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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TECHNIQUE IN PREDICTION OF THE IMPLANT TITANIUM ALLOYS BEHAVIOUR

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INTRODUCTION: The surface oxide film on titanium and its alloys in bioliquids and its stability play an important role in the understanding of titanium implant corrosion resistance. It has been reported [1] that the surface film in human body changes the thickness and composition in time. So, simulation of long-term exposure of implants using various electrochemical techniques could be a help for in vivo behaviour prediction. As electrochemical impedance spectroscopy (EIS) is a technique for studying the spontaneous passivation of metals in electrolytes, various oxide films on metal surfaces have been characterized by this technique. Despite a high corrosion resistance of titanium and its alloys, in vivo experiments showed accumulation of titanium ions in tissue adjacent to implants [2,3].

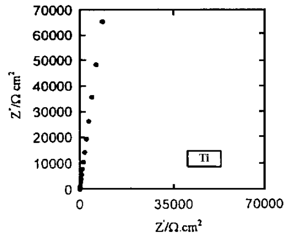
This work investigate the long-term behaviour of Ti and its implant ternary alloys in Ringer's solution of different pHs (6.98; 4.35; 2.5)

EXPERIMENTAL PART: Titanium and its alloys Ti-5Al-4V, Ti-6Al-4Fe were processed into cylindrical electrodes. All measurements were performed in Ringer 2 solution for 12,000 exposure hours. Materials and solution composition were presented in a previous work [4].The following electrochemical techniques were used: impedance spectroscopy, linear polarisation, pH measurements, and open circuit potential. Statistical treatment with Medcalc program was the instrument for the prognosis of the behaviour in time.

RESULTS AND DISCUSSIONS:

EIS data

Impedance spectra, in Nyquist and Bode forms were obtained at open circuit potential and different potentials from the passive potential range.



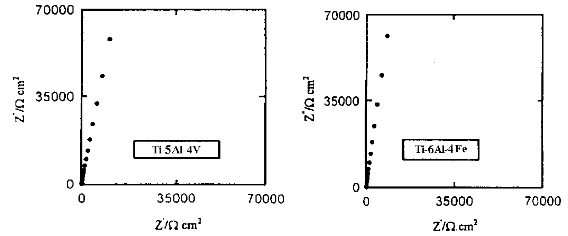


Fig. 1 Nyquist plots at open circuit potential in Ringer's solution of pH = 6.98

At open circuit potential, the impedance spectra (Fig.1) illustrate a pure capacitive behaviour (high corrosion resistance) for Ti and Ti-5Al-4V alloy. Nyquist plots for Ti-6Al-4Fe alloy included a diffusion tail, which suggested that the alloy acted as a porous electrode.

At 0 V, in the passive potential range, Bode plots (Fig.2) exhibit only a near capacitive response illustrated by a phase angle close to -90^0 over the wide frequency range, indicating a compact, passive film. Bode plots in log | Z | - log f form show linear portions (at intermediate frequencies) with slopes closed to –1.0 (from –0.92 to –0.99). This is the characteristic response of a compact, passive oxide capacitance (C_p). The same Bode plots were obtained at +0.4 V potential, in the passive range, pointing out the same protective film.

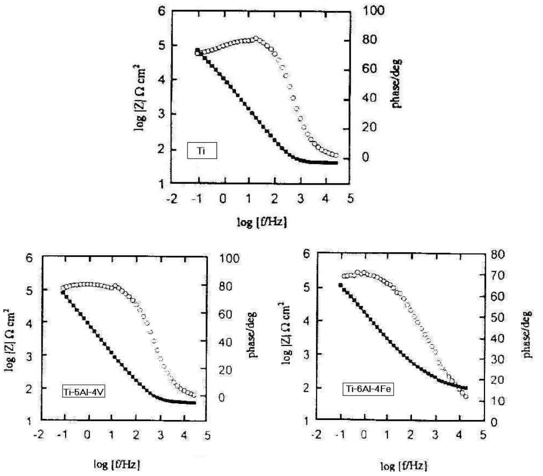


Fig. 2 Bode plots at the potential of 0 V in Ringer's solution of pH = 6.98

The impedance spectra were modelled by fitting these data with an equivalent electric circuit. In the passive potential range, an equivalent circuit with one time constant (Fig.3) was fitted for all materials and pHs of Ringer's solutions. The components of this equivalent circuit are: R_Ω - ohmic resistance of the electrolyte; R_p – resistance and C_p – capacitance of the passive film.

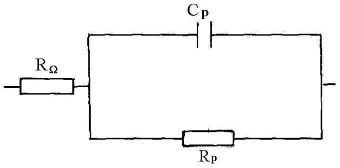


Fig.3 Equivalent electric circuit fitted in the passive potential range for Ti and its ternary alloys

The values obtained for the passive film resistance and capacitance are presented in table 1. It can be seen that the resistance of the passive films for Ti, Ti-5Al-4V and Ti-6Al-4Fe are very high, around 2 MΩ.cm^2. The very high resistance implies a good corrosion resistance, i.e. a low rate of titanium ion release and the oxide growth. In addition, the passive film capacitance is relatively low, around 15 µF/cm^2, and decreases slightly with the potential. This C_p decrease corresponds to a slow growth of the titanium oxide film, indicating a long-term stability of the passive layer.

