SEM and EDS analysis of enriched in phosphorus and copper coatings fabricated by AC-PEO treatment

Krzysztof Rokosz\textsuperscript{a}, Tadeusz Hryniewicz\textsuperscript{b}, Kornel Pietrzak\textsuperscript{c}, Łukasz Dudek\textsuperscript{d}

Division of BioEngineering and Surface Electrochemistry, Department of Engineering and Informatics Systems, Faculty of Mechanical Engineering, Koszalin University of Technology, Racławicka 15-17, PL 75-620 Koszalin, Poland

\textsuperscript{a-d}E-mail address: rokosz@tu.koszalin.pl, Tadeusz.Hryniewicz@tu.koszalin.pl, kornel.pietrzak@s.tu.koszalin.pl, lukasz.dudek@tu.koszalin.pl

ABSTRACT

In the present paper, SEM and EDS studies of coatings obtained on CP Titanium Grade 2 under sinusoidal alternating voltage (AC) with frequency 50 Hz in Plasma Electrolytic Oxidation (PEO) process at voltages of 200 \textit{V}_{pp}, 250 \textit{V}_{pp} and 300 \textit{V}_{pp} during 3-minute treatments, are displayed. Based on SEM micrographs it may be stated that the porous surfaces, which are needed for biomedical and catalysis application, are obtained only for samples fabricated at 200 \textit{V}_{pp}. It was found out that thickest and most morphologically developed surfaces were obtained at 200 \textit{V}_{pp}, too. The surfaces obtained at 250 \textit{V}_{pp} and 300 \textit{V}_{pp} are cracked and had low concentration of copper, i.e. 0.9 at\% and 1.1 at\%, respectively, while that one obtained at 200 \textit{V}_{pp} was porous and had 8.6 at\% copper.

Keywords: Plasma Electrolytic Oxidation (PEO), Micro Arc Oxidation (MAO), CP Titanium Grade 2, copper nitrate Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O

1. INTRODUCTION

Metal surface treatments by electrochemical processing have been steadily developed since many decades. Standard electropolishing (EP) [1-5], considered as a surface finishing
performed on a plateau current density level has been recently modified by extending the treatment conditions to the high-current-density electropolishing (HCEP) [6-8] or high-voltage electropolishing (HVEP) [9], with the improved results concerning nano-films or nano-coatings. Another electrochemical surface technique acquires a magnetic field [10] with the process named magnetoelectropolishing (MEP) [10-24] in which, apart from improving surface finishing [13-25], nanohardness [12], corrosion resistance [13-16, 70, 71], biological response [26], and fundamental about 90-percent de-hydrogenation is obtained [27, 28].

On the other hand, Plasma Electrolytic Oxidation (PEO) [29] also known as Micro Arc Oxidation (MAO) has been developed to form micro-coatings on metals and alloys [30-66]. These coatings are usually porous and may be enriched with chemical elements, such as phosphorus and calcium to form the hydroxyapatite-like structure [40-48]. Moreover, another elements, such as bactericidal copper [49-58], magnesium, which may accelerate the healing of wounds [43, 60, 61] as well as zinc with antibacterial properties [42, 62-65], capable for improving osteogenic characteristics and bone regenerating capacity [66-69], may be introduced into the porous coatings.

The aim of this work is to characterize coatings obtained during AC-PEO process on CP Titanium Grade 2 obtained during Plasma Oxidation Process enriched with antibacterial copper analyzed by SEM and EDS techniques.

2. METHOD

The CP Titanium Grade 2 samples with dimensions of 10 mm × 10 mm × 2 mm by plasma electrolytic oxidation (PEO) process were treated. The process was performed at voltages of 200 Vpp, 250 Vpp and 300 Vpp by using 50 Hz AC power transformer. The electrolyte composition was the following: 1 L of 85% H₃PO₄ with 500 g Cu(NO₃)₂·3H₂O. For each run, the electrolytic cell made of glass was used, containing up to 500 ml of the electrolyte.

