Formation of Ca/P ceramic coatings by Plasma Electrolytic Oxidation (PEO) on Ti6Al4V ELI alloy

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Abstract. The formation of PEO ceramic coatings on Ti6Al4V ELI alloy was investigated using a phosphate/calcium containing electrolyte at 300 and 400V at 310K for different times. The Plasma Electrolytic Oxidation (PEO) coated specimens were then heat treated at 873 and 1073K for 2 hours. Scanning electron microscopy, Energy Dispersive X-Ray Spectroscopy (EDS) and X-ray diffraction analysis were used to study the composition and the morphology of the ceramic coatings. The corrosion behaviour of the coatings was studied by Electrochemical Impedance Spectroscopy (EIS) in Simulated Body Fluid (SBF). The PEO-treated specimens primarily revealed a porous structure with thickness between 4 and 12μm, according to the voltage and process time used. The coatings are mainly composed of hydroxyapatite; however, as the voltage and anodizing time increase, the Ca/P ratio decreases. Generally, the corrosion resistance of the alloy was improved by the PEO-treated coatings, although the specimens treated at 1073K showed the presence of cracks that reduced the protective effect of the coatings.

1. Introduction
Titanium and its alloys are widely used as medical, orthopedic and dental implants due to their high biocompatibility, high strength to weight ratio, high load capacity, chemical stability, low toxicity and excellent corrosion resistance [1]. However, titanium alloys release small amounts of metal ions once they are exposed to corporal fluids, causing cytotoxic, genotoxic, carcinogenic and mutagenic effects [2,3]. Several methods have been used to modify the surface condition of the alloy, in order to produce a stable barrier layer that reduces metal ion release, while increasing alloy bioactivity [4,5]. The PEO is a method for surface finishing of important light alloy metals. It results in a multifunctional ceramic coating, which is relatively thick and contains containing amorphous and crystalline phases with enhanced corrosion, wear, dielectric and thermal barrier properties [6-8]. One of the major advantages of the PEO process is the possibility of incorporating Ca and P ions into the titanium alloy surface by controlling process parameters such as composition of the electrolyte, applied voltage, current density and treatment times [9-11]. The high temperatures in the micro discharge channels during the PEO process allow for the combinations of Ca and P ions to form a hydroxyapatite phase in the coatings [12]. The presence of hydroxyapatite enhances the bioactivity of titanium alloys [13]. This study explores the influence of voltage and treatment time on the formation of Ca and P rich PEO coating on a Ti6Al4V alloy, in order to improve the corrosion resistance of the alloy in a SBF solution.
2. Experimental

2.1. Materials and surface treatment
Samples of Ti6Al4V-ELI alloy of 13.7 mm diameter and 1.55 mm thick were grounded by 80, 120, 180, 220, 320, 400 and 600 grid SiC paper and cleaned using ultrasonic agitation in acetone, followed by rinsing in deionized water and drying in warm air. The PEO treatment was carried out using a voltage controlled DC power supply (Kepco BHK 500-0.4 MG) in an electrolyte comprising 0.06M calcium glycerophosphate (Ca-GP) and 0.3M calcium acetate monohydrate (CA). Ti6Al4V alloy samples connected to the positive output of the power supply served as a working electrode, whereas a stainless-steel sheet was used as a counter electrode. The cell was immersed in a stainless-steel vessel with water to maintain the cell temperature at 309K. The process was carried out at 300 and 400 V for 180 and 420s. The treated samples were washed with deionized water and dried with cold air. Finally, they were subjected to a crystallization heat treatment at 873 and 1073K for 2h in a Carbolite CWF 1200 furnace.

2.2. Coating characterization
Surface morphologies of the coatings were investigated using a Quanta 650 FEG Scanning Electron Microscope (SEM) equipped with microwave Energy Dispersive X-Ray Spectroscopy (EDS). The phase structure of the PEO coatings was detected by X- Ray Diffraction (XRD) using a Bruker D8 Discovery equipment. Coating thickness was evaluated using an eddy current gauge.

2.3. Electrochemical experiments
Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR) measurements were carried out at room temperature in an aqueous SBF solution described by Kokubo [14]. A standard three-electrode cell arrangement was used, in which the coated samples served as the working electrode, a platinum wire acted as the counter electrode, and an Ag/AgCl electrode was employed as reference. Electrochemical measurements were performed using a GAMRY 650 potentiostat/galvanostat, with a 23mV amplitude perturbation and a frequency scan from $10^4$ to 0.01Hz.

3. Results and discussion

3.1. Coating morphology and composition
The coating surfaces revealed micropores of different sizes and shapes. The porous structure strongly depends on the voltage and time involved in the PEO process (Figure 1) [9]. It can be clearly seen that at low voltage, fine micropores with sizes less than 1 µm in diameter are randomly distributed on the surface (Figure 1 (a) and (b)). On the other hand, micropores with diameters larger than 1 µm are observed on the samples treated at high voltage (Figure 1 (c) and (d)). The number of micropores decreases as the time and applied voltage increase. However, the diameter of the micropores is bigger for higher voltages. On the other hand, cracks of dielectric rupture were observed due to the rupture of the titanium oxide layer formed at 400V (Figure 1 (c) and (d)). The cracking is caused by the high energy values released during the PEO process, which could have increased the ionic transport towards the metal/coating interface, and therefore, could have also increased the conductivity of the coating [9]. The Ca/P ratio was obtained by EDS analysis for each PEO condition before heat treatment. It was observed that by increasing the voltage and the treatment time the Ca/P ratio decreases. The coatings are constituted of non-stoichiometric hydroxyapatite (HAp), because the Ca/P ratio is less than 1.67. However, Ca/P ratio values can be associated with other calcium phosphates. For example, in the coatings obtained at 420s and 300V, the Ca/P ratio is close to dicalcium phosphate dehydrate (CaHPO₄·2H₂O) or brushite (Ca/P: 1.0), while for the coatings obtained at 180 s and 300V the Ca/P ratio is close to tricalcium phosphate (Ca₃(PO₄)₂, Ca/P: 1.5) [15]. The previous indicated that crystals of brushite and tricalcium phosphate could be formed during PEO treatment [16].

