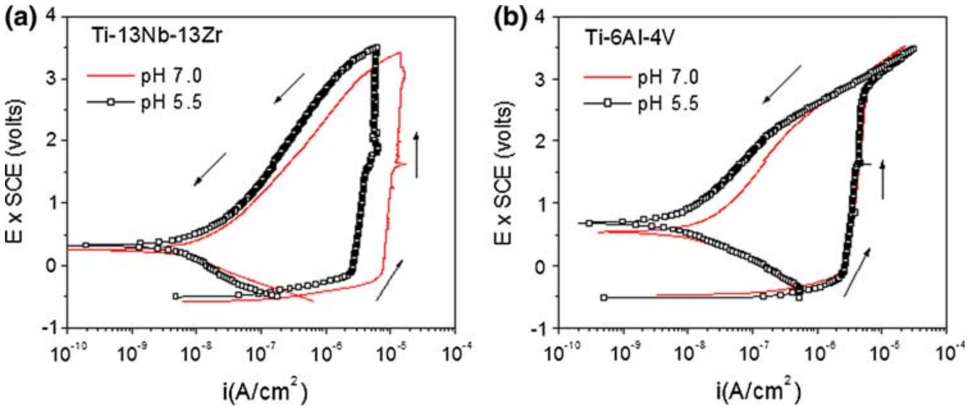

Fig. 4 Cyclic polarization results in different values of pH solution: **a** Ti-13Nb-13Zr, **b** Ti-6Al-4 V

alloy Ti-6Al-4 V in pH 5.5 that was adjust with circuit 2. This fact demonstrates that before polarization the surface of alloys present a passive film more compact or with more homogeneity. After polarization all alloys present a two time constant and their results were fitted with circuit 2, this indicate that polarization induces the formation of a porous film on the surface alloys. By the values obtained from adjust can be observed that in acid pH the alloy Ti-13Nb-13Zr shows a film less protector once the value of R_2 (4.03e5 Ω.cm^2) is lower than the value found to pH 7.0 (5.9e6 Ω.cm^2). Otherwise, Ti-6Al-4 V alloy presents an irregular surface before polarization and the resistance of barrier layer (R_2) after polarization is a little higher than the value of R_2 before polarization.

The results of cyclic polarization are presented in Fig. 4 and can be observed that both alloys did not show tendency to pitting corrosion once the pitting potential is not observed, the typical hysteresis of pit presence did not appears on the results. Another observation is that again the Ti-13Nb-13Zr alloy seems to be more sensible the pH change. A displacement in the values of current density is observed when the pH is changed. This fact reinforces the results previously showed by the other tests.

4 Conclusions

From the results obtained some remarks can be done:

- The effect of pH on corrosion resistance in Ringer's solution was more accentuated for the Ti-13Nb-13Zr alloy than for Ti-6Al-4 V alloy.
- The value of i_{corr} is bigger to Ti-13Nb-13Zr alloy when at acid pH.
- After anodic polarization both alloys presented an anodic film with two layers: one more compact (barrier layer) and other porous, independent of pH.
- The alloys did not show tendency to localized corrosion (pitting) in the Ringer's solution.

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