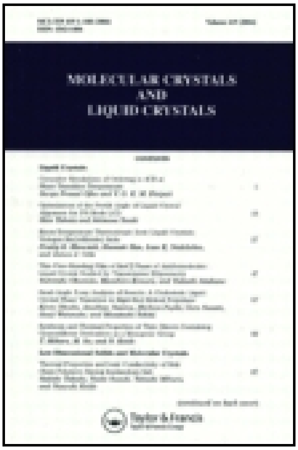

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The Stability of TiAlV Alloy in Simulated Bioliquids

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This work is an approach of surface treatment effect and ions fluoride influence on TiAlV alloy in Ringer 1 solution. Mechanical and chemical alkali treatment are the two different ways of change in surface features. The samples were examined and characterized using open circuit test (OCP), cyclic polarisation tests (CPT), electrochemical impedance spectra (EIS) and electron spectroscopy for chemical analysis (XPS). An empirical model of bio-interface is proposed based on electrochemical and surface experiments.

Keywords: CPT; EIS; Ringer 1; stability; TiAlV; XPS

INTRODUCTION

Among main requirements of hard tissue replacement materials, especially those implanted in the highly loaded bones, are high mechanical strength, low elastic modules and their ability to chemically bond to bone – the so called bio-activity [1,2].

For dental implantology, in parallel with studies about corrosion resistance and biocompatibility by increasing bio-activity, fluoride therapy is now recognized as being one of the principal methods in preventing dental caries [3].

Titanium and its alloys are one of the most important materials for medical and dental implants due to its high corrosion resistance in many bio-systems with aggressive ions. In fact, most brands of

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tooth-paste contain a fluoride concentration of about 1% while concentrations of approximately 2% are used to remove stains from enamel. However, the fluorides (e.g., in terms of NaF and/or Na_2FPO_4 [4]) contained in commercial tooth-pastes and prophylactic gels, used orally and topically to prevent dental caries or to relieve sensitivity, can be in the range of 0, 1–2%. The higher concentration where fluoride ions are present may cause Ti materials underging a corrosive process in the form of crevice and pitting, as soon as the pH drops below 2.75.

In spite of the Ti and Ti alloys being intrinsically non-bioactive, it has been shown in the scientific literature [5], that Ti and its alloys can be made bioactive by treatment of surface such as soaking in basic solution.

Recently [6], was relived that titanium, and tantalum metals and their alloys spontaneously bond to living bone if they have been previously subjected to a treatment involving a soak in NaOH solution followed by a subsequent heating treatment. These metals can therefore be called bioactive metals, and they are already subjected to clinical trials for use in artificial total hip joints.

The main objective of the present research was to use surface treatment and alkali treatment for bio-activation of TiAlV alloy and study the influence of fluoride ions on the obtained surface.

The alloy TiAlV has an excellent corrosion behaviour due to the passivity. Passivity is due to the very stable and tenaciously adherent oxide film spontaneously formed over the surface, which reform very rapidly if removed or mechanically damaged.

MATERIALS AND METHODS

The composition of TiAlV samples examined in the present study are: 0.08%C, 0.05%N_2, 0.015H_2, 0.02%O_2, 0.3%Fe, 6.75%Al, 4.5%V, 88.29%Ti.

In order to examine the surface layer effect of each specimen, the surface of each sample (10 mm^2) was treated in two different ways, A and B:

A) polished with 600 and 1000 μm emery paper, degreased with acetone and rinsed in pure water before each measurement, because it is known that an increased implant surface roughness increase the roughness of passive protective film and so, the value of cell addition, proliferation and differentiation become better [7,8].

B) after polishing the sample was immersed in 5 mol NaOH aqueous solution at 60°C for 24 h. Alkali treatment was followed by gently washing with acetone and distilled water and by drying for 24 h in air, at 40°C. The development of an alkali treatment forms a bioactive surface on the passive metallic layer for direct bonding to the bone tissue.

The samples were examined and characterized using open circuit test (OCP), cyclic polarisation tests (CPT), electrochemical impedance spectra (EIS) and electron spectroscopy for chemical analysis (XPS).

Electrochemical Tests

The corrosion test were performed in a glass cell (200 mL) containing Ringer 1 solution at 37°C with the following chemical composition: 8.6 g/L NaCl, 0.33 g/L $CaCl_2$, 3 g/L KCl.