The effect of heat treatment temperature on the morphology and Ca/P ratio of the coating was studied using the PEO treated samples at 300V for 180s. Figure 2 shows the surface morphology of PEO
coatings heat treated for 2h at 873 and 1073K. At 873K, the surface morphology showed no appreciable changes (Figure 2 (b)) with respect to the untreated sample (Fig 2 (a)). On the other hand, the sample treated at 1073K shows a rough surface (Figure 2 (c), (d)), probably due to the crystallization of amorphous species, allotropic transformations or formation of crystalline species [17]. Rutile crystals are formed above 873K [18] and tricalcium phosphate is formed on the surfaces of the PEO coatings after heat treatment at 993 K [16].

**Figure 1.** Scanning electron micrographs of PEO coatings formed on Ti6Al4V ELI alloy in 0.06M Ca-GP+0.3M CA solution. (a) 180s, 300V, (b) 420s, 300V, (c) 180s, 400V and (d) 420s, 400V.

**Figure 2.** Scanning electron micrographs of PEO coatings formed on Ti6Al4V ELI alloy in 0.06M Ca-GP+0.3M CA solution for 180s at 300V, before and after heat treatment (HT). (a) No HT, (b) HT to 873K, (c) HT to 1073K and (d) detail of condition (c).

XRD diffraction analysis indicates that the coatings are mainly composed of titanium dioxide (TiO₂), as anatase or rutile (Figure 3). The anatase phase decreases with the increase of heat treatment temperature due to its polymorphic transformation into rutile. Importantly, the presence of hydroxyapatite in the coating is confirmed. Hydroxyapatite enhanced the bioactivity properties of the coatings. Also, other phases are evident from the XRD patterns. Peaks corresponding to β-tricalcium phosphate or Whitlockite (β-Ca₃(PO₄)₂) are observed in the samples heat treated at 1073K. Whitlockite is one of the crystalline calcium phosphates and has a Ca/P ratio equal to 1.5 [15]. Brushite (CaHPO₄·2H₂O) peaks are observed for the sample heat treated at 1073K in good agreement with the SEM and EDS results. The heat treatments improve the crystallinity of TiO₂ and lead to the crystallization of amorphous calcium phosphates.

3.2. Coating thickness
Table 1 presents the average thickness measurement of the PEO coatings. The coatings formed at 400V show higher values (>10µm) than the ones formed at 300V (<5µm). At higher voltage, the energy released in the process is great enough to break the barrier layer initially formed and continue the oxidation process [18]. The potential difference applied between the cathode and the anode exceeds the dielectric limit of the coating more easily, the rupture of the formed layer occurs for longer time resulting in a thicker coating. However, the thickness of the coatings does not increase significantly as the treatment time increases.
Figure 3. XRD patterns for Ti6Al4V ELI alloy following PEO treatment in 0.06M Ca-GP+0.3M CA solution at 300V for 180s, before and after heat treatment (HT).

Table 1. Average thickness of the PEO coatings formed on Ti6Al4V ELI alloy in 0.06M Ca-GP+0.3M CA solution.

| PEO condition | 180s–300V | 420s–300V | 180s–400V | 420s–400V |
|---------------|-----------|-----------|-----------|-----------|
| Thickness (µm)| 4.75      | 5.00      | 10.63     | 12.13     |

3.3. Electrochemical behaviour of PEO coatings in SBF
The polarization resistance values of the PEO coatings are presented in Table 2. The coatings obtained at 300V for 180s and heat treated at 1073K showed the highest polarization resistance values. The heat treatment appears to have a significant effect on the polarization resistance. There is an increase of two orders of magnitude relative to the sample without heat treatment. The PEO coatings obtained showed a capacitive behaviour at high frequencies, except for the condition obtained at 180s, 300V and heat treated at 1073K, which presented a resistive behaviour. The Nyquist spectra (Figure 4) shows that the samples without heat treatment and those heat treated at 1073K, except for the 180s at 300V condition, exhibited charge transfer control (represented by a dome) and diffusion control (represented by a straight line). On the other hand, diffusion control predominated in all systems heat treated at 873K.

Table 2. Polarization resistance values of Ti6Al4V ELI alloy following PEO treatment in 0.06M Ca-GP+0.3M CA solution.

| PEO condition | Not HT | HT 873 K | HT 1073 K |
|---------------|--------|----------|-----------|
| (a) 180s–300V | 1.5E+05| 8.3E+04  | 6.7E+07   |
| (b) 420s–300 V| 2.6E+05| 8.3E+05  | 2.2E+05   |
| (c) 180s–400V | 2.5E+05| 4.4E+07  | 3.6E+04   |
| (d) 420s–400V | 2.3E+05| 6.0E+08  | 1.2E+05   |
4. Conclusions

PEO coatings rich in Ca and P were obtained on a Ti6Al4V alloy using a calcium glycerophosphate (Ca-GP) and calcium acetate monohydrate (CA) electrolyte at 300 and 400V. The Ca/P ratio remains greater than one, indicating the formation of stoichiometric or non-stoichiometric hydroxyapatite. The coatings are porous, continuous and thick. The most suitable condition to study bioactivity of the alloy is PEO treatment at 300V for 180s, which also showed high corrosion resistance in a SBF solution. Heat treatment of the coatings results in the formation of calcium phosphates such as HAp, Brushite and Whitlockite.

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