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CORROSION PROPERTIES OF ZN-TIO_2 PRODUCED BY PLASMA ELECTROLYTIC OXIDATION

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Abstract. *Surface modifications of metallic implants can be tailored to improve osseointegration and to have bactericidal ability. Zinc is one of the bactericidals elements most investigated on the biomaterial field, due to its lower toxicity and to be present in biological processes in the human body, such as acting on protein synthesis. In addition, it acts on the osmotic regulation and maintenance of ionic balance. However, one of the main concerns in the success of an implant is its resistance to the process of corrosion, which occur in the oral environment. Corrosion process can lead to the failure of the implant and release toxic ions on the human body. In this research, a titanium oxide coating doped with zinc was obtained, and its corrosion resistance was evaluated against Zn free coating. TiO_2 coatings were produced on titanium grade 4 samples by plasma electrolytic oxidation (PEO). Commercially pure titanium samples were mechanically grounded and ultrasonically cleaned. PEO was carried at 350 V for 60 s using 0.02 mol/L calcium glycerophosphate + 0.15 mol/L of calcium acetate + 0.02 mol/L of zinc acetate. The modified surfaces were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), corrosion assays. SEM images showed micropores and a homogeneous layer. Results showed a higher corrosion resistance on coatings containing zinc.*

Keywords: *biomaterials, titanium, zinc, surface modification, corrosion.*

1. INTRODUCTION

Titanium and its alloys are used in the manufacture of dental and orthopedic implants, as they have good biocompatibility and mechanical resistance. However, these implants are subject to bacterial contamination (Costerton et. al, 1999). The bacteria present on the surface of the biomaterial synthesize a protective polymeric matrix, called biofilm, capable of prevent the action of the immune system and antibiotics administered orally. The formation of the biofilm compromises the growth of formed bone on the implant, called osseointegration (Camargo et.al, 2015).

Previous research suggests the use of coatings containing bactericidal agents, preventing the survival of bacteria on the biomaterial (Cheng et. al, 2007). Zinc is one of the bactericidals elements most investigated on the biomaterial field due to its lower toxicity and to be present in biological processes in the human body, such as acting on protein synthesis, also acts on the osmotic regulation and maintenance of ionic balance (GOUDOURI et.al, 2014).

Previous works investigated the presence of calcium and phosphorus on plasma electrolyte oxidation (PEO) coatings, which is an electrochemical technique that incorporates elements present in the electrolyte forming an oxide layer, to obtain better osseointegration (Laurindo et.al, 2014), since these elements are osteoinductive. However, these surfaces do not present bactericidal activity.

One of the main concerns in the success of an implant is its resistance to the process of corrosion, which may impair the structural integrity of the implant and lead to the implant failure. Furthermore, corrosion can release toxic ions to the body and cause an adverse biological reaction of the organism (Jacobs et. al, 1998).

The objective of this work is obtaining a doped surface with calcium, phosphorus and zinc by PEO and to evaluate the influence of the zinc on the corrosion properties.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Commercially pure titanium grade 4 disks were mechanically grounded with #600 SiC abrasive paper., specimens were ultrasonically cleaned in acetone, ethanol and deionized water for 15 minutes respectively.

The PEO was carried out in potenciostatic method (constant voltage) at room temperature (23 ºC). The potential was set to value of 350 V and current density of 2A for 60 seconds, using a DC power supply (Model 62012P-600-8 Chroma) and a titanium plate as a counter electrode. After the PEO treatment the samples were washed with deionized water and air dried. Two different concentrations were used, the first contained 0.02 mol/L calcium glycerophosphate + 0.15 mol/L of calcium acetate (Ca-P) and the second was added 0.02 mol/L of zinc acetate (Ca-P-Zn).

2.2 Oxide layer characterization

The surface morphology of the samples was examined by scanning electron microscopy (Tescan Vega III). The chemical composition was determined by energy dispersive spectroscopy. The crystalline structure was characterized by X-ray diffraction (Shimadzu XRD-700).

2.3 Electrochemical behavior

First the open circuit was measured. The tests were carried out in phosphate solution (PBS) at 25 °C with a rest time of 60 min, needed for reaching to a steady-state. Then, potentiodynamic polarization tests were performed using InviumStat (Invium). The scan rate was 1 mV s^{-1} in the range of -0.500 to +0.700 V in relation to OCP. A titanium wire was used as counter electrode, a saturated calomel electrode was used as reference electrode and the exposed area of the coating was used as working electrode.

3. RESULTS AND DISCUSSION

3.1 Oxide layer characterization

SEM images of the reference sample and the surfaces obtained by PEO were performed, to evaluate the homogeneity and details of the topography, Figure 1. The samples coated by PEO showed homogeneous layer, and pores with heterogeneous diameters. Thus, the incorporation of zinc did not alter the surface morphology.

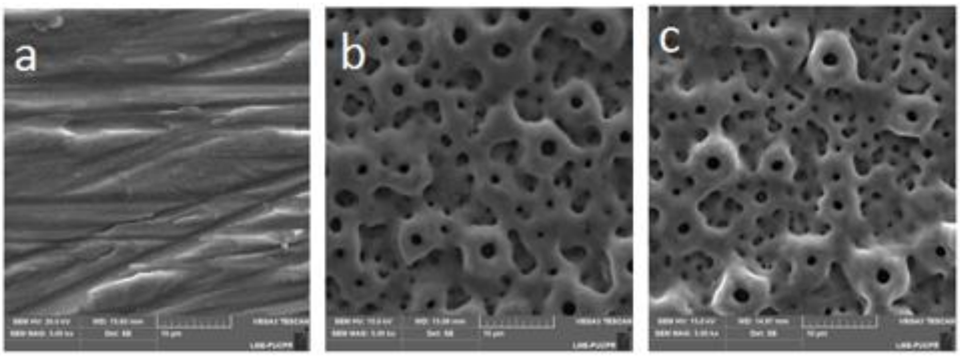

Figure 1 – SEM images magnification 5kx (a) Group Ti (b) Group Ca-P (c) Group Ca-P-Zn

The chemical compositions tests showed the presence of zinc the coating Ca-P-Zn (8.0 wt%), that is, zinc was incorporated in the coating by PEO. However, incorporation of zinc decreased the incorporation of calcium on the coating.

