Electrochemical evaluation of hydroxyapatite and titanium oxide coating made by HVOF in Kokubo's solution.

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Abstract

During the XXth century, one of the main concerns in medicine has been the deterioration of articular joints in old people, as a consequence of aging phenomenon. Metallic implants have been chosen as bone replacement material because of their mechanical properties, but also other properties, as biocompatibility and corrosion resistance in body fluids, low modulus, low density and good wear resistance have to be taken into account. In order to improve the corrosion stability of titanium, it can be alloyed with resistant materials. In this work the behavior of a hydroxyapatite/titanium oxide (60-40%) produced by high velocity oxygen fuel (HVOF) was investigated using open circuit potential measurements, and electrochemical impedance spectroscopy (EIS) in natural aerated Kokubo’s solution for 15 days. The coated samples presented open circuit potential oscillations, which were associated to the porous nature of the coating that allows the electrolyte reach the substrate causing pitting formation with activation – repassivation at the bottom of the pores. The impedance data were interpreted based on the presence of a metallic oxide layer between the HA-TiO2 coating which are attacked and / or dissolved by the Kokubo’s solution with significant influence of the bovine serum albumin (BSA).

Keywords: corrosion, EIS, hydroxyapatite.

Introduction

During the XXth century, one of the main concerns in medicine has been the deterioration of articular joints in old people, as a consequence of aging phenomenon. Metallic implants have been chosen as bone replacement material because of their mechanical properties, but also other properties, as biocompatibility and corrosion resistance in body fluids, low modulus, low density and good wear resistance have to be taken into account (1,2). In order to improve the corrosion stability of titanium, it can be alloyed with resistant materials (3).

Hydroxyapatite (HA) coatings is a vast research field which is growing very fast since the 1980’s when titanium implants have been coated with HA using thermal spray techniques. Thermal spraying processes are the fastest method to deposit hydroxyapatite (HA) coatings with good adhesion with the substrate. High Velocity Oxygen Fuel (HVOF) sprayed coatings are attractive for corrosion resistance, because they are dense and exhibit low oxidation of raw materials compared to coatings obtained by other thermal spray processes (plasma or wire arc spray) (4).

The electrochemical impedance spectroscopy (EIS) has the advantage of to be a non-destructive and transient technique, is able to separate the resistance of electrolyte from the

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processes occurring at the electrode / electrolyte interface, and as explores a high frequency range is enabling to detect events occurring in a large time constant interval .(5-7)

Considering the reduced number of works used EIS to characterize the evolution of the HA-based coatings in physiological solutions, and that is rarely electrochemical studies on HA-based coatings prepared by HVOF technique, the aim of this work is to evaluate the corrosion behavior of HA-TiO_2 composites as bioactive coatings, which may present a better corrosion resistance when compared with HA coatings and better mechanical proprieties, conserving the biological ones(7, 8).

Methodology

Ti-6Al-4V alloy was used as substrate. Before the spraying process, the substrate was degreased and grit blasted with corundum to get a rough surface with a mean roughness around 5 µm, and sufficient anchorage points between the sprayed coating and the substrate.
A spherical commercial hydroxyapatite powder, with a particle size of (31±2) µm and irregular commercial rutile powder, were sprayed using a HVOF technique by means of a Sulzer-Metco DJH 2600 HVOF system. Propylene was used as the fuel gas and compressed air as carrier gas.

Scanning electron microscope (SEM) images and energy dispersive x-ray spectroscopy (EDXS) data were acquired before and after the electrochemical techniques, using a Jeol JSM-840 equipment.

The corrosion resistance of coated and uncoated substrates was evaluated by means of electrochemical measurements carried out in an 80 mL three-electrode conventional electrochemical cell with exposing area of 0.74 cm^2 to the solution. Kokubo's solution was used as electrolyte. An Ag/AgCl/$KCl_{3mol/L}$ electrode, connected to the working solution through a Luggin capillary, was used as reference, and a Pt network as auxiliary electrode. Open circuit potential (E_{OC} *versus* time), and electrochemical impedance spectroscopy (EIS) measurements were carried out using a potenciostat-galvanostat Irvium, model VERTEX equipped with an impedance modulus. The EIS measurements were acquired for immersion times up to 15 days, and performed by applying a 10 mV (rms) sinusoidal perturbation signal to the E_{OC}, from 1 x 10^5 to 1 x 10^{-3} Hz recording 10 points per frequency decade. The first impedance diagram was acquired after 24 hours of immersion in the test solution. All electrochemical experiments were performed at 36°C. All electrochemical tests were conducted in triplicate in order to ensure the reproducibility of results.

Results and Discussion

The open circuit potential *versus* time curves of the bare and coated Ti-6Al-4V alloy samples in contact with Kokubo's solution are presented in **Figure 1**. It has been considered more appropriate to wait for 24 hours, as the studied materials did not show an immediate and clear stabilization of the electrode/solution interface at shorter immersion times. The coated sample presented higher potential values, pointing to a noble surface.

