Influence of the oxide interlayer on the electrochemical behavior of hydroxyapatite-coated titanium used as biomaterial

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Abstract

This study investigates the influence of the oxide interlayer on the electrochemical behavior of hydroxyapatite-coated titanium substrates since the biocompatibility of biomaterial implants is primarily related to their corrosion resistance. An oxide film was deposited onto titanium using the plasma-spray technique. The hydroxyapatite coating, HA, was obtained by the biomimetic method, which simulates the natural formation conditions of biological HA. Electrochemical experiments were carried out using different immersion times (24 h, 48 h and 7 days) in simulated physiological solution using electrochemical impedance spectroscopy, EIS. The main focus of this work was to show that it is possible to apply an electrochemical method to estimate the corrosion resistance of the hydroxiapatite coating on modified commercially pure titanium, cp-Ti substrates, and to model the different electrochemical interfaces based on a proposed equivalent electrical circuit. The loops observed in the graphs of the complex plane were determined by the charge transfer resistance in the high-frequency region and were also correlated to diffusion processes within the pores at region of low frequencies. Experimental data showed that the most effective protection was provided by a film of pre-coated oxides after it was immersed in physiological solution for seven days.

Keywords: hydroxyapatite coatings, titanium, plasma-spray, electrochemical impedance.

1 - Introduction

Titanium oxide coatings on titanium alloys have recently demonstrated promising *in vivo* corrosion behavior, acting as a chemical barrier against the release of metal ions from the implant. However, its chemical bonding with the living bone tissue in the body is not very strong.

Hydroxyapatite is of a substantial interest because of its chemical similarity and compatibility to calcium phosphate minerals present in bone tissue, and its ability to form a strong chemical bond with natural bone. The HA coating is expected to enhance the bioactivity and osteoconductivity by acting as an outer coating layer (1). The inner titanium oxide layer is designed to prevent the cp-Ti substrate from becoming corroded, even after the HA layer has been completely dissolved due to biological processes. Therefore, a double-layer HA-TiO_2

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coating on cp-Ti or Ti alloys should present a very good combination of biochemical stability and mechanical properties, particularly if the interfacial adhesion can be enhanced, having HA as the porous, bioactive top layer and a porous TiO_2 film as the corrosion resistant inner layer (2). However, the coating porosity may affect the corrosion behavior of the metal implant (3). The electrochemical behavior of metal implants in corrosive environments can be evaluated to estimate the implant's corrosion resistance (1).

The purpose of this work was to investigate the influence of the surface modification of cp-Ti substrates on the corrosion resistance of the HA coating in physiological solution, which simulates the body's internal environment. The electrochemical behavior of the HA coating on polished cp-Ti substrates, with and without a TiO_2 interlayer, was evaluated by EIS to estimate the corrosion resistance.

The reason for the EIS characterization of the coatings is to obtain information about system properties such as the presence of defects, the reactivity of the interface and adhesion. The equivalent electrical circuits representing the physical properties characterizing the system are proposed to model the impedance results.

2 - Material and Methods

Two pieces of cp-Ti were previously cut into small rectangular blocks (10mm x 10mm x 3mm) and polished with 150-grit wet emery paper to obtain a rough surface. A thin titanium oxide layer was deposited using a plasma spray gun (Plasma Spray Gun – METCO Perkin Elmer) onto one of the specimens roughened beforehand. The substrate was placed about 20 cm from the nozzle of the gun. The deposits were prepared with a voltage of 60V at a velocity in the range of 120-600 m s^{-1} and a temperature between 2200 and 8300°C.

Both of the samples (cp-Ti and cp-Ti/oxides film) were ultrasonically cleaned in acetone for 10 min, in alcohol for 10 min, and then in distilled water for 15 min. These samples were then subjected to treatment in the 5 mol L^{-1} solution at 60°C for 24 hours and the subsequent heat treatment was at 600°C for 1 hour.

After that, the two specimens were submersed for 7 days at 37ºC in a solution of 1.5 SBF, nearly equal to that of human blood plasma with ion concentrations (mmol.dm^3) of: Na^+, 213.0; K^+, 7.5; Mg^{2+}, 2.3; Ca^{2+}, 3.8; Cl^-, 223.0; HCO_3^{2-}, 6.3; HPO_4^{2-}, 1.5; SO_4^{2-}, 0.75). After coating, the samples were subjected to heat treatment at 800 °C for 1 hour to obtain the modified surfaces: cp-Ti/HA and cp-Ti/oxides film/HA.

