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STRUCTURAL AND CHEMICAL CHARACTERIZATION OF Ti-ZrO_2-PO_4^{-3} PROTECTIVE COATINGS FOR BIOMEDICAL APPLICATIONS[1]

CARACTERIZAÇÃO ESTRUTURAL E QUÍMICA DE REVESTIMENTOS PROTETIVOS A BASE DE Ti-ZrO_2-PO_4^{-3} PARA APLICAÇÕES BIOMÉDICAS

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ABSTRACT

The development of new materials have provided great advances in biomedical implant properties. Despite these, some problems such as chemical stability and osseointegration still have evident negative effects in many patients. To improve the properties of these materials, the main goal of this work is to develop zirconium oxide (ZrO_2) coatings containing phosphate, by sol-gel process, deposited on titanium (Ti) substrate. The precursor solution was prepared by the dissolution of zirconium acetylacetonate in a mixture of acetone, ethylene glycol, ethanol, water and phosphoric acid. The substrate has been coated with gel containing the precursor material, by a dip-coating process. For samples characterization, a crystal structure of the films by X-ray diffraction (XRD), chemical stability by voltammetry and potential balance were evaluated. The diffraction analysis of x-rays showed that it was possible to coat the titanium with zirconium pyrophosphate in the sol-gel process. An increase on corrosion resistance was observed on the titanium surface containing the film.

Keywords: biomaterials, osseointegration, prosthesis, sol-gel.

RESUMO

O desenvolvimento de novos materiais tem proporcionado grandes avanços nas propriedades implantes biomédicos. Apesar disto, alguns problemas, tais como a estabilidade química e a osteointegração ainda apresentam efeitos negativos evidentes em muitos pacientes. Para melhorar as propriedades desses materiais, o principal objetivo deste trabalho é desenvolver revestimentos a base de óxido de zircônio (ZrO_2) contendo fosfato, pelo processo sol-gel, depositados sobre titânio (Ti) como substrato. A solução precursora foi preparada pela dissolução do acetilacetonato de zircônio em mistura com acetona, etileno glicol, etanol, água e ácido fosfórico. O substrato foi revestido pelo gel contendo o material precursor, por um processo de revestimento por imersão. Para caracterização das amostras, foi avaliada estrutura cristalina dos filmes por difracção de raios-X (DRX), a estabilidade química, por voltametria e equilíbrio potencial. A difracção de análises de raios-X mostrou que foi possível revestir o titânio com dióxido de zircónio de fase pirofosfato pelo processo sol-gel. Foi observado um crescimento na resistência a corrosão de superfícies de titânio contendo o filme protetivo.

Palavras-chave: *biomateriais, osteointegração, próteses, sol-gel.*

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INTRODUCTION

The improvement on the performance of medical devices used in orthopedics and dentistry requires the development of new multifunctional materials. A recent study has been conducted to improve the mechanical characteristics, corrosion resistance and biocompatibility of prostheses currently used (CALDERON; CAVALEIRO; CARVALHO, 2015)

Stainless steel was initially used for this application, due to its good ductility and high mechanical strength. However the low corrosion resistance has limited the use of this material (NIINOMI, 2002). This problem was partially overcome with the development of Cr-Co alloys, which have excellent corrosion resistance and biocompatibility. High elastic modulus (E) of Cr-Co alloys, can generate undesirable stress shielding effect and lead to bone loss, as described in the literature (NIINOMI, 2002).

Titanium and its alloys are, currently, the most applied materials in the biomedical field. As an advantage over other materials, it has excellent biocompatibility and low elastic modulus (E) (MISHNAEVSKY et al., 2014), which gives excellent osseointegration. These materials may have some undesirable effects such as premature wear and release of ions (ESPALLARGAS; TORRES; MUÑOZ, 2015).

To overcome this problem, a significant effort has been expended by many researchers in order to develop coatings on the surface of these materials, in order to change characteristics such as mechanical strength, chemical stability and biocompatibility (VELASCO et. al., 2014). A good example is the prosthetic knees and hips that have constant movement and consequent wear in use. For this application, the protective film require, in addition to high hardness, good chemical stability to prevent corrosion and to ensure the biocompatibility of the material in body conditions (CALDERON; CAVALEIRO; CARVALHO, 2015).

Many techniques have been u3sed for obtaining the coating, highlighting the Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) (CALDERON; CAVALEIRO; CARVALHO, 2015). An alternative coating technique is the sol-gel, which has benefits such as low production cost, good adhesion and the ability to uniformly coat complex surfaces (ASRI et al., 2016). This technique, as well as the above mentioned methods, allows the use of transition metals as a base material in the matrix of the film, besides the incorporation of additional materials into the structure of that. Among the transition metals used are highlighted titanium (Ti), the zirconium (Zr), niobium (Nb) and their oxides (FUSER et al., 2016; LEPULE et al., 2015).