The electrodes used were the working electrode TiAlV, the reference electrode calomel (ESC) and a platinum one as a counter electrode.

The tested Ringer 1 with fluoride ions solutions involves a 0.01 m/L addition of NaF.

Open Circuit Test (OCP)

The electrode potential was measured over time according to the ASTM G 31-90 standard. Corrosion potential evolution was measured until 60 days. Electrode potential recording and data acquisition were carried out with ITT instruments MX20.

Cyclic Polarisation Test (CPT)

The cyclic polarisation tests were performed according to the standard ASTM G 61-86 method. The samples were immersed for 15 min in electrolyte prior to starting the polarisation scan at –800 mV. The scan was initiated in the more noble direction at a scan rate of 2 mV/s. When 4 V was reached, the scanning direction was reversed. The scan was finished when the potential reverted once again –800 mV. The potentiodynamic polarisation curves were obtained with a Voltalab 21 equipment using Volta Master Corrosion Program. They revealed a presence of passive protective layers on TiAlV electrodes after surface treatments, with or without fluoride ions.

Impedance measurements were performed with a frequency response analyzer connected to a potentiostat and controlled by a microcomputer, incorporated in an Autolab PGSTAT-30 device. The amplitude of potential modulation was 10 mV. Impedance measurements were made in the frequence range 100 kHz to 10 MHz. All value of the potential indicated here are compensated for ohmic drop.

XPS measurements were performed in a ESCALAB MKII. The energy resolution was 0.1 eV. The calibration of the energy scale was performed according to a standard procedure [9]. The basic pressure in the analyser chamber was 5×10^{-8} Pa.

RESULTS AND DISCUSSION

The evolution of corrosion potential in time (Table 1) presents the OCP variation according to the two samples immersion time in the Ringer 1 solution, with and without fluoride. For both type of samples, the OCP in Ringer solution was found to increase during the first 30 min. The initial corrosion potential for sample A is around –385 mV, and for sample B is around –320 mV. After immersion the corrosion potential gradually increases for 2 hours for sample A and 1.5 hours, for sample B, until an approximately steady value is reached.

The potential of specimen A shows a large number of oscillations, mainly in the beginning at the test, indicating passivation and repassivation phenomenon [10].

The addition of fluoride ions caused a corrosion potential shift to more negative values. Increasing the immersion time to one month caused only slight variations in the OCP, indicating that passive oxide film growth occurred even in the presence of fluoride.

The recording of E_{cor} was interrupted after 2 months, but the sample remained immersed inside the testing solution for longer measurements studies. After 24 hours the measured E_{cor} values were +120 mV (SCE) without fluoride, –150 mV with fluoride for sample A, and + 150 mV (without fluoride), –60 mV (with fluoride) for sample B. This fact indicates that there is not a real stabilization of E_{cor} during this period of time, being rather a continue slow increase. Corrosion potentials are in good agreement with the values previously reported by other authors [7,10] and our [11] working with similar electrolytes. Moreover, these values demonstrate that addition of NaF solution produces the corrosion potential of TiAlV shift to more positive values due to changes in TiO_2-layer thickness and/or structure [12,13].

TABLE 1 The Evolution of Corrosion Potential in Time

	Samples A E_{cor} (mV)		Samples B E_{cor} (mV)	
Time (days)	Without fluoride	With fluoride	Without fluoride	With fluoride
1	–250	–325	–210	–250
10	–145	–205	–125	–195
20	–120	–180	–90	–140
30	–90	–115	–85	–110

The corrosion potential increase to more noble values is attributable to the growth of film barrier on the metal surface. According to literature data [14] it is possible that hydrogel sodium titanate ($Na_2Ti_5O_{11}$) layer and rutile TiO_2 is formed on the surface of the TiAlV substrate in the case of alkali treatment B. This suggests that a similar bone like apatite layer is forming on the surface.

The voltametric curves obtained for the sample A between –800 mV and 4 V (Fig. 1) show an anodic peak around 0.25 V followed by a region with practically constant current indicating the films growth. The voltammetric curve obtained in the presence of fluoride indicated the same anodic peak, but increased anodic currents. It is an argument for fluoride ion adsorption on the passive film, which caused its dissolution and/or the formation of a porous layer [15].

