Effect of pulsed electrodeposition time on the characteristics of calcium phosphates coating on TiO₂ nanostructures

E Pájaro-Contreras¹, L C Tamayo-Durán¹, D K Sierra-Herrera¹ and D Y Peña-Ballesteros¹
¹GIC, Universidad Industrial de Santander, Bucaramanga, Colombia
E-mail: kathesihe@gmail.com, dypena@uis.edu.co

Abstract. To improve the biological performance of titanium alloys calcium phosphates (CaP) coatings are applied to the surface. Those coatings were grown by pulsed current electrodeposition on TiO₂ nanostructures, as a material proposed for biomedical implants. This study evaluated the effect of electrodeposition time variation on the morphology and the electrochemical properties of the coating. Several Ti6Al4V-ELI samples were anodized using an electrolyte of NH₄F and NH₄H₂PO₄ obtaining TiO₂ nanotubes and characterizing them by scanning electron microscopy. After that, calcium phosphates were deposited using a solution of Ca(NO₃)₂ and NH₄H₂PO₄ with a pH of 6.5; the coatings were annealed at 550°C per 1h. Finally, the coatings were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction and Electrochemical impedance spectroscopy techniques. The analysis of X-ray diffraction and Fourier transform infrared spectroscopy confirmed the formation of calcium phosphates (Hydroxypatite and β-tricalcium phosphate). The results revealed that the coatings morphology was modified with the electrodeposition time variation. Furthermore, it was observed that an increase in galvanostatic electrodeposition time leads to a higher electrochemical stability of the samples in simulated body fluid.

1. Introduction
Titanium alloys are widely used in the biomaterials field due to its low elastic modulus, exceptional biocompatibility and its corrosion resistance. The presence of titanium dioxide on the Ti6Al4V surface provides higher corrosion resistance. This oxide has 2 – 10nm thickness and it is naturally formed at room temperature in presence of air or water [1]. In order to improve the oxide properties, a new generation of biomaterials has been developed. Hence, the formation of TiO₂ nanotubes on the biomaterials surface has been studied. Furthermore, it has been demonstrated that the surface functionalization improves the response from the biomaterial to the biological medium favoring the apatite crystals precipitation, which is a stable structure that facilitates the osseointegration with the bone [2]. Many different techniques for preparing calcium phosphates have been developed, including sol-gel, deposition by pulsed laser, electrophoretic and electrochemical deposition. Among them, electrodeposition is an alternative technique that has some evident advantages as the process can be carried out at lower temperatures and the thickness and chemical composition are controlled [3]. However, when a high current density is used, hydrogen bubbles are formed in the vicinity of the cathode producing non-uniform and weakly adherent coatings [3,4]. In view of those limitations, pulsed electrodeposition (PED) has been researched as a new method [5]. PED is conducted by applying a current during a period of time where the coating is formed, followed by a relaxation time, without any current applied. This process reduces the emission of hydrogen bubbles allowing the calcium phosphate
coating deposited properly [3]. In this research evaluated the electrodeposition time influence on the morphology and electrochemical properties of coating obtained by pulsed current electrodeposition TiO$_2$ nanostructures.

2. Materials and methods

Ti6Al4V-ELI cylindrical pieces of 14mm of diameter and 3mm of thickness were used as working electrode. The samples were sanded by silicon carbide paper from 280 to 1200 grit. Then, they were ultrasonically cleaned with ethanol for 15 min and etched according to ASTM E407 using a solution of 11% V/V HF, 33% V/V HNO$_3$ y 56% V/V H$_2$O deionized. The formation of nanotubes oxide layer on Ti6Al4V alloy was carried out by anodizing using a solution 1M (NH$_4$H$_2$PO$_4$) and 0.3M (NH$_4$F) as electrolyte and a two-electrode cell using a platinum mesh as counter electrode and Ti6Al4V discs as working electrode applied 20V and 250mA for 60 min at room temperature and magnetic agitation of 300 rpm. The distance between the electrodes was 15cm approximately.

The morphologic characterization of the coatings was obtained by Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) techniques using a JOEL Quanta 650 FEG microscope. Fourier-transform infrared spectroscopy (FTIR) was applied to identify functional groups in the coating samples using the NICOLET iS50 equipment, the spectrum range was from 4000 cm$^{-1}$ to 400 cm$^{-1}$ with a number of 32 scans at the 4 cm$^{-1}$ resolution. The analysis of the crystalline phases was identified by the X-ray diffraction (XRD) using the BRUKER model D8 DISCOVER with Cu Ka radiation generated at 40 kV and 40 mA. Finally, the electrochemical evaluation of the samples was carried out by electrochemical impedance spectroscopy (EIS) technique using the AUTOLAB equipment and three-electrode cell. A graphite bar was used as a counter electrode, Ag/AgCl (KCl 3M) electrode as a reference and the sample as the working electrode. Simulated body fluid (SBF) was used as electrolyte at 37°C. It was applied a sinusoidal signal of 10 mV of amplitude in a frequency range from 100 kHz to 0.01 Hz and stabilization time of 60 min.

3. Results

Figure 1a shows SEM image of the TiO$_2$ nanostructures. The structure obtained present a growth of nanotubes with a diameter of 66 nm approximately and highly ordered. This can be related to the compounds present in the electrolyte, since it has been shown that highly ordered nanotubes are obtained with NH$_4$F, which contributes to the reduction of roughness [6]. Moreover, there are heterogeneities presented in the TiO$_2$ nanotube layer due to the vanadium phase β present in the alloy promoting layers of TiO$_2$ unstable and fragile inhibiting the suitable growth of nanostructures [1,6].