For studies, the scanning electron microscope Quanta 250 FEI with Low Vacuum and Environmental Scanning Electron Microscope (ESEM) mode and a field emission cathode as well as the Energy-Dispersive X-ray Spectroscopy (EDS) system in a Noran System Six with nitrogen-free silicon drift detector, were employed.

3. RESULTS AND DISCUSSION

In Figures 1, 2 and 3, the SEM images of coating formed on CP Titanium Grade 2 after PEO process at 200 Vpp in the electrolyte containing of 500 g Cu(NO₃)₂·3H₂O in 1 L H₃PO₄, are presented. It can be observed that irregular surface with well-developed porous morphology was obtained. In Table 1, results of EDS measurements are presented. The EDS data show the presence of copper (8.6 at%), phosphorus (48.8 at%) and titanium (42.6 at %) which signal comes partly from metallic matrix. Based on these results, copper-to-phosphorus ratio Cu/P was calculated and equal 0.18.
Fig. 1. SEM pictures with magnification 1000 times of coating formed on Titanium after PEO treatment for 3 min at 200 V\text{pp} in electrolyte containing of 500 g Cu(NO$_3$)$_2$·3H$_2$O in 1 L H$_3$PO$_4$.

Fig. 2. SEM pictures with magnification 5000 times of coating formed on Titanium after PEO treatment for 3 min at 200 V\text{pp} in electrolyte containing of 500 g Cu(NO$_3$)$_2$·3H$_2$O in 1 L H$_3$PO$_4$. 
**Fig. 3.** SEM pictures with magnification 10000 times of coating formed on Titanium after PEO treatment for 3 min at 200 V\textsubscript{pp} in electrolyte containing of 500 g Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}

**Table 1.** EDS results of coatings formed on Titanium after PEO treatment for 3 min at 200 V\textsubscript{pp} in electrolyte containing of 500 g Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}

<table>
<thead>
<tr>
<th>Atomic concentration [%]</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>P</td>
</tr>
<tr>
<td>8.6</td>
<td>48.8</td>
</tr>
</tbody>
</table>

In **Figures 4-6**, the SEM images of coating formed on CP Titanium Grade 2 after PEO process at 250 V\textsubscript{pp} in the electrolyte containing of 500 g Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O in 1 L H\textsubscript{3}PO\textsubscript{4}, are presented. The obtained surfaces are generally non-porous, displaying island-like structure with visible cracks. In **Table 2**, results of EDS measurements are presented. The EDS data show the presence of copper (1.1 at%), phosphorus (7.1 at%) and titanium (91.8 at %) which signal comes partly from the metallic matrix. Based on these results, copper-to-phosphorus ratio Cu/P was calculated and equal 0.15.
Fig. 4. SEM pictures with magnification 1000 times of coating formed on Titanium after PEO treatment for 3 min at 250 V_{pp} in electrolyte containing of 500 g Cu(NO_3)_2\cdot3H_2O in 1 L H_3PO_4.

Fig. 5. SEM pictures with magnification 5000 times of coating formed on Titanium after PEO treatment for 3 min at 250 V_{pp} in electrolyte containing of 500 g Cu(NO_3)_2\cdot3H_2O in 1 L H_3PO_4.
Fig. 6. SEM pictures with magnification 10000 times of coating formed on Titanium after PEO treatment for 3 min at 250 $V_{pp}$ in electrolyte containing of 500 g Cu(NO$_3$)$_2$•3H$_2$O in 1 L H$_3$PO$_4$

Table 3. EDS results of coatings formed on Titanium after PEO treatment for 3 min at 250 $V_{pp}$ in electrolyte containing of 500 g Cu(NO$_3$)$_2$•3H$_2$O in 1 L H$_3$PO$_4$