Figure 2 shows the cyclic voltamograms for the Ti6AlV alloy after treatment B. In this case the current density is very low, as a proof of the high corrosion resistance of the TiAlV alloy.

The potentiodynamic polarisation results in Ringer 1 solution for both samples (A, B) are presented in Table 2.

Cyclic potentiodynamic curves reveal higher corrosion and passivity current for treatment A. Regarding the corrosion potential, in the case of alkali treatment the values are more noble compared to polished electrodes. The effect of fluoride ions in both cases, independent of surface treatment are shifts to more negative values, and simultaneously increases in corrosion and passivation currents. Such data support OCP results concerning the presence of fluoride ions.

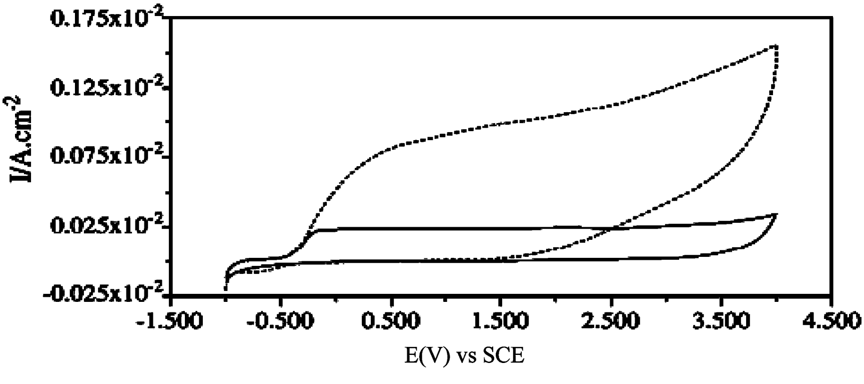

FIGURE 1 The cyclic potentidynamic curve (— without fluoride; …… with fluoride) for the sample A.

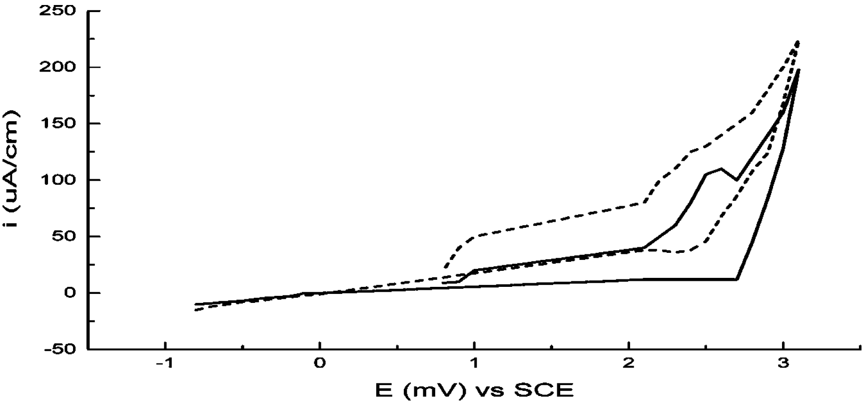

FIGURE 2 The cyclic potentidynamic curve (— without fluoride; …… with fluoride) for the sample B.

X-ray Photoelectron Spectroscopy (XPS)

As surface investigation with a depth analysis capacity of only a few nm, i.e., less than the depth of the natural oxide film formed on Ti, is well adapted to probe the elements present in TiO_2.

It is well known the excellent corrosion behavior of the TiAlV alloy, which relies on the formation of an amorphous oxide layer of 4–6 nm at the surface. Studies performed by means of XPS show [16] that the oxide layer on top of TiAlV alloy is predominantly TiO_2, with lower amounts of sub-oxides TiO and Ti_2O_3 close to the metal/oxide interface.

Figure 3 presents the XPS Ti spectra recorded for sample A in Ringer 1 solution without NaF. In this solution, the Ti $2p_{3/2}$ peak was located at binding energy of $E_b = 459\,eV$ denoting the TiO_2 presence.