An electrochemical cell with three electrodes was used containing physiological solution of the following composition (gl^{-1}): NaCl 8.74, $NaHCO_3$ 0.35, Na_2HPO_4 0.06, NaH_2PO_4 0.06, using the saturated calomel electrode as the system reference, and a Pt foil as an auxiliary electrode.

Impedance measurements were made at open-circuit potential after different immersion times using a frequency-response analyzer, Solartron 1255, connected to an electrochemical interface, Solartron 1287. An amplitude of 10 mV was applied to the potential in a frequency range that varied from 100 kHz to 10 mHz where 5 points were obtained for each frequency decade, controlled by ZPlot software and analyzed using ZView software (Scribner Associates, Charlottesville USA).

3 - Results and Discussion

The EIS spectra obtained in this study can be described in terms of an equivalent electrical circuit, based on a plausible physical model with the circuit elements representing electrochemical properties of the different electrochemical interfaces. Because of the distributed relaxation feature, which is commonly observed in titanium oxide films, a constant phase element (CPE) was utilized for data fitting instead of an ideal capacitor. The CPE is usually interpreted as the non-ideal capacitance and the inclusion of CPE in the equivalent circuit provides a parameter α, corresponding to either, the degree of distortion of the spectrum, or to surface roughness. The decrease of α as a function of time can be explained by an increasing roughness of the surface and number of pores (4).

The Figures 1 and 2 display the impedance spectra of cp-Ti/HA and cp-Ti/oxides film/HA, respectively. Both spectra exhibit three capacitive components. Figures 1A and 2A show examples of the graph clearly separating into three semicircles. The corresponding Bode plots are shown in Figures 1B and 2B. Clear separation into Bode formats is indicated by the three phase-angle maximums, highlighting and dividing the Bode graphs in three sections. The first being the high frequencies containing information regarding the porous HA layer, which is the most external layer; the second being the intermediary frequency which can be described by the morphology of the barrier of the oxides; and the third being the low frequencies, containing information regarding the substrate itself.

The equivalent electrical circuit model proposed for fitting spectra takes into account three R(CPE) elements in series with the cell resistance, R_Ω. The non-ideal capacitances, according to CPE = $(Ci\omega)\alpha$, were modeled by CPE_1, CPE_2 and CPE_3, where CPE_1 is attributed to ion diffusion to within the HA layer, CPE_2 is attributed to ion diffusion to within the oxides film and CPE_3 is attributed to metallic corrosion.

The maximum observed for the phase angles ($-\phi$) corresponding to capacitive components at regions of low and intermediary frequencies, corresponded to about 45º and 20º, respectively. This last value cannot be described by the free diffusion of the species in solution. However, when considering species diffusion in porous electrodes, the impedance will be a straight line with a slope of about 45º/2 (4).

Particularly, the loops observed in the graph of the complex planes are determined by the charge transfer resistance in the region of high frequencies and are characterized by free diffusion of the species in the solution, ($-\phi \cong 45º$) and also can be correlated to diffusion processes within the pore where $-\phi \cong 20º$ at region of low frequencies.

The differences observed in the open-circuit potential values (marked in Figures 1 and 2) for impedance measurements shows that the protection has a greater effect on the substrate ion release when the TiO_2 intermediate layer is present.

Comparing the complex plots obtained after two immersion times for different coatings, high values of the impedance modules for HA on modified substrates of cp-Ti can be observed.

However, with the increase in the immersion times, from one day to seven days, the diameter of the semicircle decreases when the TiO_2 interlayer is not present.

4 - Conclusions

EIS has proved itself to be a suitable technique to evaluate the corrosion resistance of modified surfaces of cp-Ti, and it also allows *in situ*, non-destructive analysis of coatings to determine adhesion loss. The impedance spectra obtained for hydroxyapatite coatings in a simulated physiological environment were characterized by diffusional effects within the pores. Hydroxyapatite films with an interlayer film of oxides provide greater effective protection after longer periods of submersion in simulated body fluid.

