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Electrochemical behavior of bioactive coatings on cp-Ti surface for dental application

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ABSTRACT

The surface characteristics and electrochemical properties of bioactive coatings produced by plasma electrolytic oxidation (PEO) with calcium, phosphorous, silicon and silver on commercially pure titanium were evaluated. PEO treatment produced a porous oxide layer, which improved the surface topography, and enriched the surface chemistry with bioactive elements, responsible for mimicking bone surface. The surfaces with higher calcium concentration presented antibacterial and biocompatibility properties with better responses for corrosion and barrier properties, due to the presence of rutile crystalline structure. PEO may be a promising surface treatment option to improve the electrochemical behavior of dental implants mitigating treatment failures.

1. Introduction

Titanium (Ti) and its alloys are the most common used implant materials for medical and dental applications due to their biocompatibility and corrosion resistance [1,2]. A thin oxide layer is normally formed on the substrate when exposed to air, but no strong bond is formed between them. The oxide film can be destroyed and materials can degrade when exposed to oral environment due to its constant chemical and mechanical changing, which induces the corrosion process [3,4]. This electrochemical instability can affect the biocompatibility of dental implants and lead to failure of osseointegration [5].

Different surface treatments have been developed to overcome this drawback. Plasma electrolytic oxidation (PEO) is one effective technique. It consists of an electrochemical process of oxidation to create ceramic-like bioactive coatings on Ti and its alloys when voltages higher than those used in conventional anodization process are employed [6–8]. As this coating is formed by a conversion of metal substrate into its oxide, the bonding to the substrate may be stronger than those observed with coatings produced by other techniques [9]. Further, this technique promotes the formation of micropores on the surface. This allows the different chemical elements such as calcium (Ca), phosphorous (P), silicon (Si) and silver (Ag) to be incorporated onto the surface. These novel surfaces can improve the biological response by promoting increased bone-implant contact, improving the osseointegration and the bioactivity of the surface [10–12], and providing antibacterial function [13]. The pore size and the coating type formed on the material may vary with the electrolyte solution, the time of surface treatment employed and with the system voltage and frequency [7]. Further, it is important to prepare bioactive surfaces that mimic the native bone tissue by modifying the Ca/P ratio as close as possible to the hydroxyapatite (1.67), a natural mineral phase in bone [14,15].

Another advantage of PEO procedure is that anatase and rutile crystalline structures can be formed on the porous oxide layers. These crystal phases of oxide layer have a significant role on surface characteristics. Anatase has great contribution for bone compatibility and rutile has an important role on corrosion resistance [16,17].

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Nomenclature

1-PEO	Groups treated with higher Ca/P ratio
1-CaP5	5 min of PEO treatment with higher Ca/P ratio
1-CaP10	10 min of PEO treatment with higher Ca/P ratio
1-CaPAg5	5 min of PEO treatment with higher Ca/P ratio and Ag incorporation
1-CaPAg10	10 min of PEO treatment with higher Ca/P ratio and Ag incorporation
2-PEO	Groups treated with lower Ca/P ratio
2-CaP5	5 min of PEO treatment with lower Ca/P ratio
2-CaP10	10 min of PEO treatment with lower Ca/P ratio
2-CaPSi5	5 min of PEO treatment with lower Ca/P ratio and Si incorporation
2-CaPSi10	10 min of PEO treatment with lower Ca/P ratio and Si incorporation
BHI	Brain hearth infusion
CPE	Constant phase element
E_{corr}	Corrosion potential
EIS	Electrochemical impedance spectroscopy
hMSCs	Human mesenchymal stem cells
I_{corr}	Corrosion current density
I_{pass}	Passivation current density
OCP	Open circuit potential
PEO	Plasma electrolytic oxidation
Q_{in}	Constant phase element of the inner compact layer
Q_{out}	Constant phase element of the outer porous layer
Rp	Polarization resistance
Rp$_{in}$	Polarization resistance of the inner compact layer
Rp$_{out}$	Polarization resistance of the outer porous layer
R_{sol}	Polarization resistance of the electrolyte
SCE	Saturated calomel electrode
W_{diff}	Warburg diffusion element

It is imperative to investigate ideal film process parameters to develop better surface characteristics, such as enhanced mechanical properties, surface roughness, corrosion and wear resistance and biocompatibility [16].

Some *in vitro* [13] and *in vivo* [18] studies have been performed to evaluate PEO coatings. The results showed improved bone healing during osseointegration process and the bioactivity of Ti [8,13,18]. However, the literature on the corrosion behavior of the oxide layers formed on commercially pure titanium (cp-Ti) using electrolytes mixed with Ca, P, Si and Ag are scarce [8,19,20]. A comprehensive investigation is needed for a complete understanding of the coating formation, characterization and corrosion resistance behavior.