TABLE 2 Potentiodynamic Polarisation Data Sample B

Sample	E_{cor} (mV)	I_{cor} (nA/cm^2)	I_{pas} (μA/cm^2)
A with NaF	–185	21	51
A without NaF	–90	18	31
B with NaF	–80	15	40
B without NaF	–59	11	26

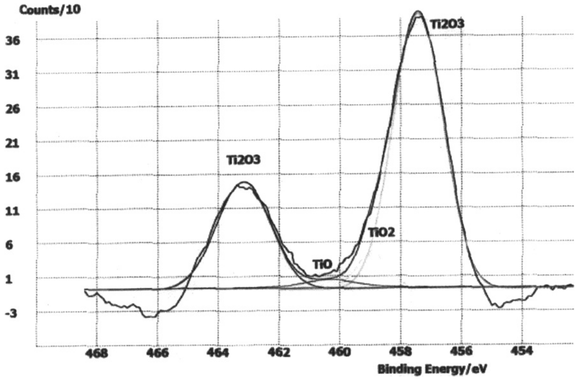

FIGURE 3 The XPS Ti spectra recorded for sample A.

Impedance Measurement

The EIS spectra for the sample A were obtained at the open circuit potential for various immersion times in Ringer solution, with and without the addition of 0.1 mol/L of NaF.

The Nyquist plots after one hour of exposure in both solution (Fig. 4) show an almost capacitive behaviour, with a decrease of the total impedance and a depression of the capacitive loop in the fluoride media, indicating the formation of a more porous film.

Increasing the immersion time from 1 to 10 days established in Bode plots an enhanced polarisation resistance and a maximum phase

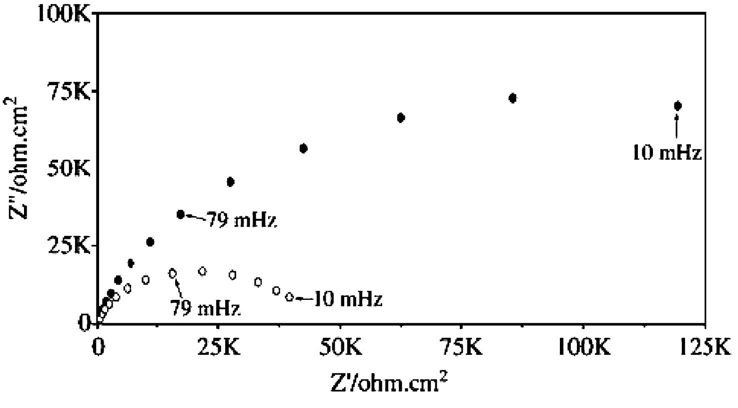

FIGURE 4 Nyquist plots obtained for the alloy at OCP after one hour in the serum (•) and with 0.1 mol/L (o).

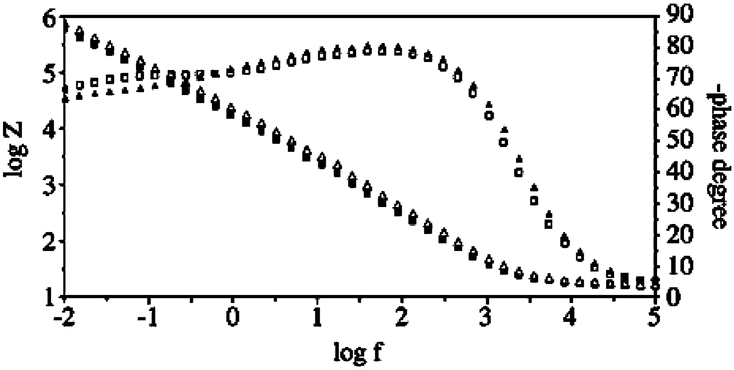

FIGURE 5 Bode plots obtained for Ti6Al4V at OCP in the serum after 1 day (□ ■) and 10 days (▲ △) of immersion.

angle close to 80°, indicating greater stability of the oxide fill in Ringer 1 electrolyte (Fig. 5).