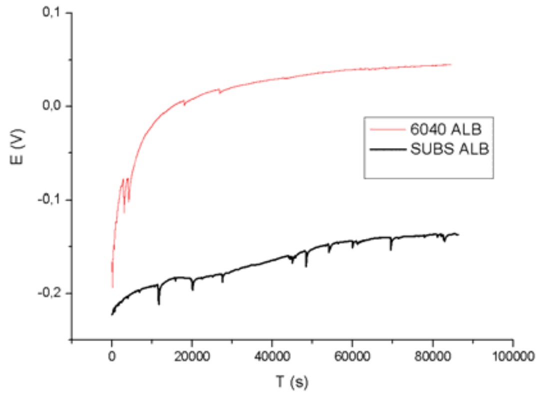

Figure 1: Open circuit potentials acquired at the first 24 hours of immersion in Kokubo's solution.

Figure 2 displays the impedance complex plane for the Ti4Al6V alloy coated with 60-40% HA-TiO2. In the Bode phase angle diagram it presented 2 distinct time constant one at the high frequency (HF) related to the interfacial process through the coating pore and one at medium frequency (MF) range related to the coating response. As time elapses, another time constant can be seen at MF region and there is a decrease of the MF time constant, which is associated with an accelerated interfacial process at the metal surface concomitantly with the degradation of the coating. After seven days, this system goes to a two time constant system again similar to degraded systems with one time constant with high phase angle modulus at the MF region and another one at the high frequency. In Nyquist plot shows that the coated sample presented larger capacitive loop than the capacitive loop displayed by the substrate at day 0 (D0).

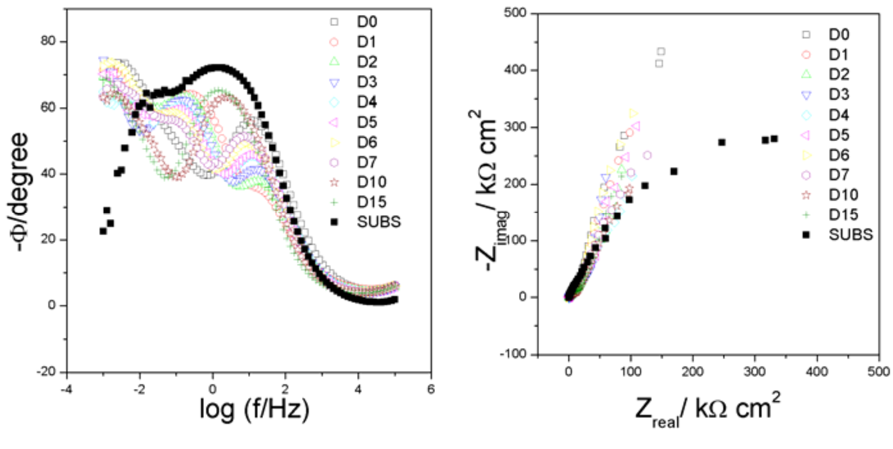

Figure 2: Experimental complex plane for 6040 sample; Bode plots -ϕ *versus* log(f) and Nyquist, for different immersions times in Kokubo's solution and for the bare substrate at the first period.

SEM images of the coated sample before and after 28 day of electrochemical measurements respectively are presented in Figure 3 and the unravel that as time elapses, the coating tend to dissolve, probably due to the shift of the local pH and leaves the metal surface exposed. This scenario corroborates with the behavior sustained by the EIS data.

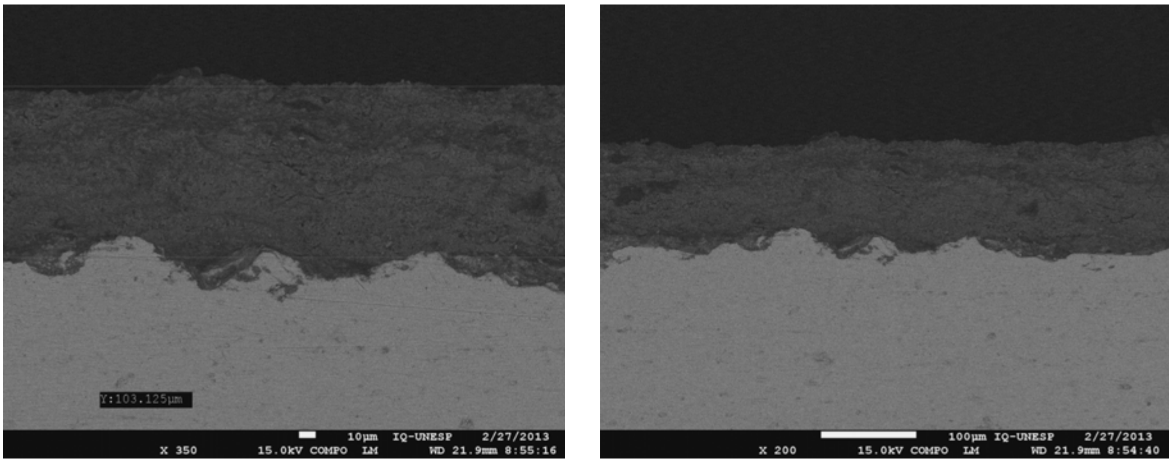

Figure 3: SEM images of the 60HA40TI sample before and after 28 day of electrochemical measurements respectively.

Conclusion

- It was possible to evaluate the Hydroxyapatite – Titanium oxide film by means of electrochemical impedance spectroscopy.
- The coated samples presented larger capacitive loop than the bare substrate, pointing to a better corrosion resistance.
- SEM images points that the 60HA40TI sample dissolves, loosing thickness.

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