In this study, the use of sol-gel process is proposed for Ti coating as substrate. The samples, after a polishing and cleaning process, received the deposition of a variable number of layers by immersion and subsequent removal of the substrate from the gel from 1 to 3 times using a dip coating system. The optimization of parameters such as the gel composition, deposition steps (number of layers) and heating levels (temperature and time), have decisive influence on the final results of adhesion of the film on the substrate (CALDERON; CAVALEIRO; CARVALHO, 2015). The main goal of this work is to develop and characterize a surface coating of zirconium oxide and phosphate. This combination align the best mechanical performance of ZrO_2 and phosphate osseointegration capacity, increasing the chemical stability of titanium.

MATERIALS AND METHODS

SOL-GEL DEPOSITION

Samples of cp-Ti (commercially pure titanium) grade 1 (99.8% Ti) were coated by the sol-gel technique, associated with the dip-coating process. Prior to deposition of the films, the samples were polished using grit paper 80-600, followed by surface cleaning with ethanol. To obtain the gel to be deposited on the cp-Ti samples, a solution containing H_3PO_4 (phosphoric acid) (2g) and $Zr\ (C_6H_7O_2)_4$ (acetylacetonate Zirconium) (2g) was prepared as a precursor material. These materials were dissolved in ethylene glycol (15g), acetone (5g), ethanol (20g), H_2O (10g). For the transformation of sol gel, the material was heated up to 70 °C and kept under stirring for a period of 2h. As the temperature rose the solution occurred evaporation of the solvent, until the desired viscosity of the sol-gel was achieved.

The cp-Ti substrate was coated by the gel containing a precursor material, by dip-coating process, and the sample was immersed and removed off the gel, to form the first layer film as shown in figure 1(a). After being subjected to the gel, the sample was placed into the muffle furnace for the sintering process as shown in figure 1(b). The heating of the parts was conducted stepwise at 110 °C for 2h, 450 °C for 4h and 700 °C for 2h. The samples with 2 and 3 layers of coatings followed the same process in which the dip-coating process repeated after sintering each layer.

Figure 1(a) - Dip-coatings process.

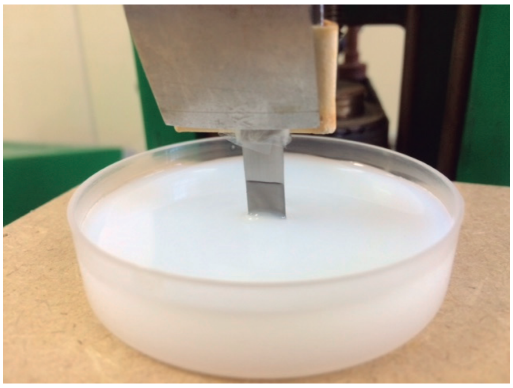


Figure 1(b) - Ti samples inside the oven.

X-RAY DIFFRACTION (XRD)

The crystalline phases of the films were identified by the technique of X-ray diffraction (XRD), before and after heat treatment using a diffractometer Bruker Advance D2 copper tube (Ka radiation = 1.5418 Å) and the voltage and current of 30 kV and 30 mA, respectively. The diffractometer used has geometry θ - θ. The goniometer scanning rate was 0.1 °/s, and the scan interval from 5º to 75º.

CHEMICAL STABILITY

The chemical stability of the films was evaluated by potentiometric and voltametric electrochemical measurements using the potentiostat-galvanostat AUTOLAB of Metrohn PGSTAT model 30. For these measurements a glass cell has been used with joints for fixing the electrodes; being a platinum plate of 4 cm^2 area as counter electrode and the Ag/AgCl electrode in 1 mol dm^{-3} KCl as reference electrode. The work electrodes are rectangular strips of Ti (99.5%, Alfa Aesar) with dimensions of 350 mm x 50 mm and 0.3 mm thick, being exposed to the solution for electrochemical measurements an area of 10 mm^2. Before the experiments, the Ti electrode has been polished with sandpaper 600 and washed with water. Measurements were made in artificial saliva solution, according to the composition described in table 1 (FUSAYAMA; KATAYORI; NOMOTO, 1963).

Table 1 - Artificial salive composition.

Components	Dosage
NaCl	400 mg/L
KCl	400 mg/L
$CaCl_2 \cdot 2H_2O$	795 mg/L
$NaH_2PO_4 \cdot H_2O$	690 mg/L
KSCN	300 mg/L
$Na_2S \cdot 9H_2O$	5 mg/L
Urea	1000 mg/L).