Figure 6 shows the Nyquist plots obtained for the sample A at OCP in Ringer solution with NaF after 1 and 10 days immersion. The figure shows

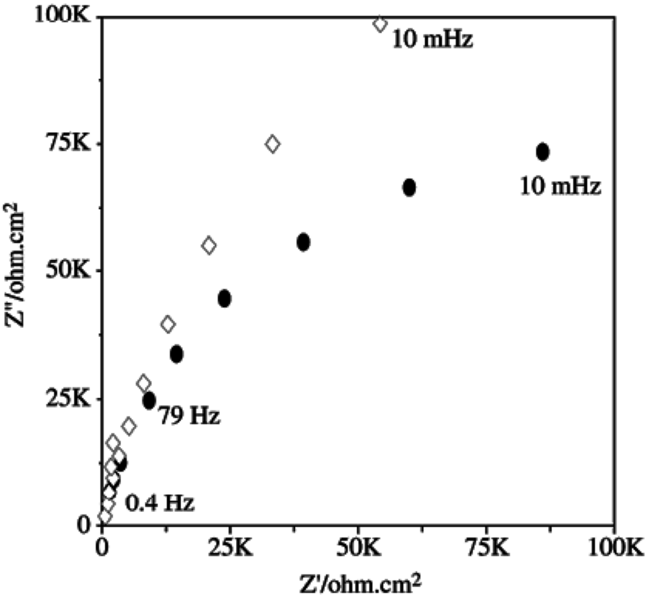

FIGURE 6 Nyquist plots obtained for the alloy at OCP in Ringer 1 with floride after 1 day (●) and 10 days (◇) of immersion.

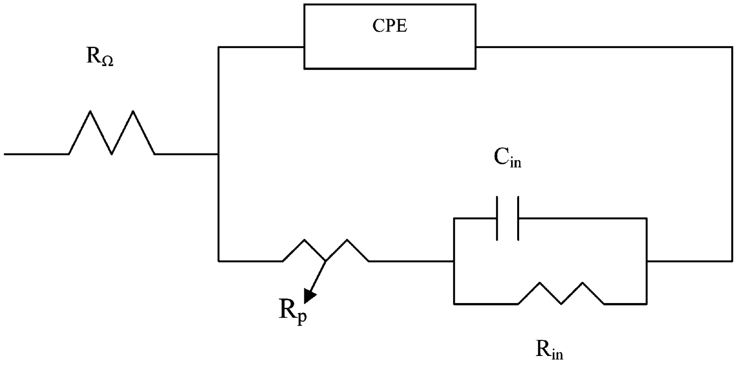

FIGURE 7 Equivalent circuit of passive film on TiAlV substrate in Ringer 1 solution.

two over lapping time constants in the middle and low frequency range, which may be related to an adsorption process on the electrode surface.

The equivalent electrical circuit fitting the experimental data sample is shown in Figure 7. The total impedance is a combination of the following elements:

- CPE is constant phase element = capacitance of intact (total) passive film. Its value is much smaller than a typical double layer capacitance. Its units are pF or nF, not μF
- R_Ω resistance of the electrolyte
- C_{in} interlayer capacitance. The interface between inner and outer part of passive film is modeled as a double layer capacity in parallel with kinetically controlled charge transfer reaction
- R_i charge transfer resistance in the inner part of the passive layer.
- R_p charge transfer resistance in the outer part of the passive layer.

The equivalent circuit confirms the idea that the passive protective film consists of two components: an inner crystalline layer of TiO_2 and a second one, of porous outer layer oxide/hydroxide surface. This surface seems to determine the adsorption of calcium ions in the pores as atomic absorption spectroscopy data already confirmed. According to our study and recent literature data which introduce complexes as titanates at bio-interface [17,18], an empirical model could be proposed with the following multi-layers:

TiAlV metallic + $[TiO + T_2O_3 + TiO_2]$ inner crystalline layer;

$[(TiO_2 + TiOH) + (Ca + Na)$ titanate$]$ outer amorphous layer.

This suggests that a similar bone-like layer could form on the surface of TiAlV upon implantation.

CONCLUSIONS

1. The stability of the oxide film is supported by all electrochemical investigations: open circuit test, cyclic polarization and electrochemical impedance. The EIS spectra show an almost capacitive behaviour, with a decrease of the total impedance and a depression of the capacitive loop in the fluoride media, indicating the formation of a more porous film.
2. Studies performed by XPS show that the oxide layer on top of TiAlV alloy is predominantly TiO_2, with lower amount of suboxides TiO and Ti_2O_3 close to the metal/oxide interface. An empirical model of the bio-interface is proposed, based on electrochemical and surface experiments.
3. In spite of the well known aggressiveness of the fluoride ions in Ringer 1 solution, the passive film remain protective and no breakdown phenomenon was noticed.

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