SEM and EDS studies of porous coatings enriched in calcium and zinc obtained by PEO with ramp voltage

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ABSTRACT

In this work, the SEM and EDS results of porous and enriched in calcium or zinc coatings, which were obtained during 3-minute treatments using Plasma Electrolytic Oxidation (Micro Arc Oxidation) processes on CP Titanium Grade 2 at ramp potentials (linear polarization) from 0 up to 650 V\textsubscript{DC} in electrolytes containing 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O and/or 500 g Zn(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}, are presented. It was found that obtained coatings have pores with different shapes and diameters. The Ca/P and Zn/P ratios by atomic concentration are the same and equal to 0.2, what may suggest hydroxyapatite-like structure (M,Ti)\textsubscript{x} (PO\textsubscript{4})\textsubscript{y}, where M= \{Ca, Zn\}.

\textbf{Keywords:} Plasma Electrolytic Oxidation (PEO), Micro Arc Oxidation (MAO), CP Titanium Grade 2, calcium nitrate Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O, zinc nitrate Zn(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O, ramp voltage, linear polarization
1. INTRODUCTION

Nanometric passive films and micrometric coatings are important aims of activity in the field of surface engineering. Various surface treatment techniques have been employed to enhance the mechanical and tribological properties, the corrosion resistance and the bioactivity. Among the different surface modification techniques, electropolishing, anodic oxidation, especially the plasma electrolytic oxidation (PEO), have become increasingly growing due to their advantages over other methods of surface modification [1-5].

The standard electropolishing (EP) [3-7], magnetoelectropolishing (MEP) [7-19] or high-current density electropolishing (HDEP) [20-23] are used to obtain nano-coatings, while the micro-coatings may be formed during the Plasma Electrolytic Oxidation (PEO), also known as Micro Arc Oxidation [1,2,24-38]. The PEO techniques are used to create porous coatings on biomaterials, such as titanium [24-32] and its alloys [1, 33-38], which may be enriched in chemical elements, such as phosphorus and calcium to form the hydroxyapatite-like structure [39-43], with bactericidal copper [44-54] as well as with magnesium, which may accelerate the healing of wounds [55-56].

The aim of this work is to present fabricating and study of porous coatings enriched in calcium and zinc on CP Titanium Grade 2, obtained by PEO treatment under ramp voltage from 0 up to 650 V\textsubscript{DC}. SEM and EDS studies were used to characterize these coatings.

2. METHOD

The samples of CP Titanium Grade 2 with dimensions 10×10×2 mm were treated by Plasma Electrolytic Oxidation (Micro Arc Oxidation) for the surface studies. The plasma electrolytic oxidation (PEO) was performed at the ramp voltages from 0 up to 650 V\textsubscript{DC} in time of 600 s. For the studies, the electrolytes based on orthophosphoric acid H\textsubscript{3}PO\textsubscript{4} with 500 g/L of calcium nitrate Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O or copper nitrate Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O were used. For each run, the electrolytic cell made of glass was used, containing up to 500 ml of the electrolyte.

Scanning Electron Microscope (SEM) FEI Quanta 650 FEG equipped with Energy-Dispersive X-ray Spectroscopy (EDS) for surface analysis was used. The microscope operated under the following conditions: voltage 15 kV, current 8-10 nA, beam diameter 6 μm, decreased vacuum in the chamber with the pressure of 50 Pa. The identification of spectral lines was performed by means of a spectral decomposition using the holographic peak de-convolution function.

3. RESULTS AND DISCUSSION

In Figures 1-5, the SEM pictures of coating formed on Titanium after PEO treatment at ramp voltages from 0 till 650 V\textsubscript{DC} (linear polarization) in electrolyte containing of 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4} are presented. The obtained surfaces have closed and opened pores, which are visible specifically in Figures 3-5. The EDS spectrum of the obtained coating is displayed in Figure 6. This way recorded the EDS peaks of phosphorus, titanium and calcium show that formed PEO coating is built mainly of phosphorus-titanium-calcium compounds, what may suggest the existence of hydroxyapatite-like structure.
Fig. 1. SEM picture of coating formed on Titanium after PEO treatment at ramp voltages from 0 till 650 V\textsubscript{DC} in electrolyte containing of 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}. Magnification 500 times

Fig. 2. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V\textsubscript{DC} in electrolyte containing of 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}. Magnification 2500 times
Fig. 3. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V$_{DC}$ in electrolyte containing of 500 g Ca(NO$_3$)$_2$·4H$_2$O in 1 L H$_3$PO$_4$. Magnification 2 500 times