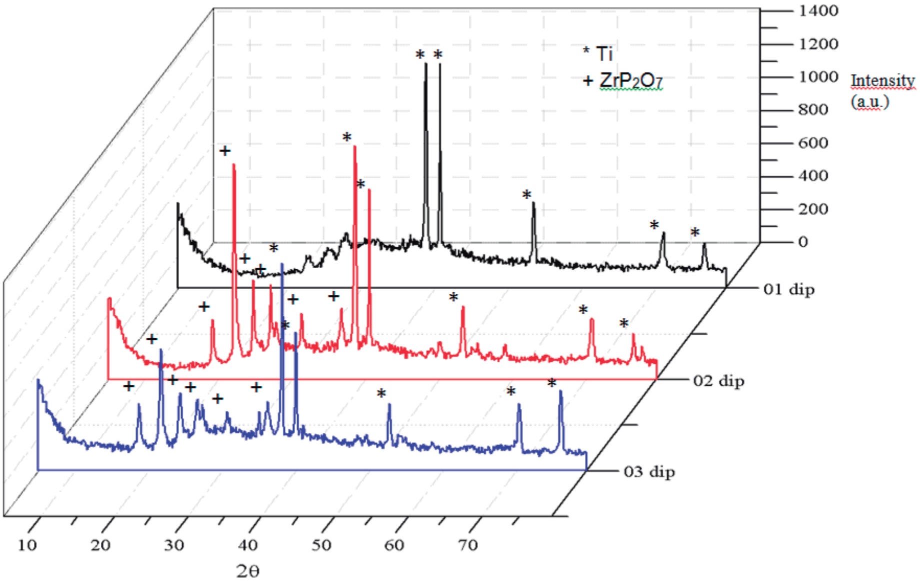
Source: Fusayama, Katayori and Nomoto (1963).

RESULTS AND DISCUSSION

X-RAY DIFFRACTION (XRD)

Figure 2 shows the evolution of the crystalline phases produced in the film surface of the titanium samples as a function of the variation of thickness of layers, deposited on the substrate. In the diffractogram of the film with only 1 coating dip, no clear formation of phase ZrP_2O_7 has been detected. The main diffraction peaks of cp-Ti substrate were observed in range 5-75°, which is a compact hexagonal structure (HC) as shown in the index record PDF 01-073-2296. The XRD patterns for samples 2 and 3 layers showed besides the characteristic peaks of the substrate, crystal formation of the protective film in the presence of zirconium and phosphorus. The diffraction peaks have shown the formation of ZrP_2O_7 phase, clearly demonstrating the fixation of the gel precursor materials, the formation of the protective film.

Figure 2 - X-Ray Diffraction of Ti/oxide.



CHEMICAL STABILITY

The results showing the open circuit potential measurements (E_{CA}) versus time are shown in figure 3. The polished Ti figure 3(a) increases the value of E_{CA} after an initial decline during measurement, which is an evidence of the formation of a protective oxide film on the metal surface, that tends to inhibit the dissolution process (ROBIN et al., 2008). The final value of the open circuit potential for polished Ti was 0.0249 V. The coated electrodes with zirconium oxide film exhibit a potential shift to the anodic region (more positive values). The E_{CA} for the electrode with 1-dip increases rapidly to a maximum steady-state value of 0.0508 V. Increasing the number of dips the potential shifts to more positive values reaching a stable value of 0.0562V after 1500 s. The existence of the film requires an increase in the E_{CA} as the layer becomes less permeable to corrosive environment. There is an increase in stability by increasing the number of dips, which may be associated with the existence of lower density cracks in the film, acting as a barrier to ion transport. In figure 3(b) after 1200s a drop in the E_{CA} has been observed, which may be associated with porosity of the film produced with 1 dip and rapid passivation returning the potential value to 0.0508 V. The response of the film with 3 dips (Figure 3 (c)) is stable, indicating that the film is stable.

The cyclic voltammograms have been performed by varying the potential applied to the electrode from -1.0 V to 3 V, as shown in figure 4. Before each measurement the electrode immersed in the solution is cathodically polarized at - 1.0 V for 1 min to remove any film formed spontaneously on the surface. The potential scanning in the positive direction of the Ti electrode shows an anodic current starting at -0.8 V corresponding to sub-forming oxides TiOOH and Ti_2O_3. The current peak at about 0.25 V indicates that the oxide composition of the film varies from Ti (III) to Ti (IV), the most stable oxide **(**PANKUCH; BELL; MELENDERS, 1993**).** With the increase of the potential, the current density is constant up to 2 V indicating the thickness increment of the anode film and leveling the surface with decreasing area **(**SCHMIDT et. al., 1998). The film is amorphous and according to the literature consisting of hydrated TiO_2 surface and sub oxide (Ti_2O_3) in the interface metal/film (PANKUCH; BELL; MELENDERS,1993). The anodic peak near 2.3 V is attributed to oxidation of the solution (oxygen evolution) occurs by transfer of electrons through the oxide film without the transpassive dissolution of Ti **(**BODDY, 1968**).** When the potential increases beyond 2.5 V the current drops to a value corresponding to a second level, due to growth of oxide film. The different threshold currents display different oxide growth mechanisms and the oxide phase transformation occurs near 2.5 V.