XRD results showed peaks related to phases present in the coating, they are titanium, rutile and anatase (figure 2). There are no peaks related to zinc, which shows zinc was incorporated as an amorphous phase. The oxide layer observed mainly consists of anatase, previous investigations showed that crystalline surfaces present better bioactivity than amorphous layers (Sul et. al, 2001).

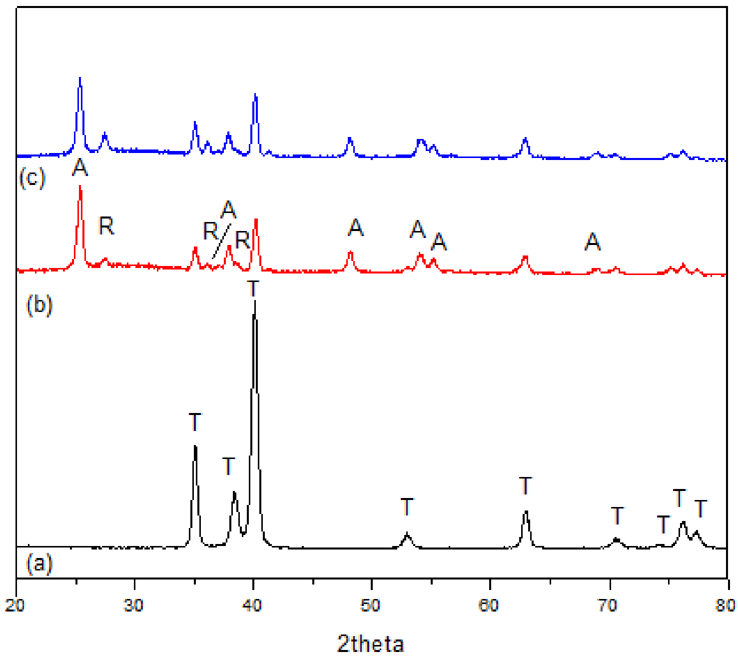

Figure 2 – XRD spectra results of (a) Group Ti (b) Group Ca-P and (c) Group Ca-P-Zn. Labels T, A and R in the figure refer, respectively to titanium, anatase and rutile phases.

3.2 Electrochemical behavior

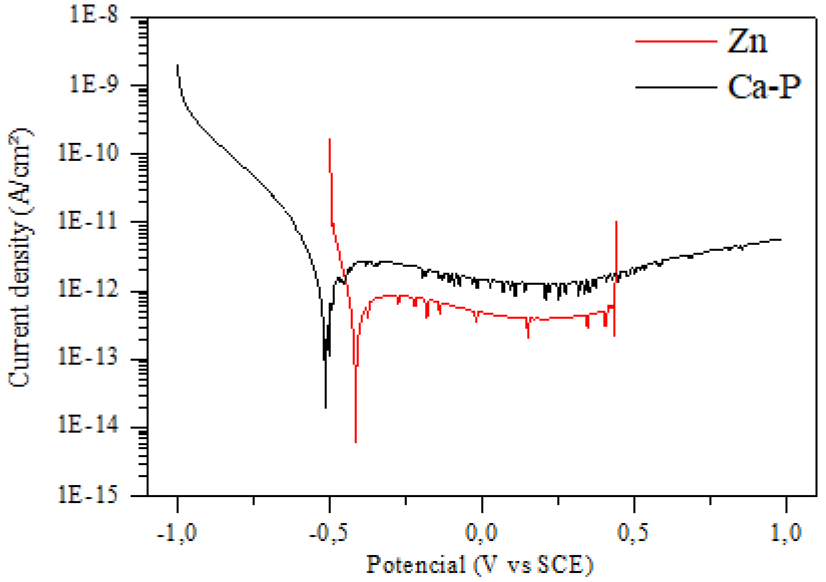

Figure 3 – Potenciodynamic polarization curves of samples in SBF solution.

Plots on semi-logarithmic scale of current densities corresponding to all PEO conditions are shown in Fig. 3. The values of corrosion potential (Ecorr) and current corrosion (Icorr) from the potentiodynamic polarization curves in SBF solution can be observed in table 1**.** It can be observed the Ca-P-Zn presented higher corrosion potential (Ecorr) and lower corrosion current (Icorr) in comparison to Ca-P samples.

Table 1 – Electrochemical parameters from the potentiodynamic polarization curves

Groups	**Ecorr. (V)**	**Icorr. (A)**
Ca-P-Zn	-0.4128	2.6E-8

Ca-P	-0.5125	3.69E-05

Results showed higher corrosion resistance on coatings containing zinc. Further research will show the origin of this resistance, which may be caused, for example, by the increase in coating thickness.

4. CONCLUSION

It was possible to obtain coatings doped with calcium, phosphorus and zinc by PEO. The microstructure of the surface was characteristic of this type of coating, which is already known to promote osseointegration. That is, the morphology with zinc incorporation was not altered.

After analysis of the results it is possible to observe that the coating containing zinc has higher value of corrosion potencial (Ecorr) than coating zinc free, which could indicate a better corrosion resistance.

5. ACKNOWLEDGMENTS

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