Table 1 Capacitance and resistance of the film

Paraameter	Potential (mV) vs.SCE	Maaterial		
		Ti	Ti5Al4V	Ti6Al4Fe
C (µF/cm^2)	-800	24	30	46
	-650	27	26	30
	-500	12	15	22
	0	14	14	18
	+200	9	12	7
	+400	9	9	11
R (MΩ.cm^2)	-800	0.169	0.221	0.251
	-650	0.039	0.191	0.347
	-500	-	1.5	1.63
	0	0.371	2.07	-
	+200	0.454	1.11	-
	+400	0.212	1.42	1.89

Open circuit potentials for 12,000 exposure hours

The open circuit potentials, corrosion potentials (E_{corr}) in Ringer's solution of different pHs for Ti and its alloys decrease in the first 2000 exposure hours, then increase oscillating around –0.1 V ÷ -0.3 V potential values. These values denote a stable passive film. No pitting corrosion was detected for 12,000 h.

The statistical treatment of the open circuit potential variations in time using the regression procedure permitted the best approximation of scatter diagrams, regression equations and coefficients of determination (table 2).

Table 2 Regression equations and coefficients of determination (D)

Material	pH	Regression equation	D
Ti	6.98	$y=-271.7+0.15x-4.4.10^{-5}x^2+4.9.10^{-9}x^3-1.8.10^{-13}x^4$	0.85
	4.35	$y=-307.9+0.014x-3.91.10^{-7}x^2$	0.73
	2.5	$y=-127.76+0.028x^2-2.15.110^{-6}x^3$	0.72
Ti5Al4V	6.98	$y=-11611.9-0.002x+3.75.10^{-7}x^2$	0.46
	4.35	$y=-291.3-0.02x+1.42.10^{-6}x^2$	0.64
	2.5	$y=-248.6-0.011x+2.4.10^{-7}x^2$	0.84
Ti6Al4Fe	6.98	$y=-397.9+0.07x-4.9.10^{-6}x^2$	0.61
	4.35	$y=-205.3+o.05x-1.10^{-5}x^2+4.8.10^{-6}x^3$	0.62
	2.5	$y=-321.7+0.01x+4.3.110^{-7}x^2$	0.88

The most important thing in using regression analysis (especially in the cases with a convenient determination coefficient) is the possibility to make some prognosis; in our case, it is a chance to estimate potential for longer time. For example, if in the polynomial equations, the value of time is 15,000 hours, the potential values become close to our experimental values for this time.

It is to point out that in the bioliquids, such predications need more precautions than in other cases, taking into account that the human body being very complex, unexpected phenomenon could take place any time.

Corrosion rates

The corrosion rates of titanium, Ti-5Al-4V and Ti-6Al-4Fe alloys were obtained by linear polarisation for 12,000 exposure hours. From table 3 can be seen that the alloys have lower corrosion rates than the titanium. Both titanium and its ternary alloys have very good corrosion resistance in Ringer's solution at 37^{0}C for 12,000 exposure hours. These corrosion rates will be periodically monitored.

Table 3 Corrosion rates (mm/yr) of titanium and its alloys in Ringer's solutions of different pHs, for 12,000 exposure hours

Material	Time (h)	Corrosion rate (mm/yr)		
		PH=6.98	PH=4.35	PH=2.5
Ti	2500	$4.84x10^{-3}$	$4.06x10^{-3}$	$4.96x10^{-3}$
	5000	$5.01x10^{-3}$	$4.22x10^{-3}$	$5.08x10^{-3}$
	10000	$6.12x10^{-3}$	$5.81x10^{-3}$	$6.15x10^{-3}$
	12000	$6.51x10^{-3}$	$6.68x10^{-3}$	$6.72x10^{-3}$
Ti-5Al-4V	2500	$4.2x10^{-3}$	$3.02x10^{-3}$	$3.11x10^{-3}$
	5000	$4.25x10^{-3}$	$3.11x10^{-3}$	$4.15x10^{-3}$
	10000	$5.44x10^{-3}$	$5.02x10^{-3}$	$5.88x10^{-3}$
	12000	$6.48x10^{-3}$	$6.59x10^{-3}$	$6.61x10^{-3}$
Ti-6Al-4Fe	2500	$3.71x10^{-3}$	$3.12x10^{-3}$	$3.54x10^{-3}$
	5000	$4.08x10^{-3}$	$3.21x10^{-3}$	$4.10x10^{-3}$
	10000	$5.42x10^{-3}$	$5.15x10^{-3}$	$5.21x10^{-3}$
	12000	$6.56x10^{-3}$	$6.51x10^{-3}$	$6.69x10^{-3}$

CONCLUSIONS:

1. EIS permitted *in situ* characterisation of passive films; impedance parameters indicated a slow

growth of oxide layer, corresponding to long-term stability.

2. An equivalent circuit with one time constant was fitted for Ti and its alloys in Ringer's solution.

3. The open circuit potentials values for very long-term denote a stable passive film; no pitting corrosion was detected.

4. The statistical treatment permitted to obtain scatter diagrams, regression equations and coefficients of determination.

5. Both titanium and its ternary alloys have low corrosion rates, a very good corrosion resistance in Ringer's solution at 37^0C, for 12,000 exposure hours.

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