Synthesis and characterisation of porous, calcium enriched coatings formed on Titanium via Plasma Electrolytic Oxidation

Krzysztof Rokosz\textsuperscript{1a}, Tadeusz Hryniewicz\textsuperscript{1b}, Kornel Pietrzak\textsuperscript{1c}

\textsuperscript{1}Division of Bioengineering and Surface Electrochemistry, Department of Engineering and Informatics Systems, Faculty of Mechanical Engineering, Koszalin University of Technology, Raclawicka 15-17, PL 75-620 Koszalin, Poland

\textsuperscript{a}rokosz@tu.koszalin.pl, \textsuperscript{b}Tadeusz.Hryniewicz@tu.koszalin.pl, \textsuperscript{c}kornel.pietrzak@s.tu.koszalin.pl

*Corresponding Author: Tadeusz.Hryniewicz@tu.koszalin.pl

ABSTRACT

The SEM and EDS study results of porous and calcium enriched coatings obtained via Plasma Electrolytic Oxidation (Micro Arc Oxidation) on the Commercial Purity Titanium Grade 2 samples, at three potentials 450 V\textsubscript{DC}, 550 V\textsubscript{DC}, 650 V\textsubscript{DC} in electrolytes containing 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 1000 mL H\textsubscript{3}PO\textsubscript{4}, are presented in the paper. In the same electrolyte three Titanium samples, one after other, were treated, with the PEO processing time equaling 3 minutes after each immersion. Based on SEM and EDS results, it was possible to state that all obtained coatings are porous and their calcium-to-phosphorus (Ca/P) ratio decreases with decreasing PEO voltage. In addition, it was found out that electrolyte aging results in decreasing Ca/P ratio, too.

Keywords: Plasma Electrolytic Oxidation (PEO), Micro Arc Oxidation (MAO), CP Titanium Grade 2, calcium nitrate tetrahydrate Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O, 85% orthophosphoric acid H\textsubscript{3}PO\textsubscript{4} (98 g/mole)
1. INTRODUCTION

Nanolayers on metals and alloys may be obtained by standard electropolishing (EP) [1-10], magnetoelectropolishing (MEP) [7-22] or high-current density electropolishing (HDEP) [23-25]. The micro-coatings may be fabricated electrochemically by the Plasma Electrolytic Oxidation (Micro Arc Oxidation) [26-51]. The titanium [26-34, 47-51] and its alloys [35-41, 45] may be enriched on their surface in chemical elements, such as phosphorus and calcium [26-28, 42-46], phosphorus and copper [47-49], calcium and zinc [50], magnesium and copper [51], and phosphorus and zinc [52].

The aim of this paper is to present the fabrication method, and characterization of porous, calcium enriched PEO coatings on CP Titanium Grade 2. Scanning Electron Microscopy (SEM) and EDS spectra were used for the studies. The effect of electrolyte aging has been investigated. Specifically, the calcium-to-phosphorus Ca/P ratios obtained after consecutive immersions of Ti samples in the same electrolyte are determined.

2. METHOD

The Commercially Pure Titanium Grade 2 samples with dimensions $10 \times 10 \times 2$ mm were treated by Plasma Electrolytic Oxidation (PEO), also known as Micro Arc Oxidation (MOA). The PEO processes were performed at three potentials, i.e. 450 V$_{DC}$, 550 V$_{DC}$, 650 V$_{DC}$. In addition, in the same electrolyte three samples, one after another, were treated. For the studies, the electrolyte based on 1000 mL concentrated 85% analytically pure orthophosphoric acid H$_3$PO$_4$ (98 g/mole) with 500 g/L of calcium nitrate tetrahydrate Ca(NO$_3$)$_2$$\cdot$4H$_2$O in it, was used. For each run, the electrolytic cell made of glass was used, containing up to 500 ml of the electrolyte. The PEO processing time after each immersion was equal to 3 minutes.

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 $\mu$m, 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 deconvolution function.

3. RESULTS AND DISCUSSION

In Figure 1, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 450 V$_{DC}$ as the first immersion in electrolyte containing of 500 g Ca(NO$_3$)$_2$$\cdot$4H$_2$O in 1 L H$_3$PO$_4$, are presented. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (44.6 wt% | 35.2 at%), which is a substrate, and which signal may partly come from matrix, phosphorus (45.4 wt% | 55.4 at%) and calcium (10.0 wt% | 9.4 at%) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal 0.22 (by weight per cent concentration) and 0.17 (by atomic concentration).
Voltage: 450 V<sub>DC</sub>; Electrolyte: 500 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in 1000 mL H<sub>3</sub>PO<sub>4</sub>; first sample

Fig. 1. SEM pictures (a–c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 450 V in electrolyte consisting of 500 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O dissolved in 1000 mL H<sub>3</sub>PO<sub>4</sub>. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×

In Figure 2, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 450 V<sub>DC</sub> as the second one in the same electrolyte containing of 500 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in 1 L H<sub>3</sub>PO<sub>4</sub>, are presented. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (49.9 wt% | 40.2 at%), which is a substrate, and which signal may partly come from matrix, phosphorus (41.2 wt% | 51.3 at%) and calcium (8.9 wt% | 8.5 at%) were also recorded. In addition, the
calcium-to-phosphorus Ca/P ratios were found to be equal 0.22 (by weight per cent concentration) and 0.17 (by atomic concentration).