Figures 1(b) and 1(c) show SEM images of the calcium phosphates coatings on TiO$_2$ nanostructures by pulsed electrodeposition. The coating obtained present a total cover of the samples without irregularities. The coatings morphology exhibits small needle-like acicular crystals and aggregates of globular crystals, being the last ones more relevant in the 60 min deposition (Figure 1d and 1e). The needle-like are thinner in the pulsed electrodeposition condition of 30 min with 725 nm thickness approximately, against 850 nm in the 60 min one. That could happen as a result of the higher time of electrodeposition, allowing a higher growth of the deposited crystals.

The molar ratio Ca/P of the coatings were obtained by EDS showing a result of 1.28 and 1.35 for the 30 min and 60 min coatings respectively. Results show that coating can correspond to different calcium phosphate close to this range as octacalcium phosphate, calcium triphosphate (TCP) and calcium deficient hydroxyapatite (CDHA) [7-9], which are reason of interest in the biomedical field.

Figure 2 represents the FTIR spectra of the calcium phosphates coating. The characteristic bands for phosphate group (PO$_4$)$^{3-}$ with the P-O bands appear at 1094 and 1027 cm$^{-1}$ attributed to the asymmetric stretching mode, the bands at 950, 600, 560 and 520 cm$^{-1}$ correspond to the phosphate ion under the symmetric stretching vibration mode. There is another vibration of the P-O band at 1220 cm$^{-1}$, this could be due to the presence of HPO$_4^{2-}$ ion which is usually found in solutions of intermediate basicity. The hydroxyl group is observed with the band of the O-H bond at 632 cm$^{-1}$ [9-12].
Figure 1. SEM morphologies of: (a) TiO$_2$ coating and TiO$_2$ nanostructures by pulsed electrodeposition with a total time of (b) 30 minutes (Mag x500). (c) 60 minutes (Mag x500). (d) 30 minutes (Mag x20000) and (e) 60 minutes (Mag x20000).

Figure 2. FT-IR spectra of coating obtained by pulsed electrodeposition with a total time of (a) 30 min (b) 60 min.
The XRD patterns of the coatings are presented in Figure 3. Qualitative analysis was obtained by comparing the observed profiles with the diffraction profiles reported in the PDF-2 (2014) database of the International Diffraction Data Center (ICDD). The diffractograms obtained show that calcium phosphate coatings are composed of several kinds of phosphates such as hydroxyapatite, tricalcium phosphate ($\alpha$ and $\beta$) and apatite (CaOH). The diffraction peaks are observed at 2$\theta$ values for HA approximately at 25.8°, 32.1°, 40.4° and 53.1° for tricalcium phosphate is evidenced by the peaks at 2$\theta$ = 34.1°, 43.8° and 46.6°, and the presence of apatite is observed with the peaks 2$\theta$ = 28.12° and 49.39°.

EIS was studied to determine the electrochemical characteristics of TiO$_2$ nanostructures and coated samples, and the impedance spectra were fitted with an equivalent circuit using ZPlot software. The Figures 4, 5 and 6 show the results obtained by EIS. The uncoated Ti6Al4V shows a trend with the semicircle shape. This response is related with the metallic titanium resistance. This behavior is represented by a Randles circuit, the system presents a single time constant which indicates a capacitive behavior, where $R_s$ corresponds to the resistance of the electrolyte, $R_1$ is the charge transfer resistance ($R_{tc}$) and $CPE_1$ is the double layer's constant phase element (Figure 6) [6].

The Nyquist diagram of the TiO$_2$ nanotubes sample shows a decrease in $R_p$ with respect to the uncoating Ti6Al4V-ELI sample (Figure 5). This behavior can be attributed to an increase in the electrochemically active surface area related with the heterogeneities in the TiO$_2$ nanotube layer present. Hence, it produced an increase in the current density, promoting a decrease in impedance according to the ratio $Z = V/I$. The Bode-phase diagram confirms these results by showing a shift the graph to the
right related to a decrease in capacitive behavior [13]. The behavior of the TiO₂ samples was modeled by an equivalent circuit with two-time constants. The first constant is related with the nanotube layer faradic behavior, the second to the substrate/nanotube interface. Therefore, R2 represents the resistance of the nanostructure layer and CPE2 its constant phase element [10].

The coated samples showed a decrease in Rp with respect to the sample with TiO₂ nanotubes. This behavior could be explained due to the coating’s porous nature allowing the electrolyte invasion and their solubility in the simulated body fluid. The results obtained from the samples with coating were modeled using equivalent circuit modeling with three-time constants related to the interfaces coating/electrolyte, coating/nanostructures and nanostructures/substrate (Figure 6). R2 and R3 correspond to the nanotube resistance and coating's resistance respectively [10]. Furthermore, the electrodeposited samples for 60min present higher Rp values against the samples of 30min. This could to related to decreasing in the electrochemically active surface area due to the increase in the crystals size of the coating shown in the SEM images (Figure 1(e)) promoting the decrease in the specific surface area.

4. Conclusion
Calcium phosphates coatings with needle-like morphology were obtained varying the time of electrodeposition. Results showed the time influence on the coatings characteristics and the electrochemical properties. The SEM results revealed that the size of the crystals varies with the increase of the time. The presence of TiO₂ nanotubes on the substrate and the increase of the deposition time allowing to the formation of uniform coatings, as shown in the SEM images. The increase of the deposition time medicated the polarization resistance of the samples. The coatings obtained to a higher time in the pulsed electrodeposition present crystals with higher size exhibiting a greater electrochemical stability in simulated body fluid (SBF). That behavior is related to the decrease in the electrochemically active surface area.
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