Figure 3 - E_{CA} x time to (a) polished Ti, (b) 1 dip of Zr oxide and (c) 3 dips of Zr oxide.

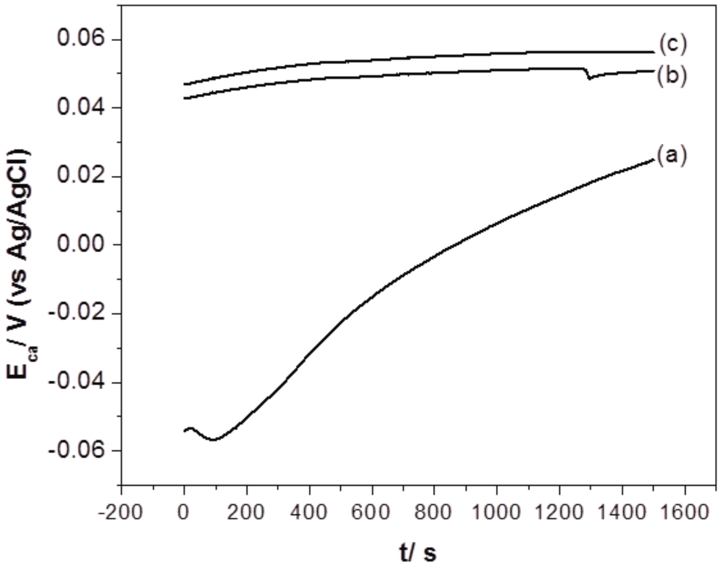
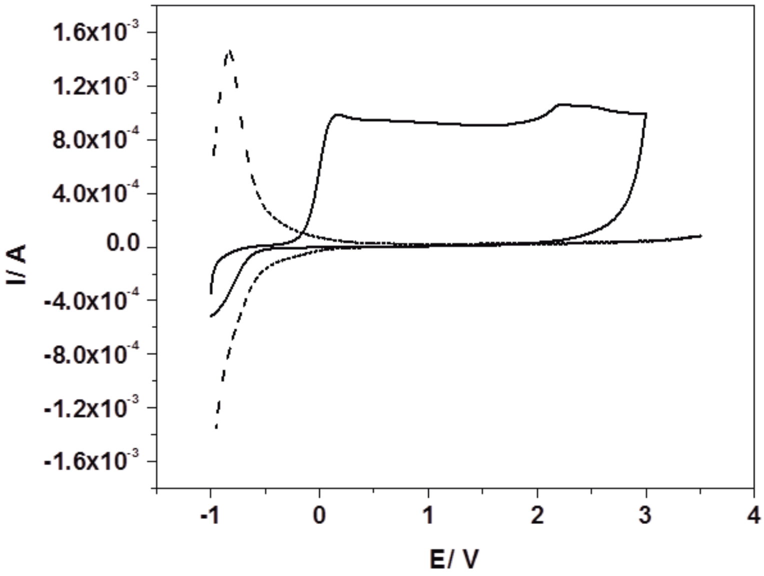


Figure 4 - Cyclic voltammograms recorded at 50 mV s-1 in artificial saliva for (___) polished Ti (- - -) and Ti/ZrO prepared with 3 dips.



The electrochemical response of the coated electrode with zirconium oxide film is presented in figure 4, after the polarization -1 V. At 1 min a rapid increase of anodic current is observed with a peak at -0.82 V followed by a rapid decrease of current to currents of the order of 3 10-6 a, which is approximately 100 times smaller than current of Ti passivated in this potential region. This indicates that the film gives a higher corrosion protection to Ti than Ti oxide grown in potentiodynamic conditions during anodic scan. The reversible process with the anodic peak at -0.82 V is associated with water reduction reaction that is anticipated on the Ti/zirconium pyrophosphate electrode surface.

CONCLUSIONS

It was possible to deposit a layer of zirconium oxide on the titanium using the sol-gel technique associated with the dip-coating process. With the increasing number of dips, an increase in film thickness occurred, as demonstrated by X-ray diffraction technique due to an increase in the peaks intensity corresponding to zirconium-phosphate oxide phase. The zirconium-phosphate oxide film gives a higher corrosion protection to Ti in the artificial salive environment. This inhibition of corrosion is observed by the decreasing of anodic current during the anodic scan as compared to pure cp-Ti. This system might be a valuable progress in nanotechnology barrier films for future applications in biomedical devices.

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