Acknowledgments

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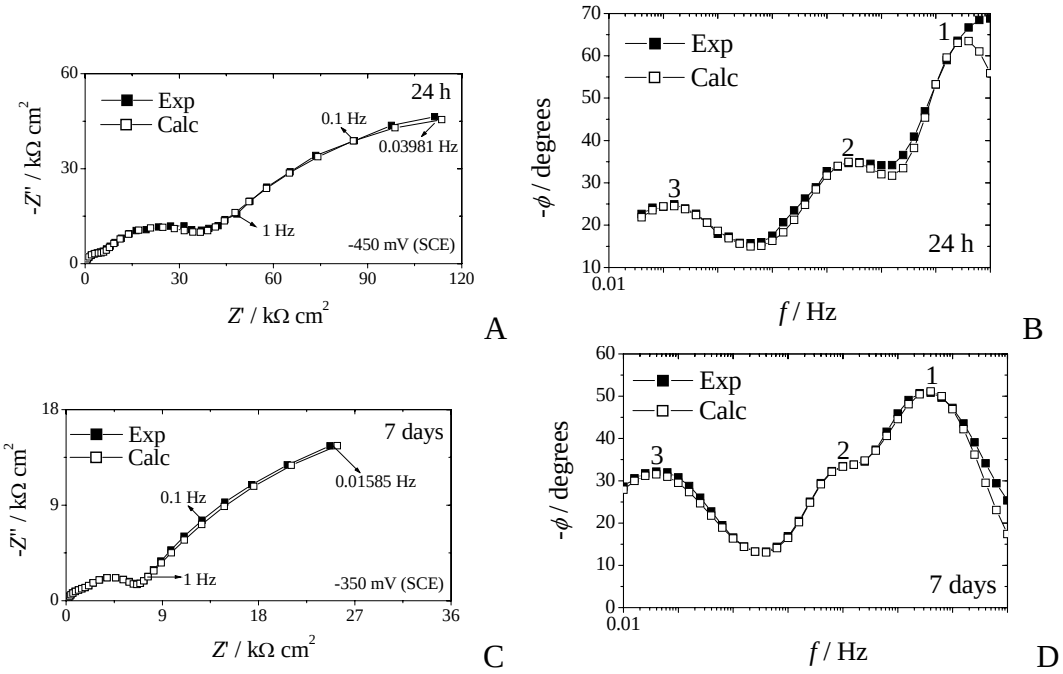

Figure 1: EIS spectra obtained at open-circuit potential for cp-Ti/HA after 24 h and 7 days immersion in simulated physiological solution: complex plane (A, C) and Bode [$-\phi(f)$] format (B, D).

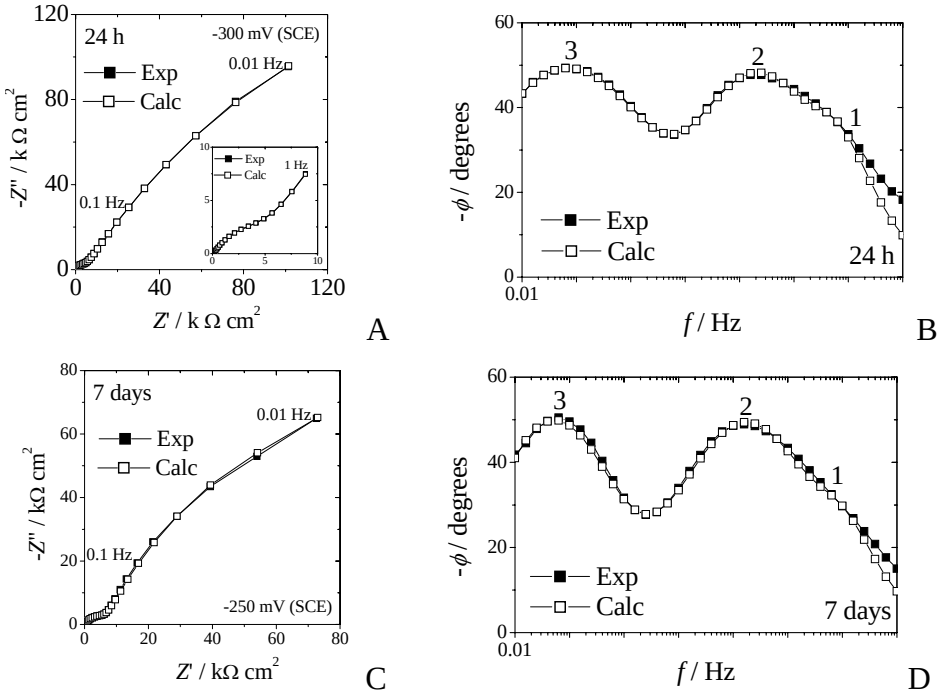

Figure 2: EIS spectra obtained at open-circuit potential for cp-Ti/oxides film/HA after 24 h and 7 days immersion in simulated physiological solution: complex plane (A, C) and Bode [$-\phi(f)$] format (B, D).