Therefore, the aims of the present study were (i) to create and characterize bioactive Ti-coatings doped with Ca, P, Si and Ag produced by plasma electrolytic oxidation (PEO) to improve biological, chemical and mechanical properties for implants surfaces, (ii) to investigate the corrosion behavior of cp-Ti treated with PEO with different Ca/P proportions and incorporation of Si and Ag and (iii) to evaluate antibacterial and biocompatibility properties.

2. Materials and methods

Cp-Ti discs (American Society for Testing of Materials—Grade II) (MacMaster Carr) with 15 mm in diameter and 2 mm thickness were ground with #320, #400, and #600 SiC abrasive paper (Carbimet 2, Buehler). The composition in wt% of cp-Ti was Ti (99.7), C (0.006), Fe (0.12), O_2 (0.16), N_2 (0.004), and H_2 (0.0019) [4,21].

The experimental design of this study (Fig. 1) consists of 2 main groups for PEO treatment, 1-PEO and 2-PEO, according to the electrolytes main composition (Ca and P) and control groups. For each electrolyte, the PEO treatment duration was set up either in 5 or 10 min. Two control groups were considered in the present study: a Ti surface (untreated) polished as described above and a sandblasted, large-grit, acid-etched surface (Al oxide). The second control group was used to compare the proposed surface treatment to a well established surface treatment.

For the Al oxide group, the discs were sandblasted with aluminum oxide particles of 150 μm at a distance of 50 mm and an angle of 90°. The air pressure used was 0.45 MPa for 30 s [22]. Subsequently, the discs were washed in an ultrasonic bath containing distilled water for 15 min and allowed to dry at room temperature. Subsequently, the surface of the discs were etched by a mixture of 0.1 mol/L of HCl and 8.8 mol/L of H_2O_2 at a temperature of 80° for 20 min and then rinsed in distilled water and oven dried at 50 °C for 12 h and finally heated in air at 400 °C for 1 h and cooled in an electric oven [23]. The discs were washed in distilled water and vacuum dried.

2.1. Preparation of plasma electrolytic oxidation ceramic coatings

Prior to plasma electrolytic oxidation (PEO) treatment, the specimens were washed and degreased with acetone, alcohol and distilled water for 10 min each in an ultrasonic bath and then air dried. PEO treatment was carried out for 5 and 10 min using a pulsed DC power supply (Plasma Technology Ltd.). The treatment was performed in a stainless steel beaker with recirculating cooling system that maintained the temperature of the electrolyte at approximately 20 °C. This electrolytic solution container was used as cathode while titanium discs were placed in the electrolytic cell as the anode. The specimen holder was designed to allow complete exposure of the sample to the electrolyte. The voltage, frequency and duty cycle were set at 290 V, 250 Hz, 60% respectively. The electrochemical treatments were performed using four different electrolytes and two different treatment duration (5 and 10 min) resulting in 8 experimental groups. All PEO treated surfaces were generated in the electrolyte based on calcium acetate ($Ca(CH_3CO_2)_2$) (Sigma–Aldrich) and glycerophosphate disodium ($C_3H_7Na_2O_6P$) with different Ca/P concentrations (higher-0.3 M/0.02 M and lower-0.1 M/0.03 M). The first main solution with higher Ca/P ratio (1-PEO) generated four groups with or without Ag incorporation by dissolving Ag nanoparticles (Sigma–Aldrich) in the electrolyte (1-CaP5, 1-CaP10, 1-CaPAg5, 1-CaPAg10). The second main solution with lower Ca/P ratio (2-PEO) also generated four groups with the incorporation or not of Si, by adding sodium silicate (Na_2SiO_3) (Vetec Quimica Fina Ltda.) in the electrolyte (2-CaP5, 2-CaP10, 2-CaPSi5 and 2-CaPSi10) (Fig. 1). More details can be found in Table 1. After PEO, the samples were rinsed with deionized water and air dried.

2.2. Surface characterization

The surface roughness ($n = 10$) parameter Ra of cp-Ti was measured using a profilometer (Dektak D150; Veeco). Three measurements of 500 μm length were performed at different areas during 12 s on each disc for each PEO condition and the mean value was calculated. The wettability ($n = 10$) was evaluated from water contact angle measurements using deionized water as test liquid and an automatic goniometer (Ramé-Hart Instrument Co., 0.100-00). The phase composition of the coatings was determined by a X-ray diffractometer (XRD; X'Pert Powder) using Cu-Kα radiation ($\lambda = 1{,}540598$ Å) at 45 kV and 40 mA. The coatings morphologies were observed with scanning electron microscopy (SEM; JEOL JSM-6010LA) and the chemical composition was evaluated with an energy dispersive X-ray spectroscopy (EDS) device attached to the SEM. Three different regions were selected to perform the EDS

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