<table>
<thead>
<tr>
<th>Atomic concentration [%]</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.1</td>
</tr>
<tr>
<td>P</td>
<td>7.1</td>
</tr>
<tr>
<td>Ti</td>
<td>91.8</td>
</tr>
<tr>
<td>Cu/P</td>
<td>0.15</td>
</tr>
</tbody>
</table>

In Figures 7-9, the SEM images of coating formed on CP Titanium Grade 2 after PEO process at 300 $V_{pp}$ in the electrolyte containing of 500 g Cu(NO$_3$)$_2$•3H$_2$O in 1 L H$_3$PO$_4$, are displayed. The obtained surfaces are generally non-porous, of island-like structures with visible cracks. In Table 3, results of EDS measurements are presented. The EDS data show the presence of copper (0.9 at%), phosphorus (12.9 at%) and titanium (86.2 at%) which signal comes partly from the metallic matrix. Based on these results, copper-to-phosphorus ratio Cu/P was calculated and equal 0.07.
Fig. 7. SEM pictures with magnification 1000 times of coating formed on Titanium after PEO treatment for 3 min at 300 V_{pp} in electrolyte containing of 500 g Cu(NO_3)_2\cdot3H_2O in 1 L H_3PO_4

Fig. 8. SEM pictures with magnification 5000 times of coating formed on Titanium after PEO treatment for 3 min at 300 V_{pp} in electrolyte containing of 500 g Cu(NO_3)_2\cdot3H_2O in 1 L H_3PO_4
Fig. 9. SEM pictures with magnification 10000 times of coating formed on Titanium after PEO treatment for 3 min at 300 V$_{pp}$ in electrolyte containing of 500 g Cu(NO$_3$)$_2$·3H$_2$O in 1 L H$_3$PO$_4$

Table 3. EDS results for coatings formed on Titanium after PEO treatment for 3 min at 300 V$_{pp}$ in electrolyte containing of 500 g Cu(NO$_3$)$_2$·3H$_2$O in 1 L H$_3$PO$_4$

<table>
<thead>
<tr>
<th>Atomic concentration [%]</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.9</td>
</tr>
<tr>
<td>P</td>
<td>12.9</td>
</tr>
<tr>
<td>Ti</td>
<td>86.2</td>
</tr>
<tr>
<td>Cu/P</td>
<td>0.07</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The studies carried out on porous coatings on titanium, fabricated by AC-PEO treatment allowed to formulate the following conclusions:

- It is possible to obtain coatings on titanium with the use of AC-PEO method
- The applied voltage higher than 200 V$_{pp}$ may result in island-like and cracked surfaces.
- The coatings obtained at 200 V$_{pp}$ contain more copper (8.6 at%) than coatings obtained at 250 V$_{pp}$ (1.1 at%) and 300 V$_{pp}$ (0.9 at%).
Acknowledgements

This work was supported by subsidizing by Grant OPUS 11 of National Science Centre, Poland, with registration number 2016/21/B/ST8/01952, titled "Development of models of new porous coatings obtained on titanium by Plasma Electrolytic Oxidation in electrolytes containing phosphoric acid with addition of calcium, magnesium, copper and zinc nitrates". Prof. Winfried Malorny from Hochschule Wismar-University of Applied Sciences Technology, Business and Design, Faculty of Engineering, DE 23966 Wismar, Germany, is given thanks for providing access to the SEM/EDS apparatus allowing to perform the studies.

References


[14] Rokosz K., Electrochemical Polishing in magnetic field (Polerowanie elektrochemiczne w polu magnetycznym), Koszalin University of Technology Publishing House (in Polish), 2012


[51] Rokosz K., Hryniewicz T., Dudek Ł., Matýsek D., Valiček J., and Harničárová M., SEM and EDS Analysis of Surface Layer Formed on Titanium After Plasma Electrolytic Oxidation in H 3 PO 4 with the Addition of Cu(NO₃)₂, *Journal of Nanoscience and Nanotechnology*, 16(8) (2016) 7814-7817