Fig. 4. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V$_{DC}$ in electrolyte containing of 500 g Ca(NO$_3$)$_2$·4H$_2$O in 1 L H$_3$PO$_4$. Magnification 5 000 times
Fig. 5. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V_{DC} in electrolyte containing of 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}. Magnification 10 000 times

Fig. 6. EDS result of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V_{DC} in electrolyte containing of 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}. Done by magnification of 500 times
In the PEO coating, apart from titanium (46.5 wt% | 37.1 at%), which comes from substrate, of which the signal partly comes from the matrix, phosphorus (42.3 wt% | 52.2 at%) and calcium (11.2 wt% | 10.7 at%) were also recorded, with the results presented in Table 1. In case of surface characterization, the Ca/P ratio equaling to 0.26 (by wt%) | 0.20 (by at%) was found.

In Figures 7-11, the SEM pictures of coating formed on Titanium after PEO treatment at ramp voltages from 0 till 650 V\textsubscript{DC} (linear polarization) in electrolyte containing of 500 g Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4} are presented. The obtained surface is similar to that one obtained in electrolyte containing Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O, however the shapes and diameters of pores are different, what is shown in Figures 9-11. The EDS spectrum of obtained coating is displayed in Figure 12.

This way recorded the EDS peaks of phosphorus, titanium and zinc show that formed PEO coating is built mainly of phosphorus-titanium-zinc compounds, in which apart from titanium (47.8 wt% | 41.4 at%), which comes from the substrate, phosphorus (36.3 wt% | 48.5 at%) and zinc (15.9 wt% | 10.1 at%) were also recorded, and they are presented in Table 1. In case of surface characterization, the Zn/P ratio equaling to 0.43 (by wt%) | 0.20 (by at%) was found.

**Fig. 7.** SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V\textsubscript{DC} in electrolyte containing of 500 g Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}. Magnification 500 times
Fig. 8. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V_{DC} in electrolyte containing of 500 g Zn(NO_3)_2\cdot6H_2O in 1 L H_3PO_4. Magnification 1 000 times

Fig. 9. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V_{DC} in electrolyte containing of 500 g Zn(NO_3)_2\cdot6H_2O in 1 L H_3PO_4. Magnification 2 500 times
Fig. 10. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V<sub>DC</sub> in electrolyte containing of 500 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 1 L H<sub>3</sub>PO<sub>4</sub>. Magnification 5 000 times

Fig. 11. SEM picture of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V<sub>DC</sub> in electrolyte containing of 500 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 1 L H<sub>3</sub>PO<sub>4</sub>. Magnification 10 000 times
Fig. 12. EDS result of coating formed on Titanium after PEO treatment at voltages from 0 till 650 V_{DC} in electrolyte containing of 500 g Zn(NO_3)_2∙6H_2O in 1 L H_3PO_4. Done by magnification 500 times.

Table 1. EDS results of coating formed on Titanium after PEO treatment at ramp voltages from 0 up to 650 V_{DC} in electrolyte containing 500 g Ca(NO_3)_2∙4H_2O and/or 500 g Zn(NO_3)_2∙6H_2O in 1 L H_3PO_4.

<table>
<thead>
<tr>
<th>Ca(NO_3)_2∙4H_2O</th>
<th>Zn(NO_3)_2∙6H_2O</th>
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<tr>
<td><strong>Element</strong></td>
<td><strong>Weight %</strong></td>
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<tr>
<td>Ca/P</td>
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4. CONCLUSIONS

The investigation carried out using SEM and EDS measurements on CP Titanium Grade 2 after PEO processing allowed to formulate the following conclusions:
it is possible to obtain the porous surface enriched in calcium and phosphorus in electrolyte containing 500 g Ca(NO$_3$)$_2$·4H$_2$O in 1 L H$_3$PO$_4$ by applying a linear polarization (ramp voltage) from 0 till 650 V$_{DC}$

it is possible to obtain the porous surface enriched in zinc and phosphorus in electrolyte containing 500 g Zn(NO$_3$)$_2$·6H$_2$O in 1 L H$_3$PO$_4$ by applying a linear polarization (ramp voltage) from 0 till 650 V$_{DC}$

obtained coatings have pores with different shapes and diameters

the Ca/P and Zn/P ratios by atomic concentration are the same and equal to 0.2, which may suggest hydroxyapatite-like structure (M,Ti)$_x$(PO$_4$)$_y$, where M = {Ca, Zn}.

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