Voltage: 450 V\textsubscript{DC}; Electrolyte: 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O in 1000 mL H\textsubscript{3}PO\textsubscript{4}; second sample

**Fig. 2.** SEM pictures (a-c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 450 V in electrolyte consisting of 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O dissolved in 1000 mL H\textsubscript{3}PO\textsubscript{4}. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×

In **Figure 3**, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 450 V\textsubscript{DC} as the third immersion in the same 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}, are presented. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (45.2 wt% | 35.8
at\textsuperscript{\%}), which is a substrate, and which signal may partly come from matrix, phosphorus (44.7 wt\% | 54.7 \textsuperscript{at\%}) and calcium (10.1 wt\% | 9.5 \textsuperscript{at\%}) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal to 0.22 (by weight per cent concentration) and 0.17 (by atomic concentration).

**Voltage:** 450 V\textsubscript{DC}; **Electrolyte:** 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O in 1000 mL H\textsubscript{3}PO\textsubscript{4}; third sample

![SEM pictures](https://example.com/sem_pictures.png)

**Fig. 3.** SEM pictures (a-c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 450 V in electrolyte consisting of 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O dissolved in 1000 mL H\textsubscript{3}PO\textsubscript{4}. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×

In **Figure 4**, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 550 V\textsubscript{DC} as the first immersion in the same 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}, are presented. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (49.2 wt% | 39.7 at%), which is a substrate, and which signal may partly come from matrix, phosphorus (40.3 wt% | 50.2 at%) and calcium (10.5 wt% | 10.1 at%) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal to 0.26 (by weight per cent concentration) and 0.20 (by atomic concentration).

**Voltage: 550 V<sub>DC</sub>; Electrolyte: 500 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in 1000 mL H<sub>3</sub>PO<sub>4</sub>; first sample**

![SEM pictures (a-c) and EDS spectrum (d)](image)

**Fig. 4.** SEM pictures (a-c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 550 V in electrolyte consisting of 500 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O dissolved in 1000 mL H<sub>3</sub>PO<sub>4</sub>. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×
In Figure 5, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 550 V$_{DC}$ as the second one in the same electrolyte containing of 500 g Ca(NO$_3$)$_2$·4H$_2$O in 1 L H$_3$PO$_4$, are presented. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (46.8 wt% | 37.3 at%), which is a substrate, and which signal may partly come from matrix, phosphorus (43.3 wt% | 53.3 at%) and calcium (9.9 wt% | 9.4 at%) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal to 0.23 (by weight per cent concentration) and 0.18 (by atomic concentration).

**Voltage: 550 V$_{DC}$; Electrolyte: 500 g Ca(NO$_3$)$_2$·4H$_2$O in 1000 mL H$_3$PO$_4$; second sample**

![SEM pictures (a-c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 550 V in electrolyte consisting of 500 g Ca(NO$_3$)$_2$·4H$_2$O dissolved in 1000 mL H$_3$PO$_4$. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×.](image)

-35-
In Figure 6, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 550 V$_{DC}$ as the third immersion in the same electrolyte containing of 500 g Ca(NO$_3$)$_2$·4H$_2$O in 1 L H$_3$PO$_4$, are presented. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (51.5 wt% | 41.7 at%), which is a substrate, and which signal may partly come from matrix, phosphorus (39.6 wt% | 49.6 at%) and calcium (8.9 wt% | 8.7 at%) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal to 0.23 (by weight per cent concentration) and 0.17 (by atomic concentration).

**Voltage: 550 V$_{DC}$; Electrolyte: 500 g Ca(NO$_3$)$_2$·4H$_2$O in 1000 mL H$_3$PO$_4$; third sample**

![SEM pictures and EDS spectrum](image)

**Fig. 6.** SEM pictures (a-c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 550 V in electrolyte consisting of 500 g Ca(NO$_3$)$_2$·4H$_2$O dissolved in 1000 mL H$_3$PO$_4$. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×
In Figure 7, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 650 V\textsubscript{DC} as the first immersion in the same 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}, are presented. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (51.7 wt% | 42.1 at%), which is a substrate, and which signal may partly come from matrix, phosphorus (37.8 wt% | 47.6 at%) and calcium (10.5 wt% | 10.3 at%) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal to 0.28 (by weight per cent concentration) and 0.22 (by atomic concentration).

**Fig. 7.** SEM pictures (a–c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 650 V in electrolyte consisting of 500 g Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O dissolved in 1000 mL H\textsubscript{3}PO\textsubscript{4}. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×
In Figure 8, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 650 V\textsubscript{DC} as the second one in the same 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. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (51.0 wt\% | 41.3 at\%), which is a substrate, and which signal may partly come from matrix, phosphorus (38.9 wt\% | 48.8 at\%) and calcium (10.1 wt\% | 9.9 at\%) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal to 0.26 (by weight per cent concentration) and 0.20 (by atomic concentration).

![Voltage: 650 V\textsubscript{DC}; Electrolyte: 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 1000 mL H\textsubscript{3}PO\textsubscript{4}; second sample](image)

**Fig. 8.** SEM pictures (a-c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 650 V in electrolyte consisting of 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O dissolved in 1000 mL H\textsubscript{3}PO\textsubscript{4}. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×
In Figure 9, the SEM pictures and EDS spectrum of porous coating formed on Titanium after PEO treatment at voltage of 650 V\textsubscript{DC} as the third immersion in the same 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. These 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 inter alia hydroxyapatite-like structure. In the PEO coating, apart from the titanium (50.7 wt% | 41.1 at%), which is a substrate, and which signal may partly come from matrix, phosphorus (39.2 wt% | 49.2 at%) and calcium (10.1 wt% | 9.7 at%) were also recorded. In addition, the calcium-to-phosphorus Ca/P ratios were found to be equal to 0.26 (by weight per cent concentration) and 0.20 (by atomic concentration).

**Voltage: 650 V\textsubscript{DC}; Electrolyte: 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 1000 mL H\textsubscript{3}PO\textsubscript{4}; third sample**

![SEM pictures](image)

**Fig. 9.** SEM pictures (a-c) and EDS spectrum (d) of porous coating formed on CP Titanium Grade 2 after PEO treatment at voltage of 650 V in electrolyte consisting of 500 g Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O dissolved in 1000 mL H\textsubscript{3}PO\textsubscript{4}. Magnifications: (a) 1000×, (b) 2500×, (c) 10000×
Setting-up of the Ca/P ratio results, calculated as of atomic per cent concentration, after PEO treatments performed under three voltages, 450 V\textsubscript{DC}, 550 V\textsubscript{DC}, 650 V\textsubscript{DC}, are given in Fig. 10. In the picture, results of Titanium PEO treatments after three consecutive immersions in the same electrolyte are displayed. One can easily see that there is no difference in Ca/P ratio after 450 V\textsubscript{DC} voltage, a proportional decrease is observed after 550 V\textsubscript{DC}, and a sharp decrease after 650 V\textsubscript{DC}, between the first and consecutive immersions noticed in the same electrolyte.

Fig. 10. Juxtaposition of Ca/P ratio results (as of at\%) after PEO treatments under three voltages: 450 V\textsubscript{DC}, 550 V\textsubscript{DC}, 650 V\textsubscript{DC}, and subsequent Ti sample immersion (1\textsuperscript{st}, 2\textsuperscript{nd}, 3\textsuperscript{rd}) in the same electrolyte

4. CONCLUSIONS

The experiments carried out on CP Titanium Grade 2 by using Plasma Electrolytic Oxidation (PEO) allowed to formulate the following conclusions:

- it is possible to obtain porous PEO coatings enriched in calcium, in electrolyte containing nitrate tetrahydrate Ca(NO\textsubscript{3})\textsubscript{2}\cdot4H\textsubscript{2}O dissolved in concentrated 85\% analytically pure orthophosphoric acid H\textsubscript{3}PO\textsubscript{4} (98 g/mole) at voltages 450 V\textsubscript{DC}, 550 V\textsubscript{DC}, 650 V\textsubscript{DC}

- the highest Ca/P ratio was found out after PEO treatment at 650V\textsubscript{DC}

- the smaller PEO voltage, the smaller Ca/P ratio by atomic concentration was found

- the more aged PEO electrolyte was used, the smaller Ca/P ratio by atomic concentration was obtained.
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".

Assoc. Prof. Jan Valíček and Dr Dalibor Matýsek from Vysoká škola báňská - Technická univerzita Ostrava - VŠB-TUO, Czech Republic, are given thanks for providing access to the SEM/EDS apparatus allowing to perform the studies.

References


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


[52] Rokosz K., Hryniewicz T., Pietrzak K., Dudek Ł., Malorny W., SEM and EDS characterization of porous coatings obtained on Titanium by Plasma Electrolytic Oxidation in electrolyte containing concentrated phosphoric acid with zinc nitrate, *Advances in Materials Science*, 17(2)/52 (2017) 41-54

(Received 19 July 2017; accepted 11 August 2017)