

# Fabrication and Characterisation of Porous Coatings Enriched with Copper on CP Titanium Grade 2 under Plasma Electrolytic Oxidation

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**Abstract:** In the present paper, coatings obtained on CP Titanium Grade 2 samples by Plasma Electrolytic Oxidation (PEO) in electrolyte containing concentrated phosphoric acid  $H_3PO_4$  with copper nitrate  $Cu(NO_3)_2 \cdot 3H_2O$ , are studied with Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Photoelectron Spectroscopy (XPS) and Glow Discharge Optical Emission Spectroscopy (GDOES). A three-layer model is proposed on the basis of GDOES depth profile signals and their first and second derivatives. It was found that the time of Plasma Electrolytic Oxidation process has an influence on the chemical composition and the thickness of the obtained porous coatings. The longer time the PEO treatment is applied, the thinner porous coatings are obtained and the lowest amounts of copper, phosphorus and oxygen inside them are found. The proposed model of PEO coatings consists of three layers, i.e. the top one "A", having a thickness corresponding to the sputtering time in GDOES of about 100 s; the operating conditions applied provide very porous and contaminated by organic substances layer down to about 50 s by sputtering time; the semi-porous sub-layer named "B" has a thickness that depends on the PEO treatment time. The sub-layer "B" of PEO coating is the thickest after one-minute PEO treatment and it decreases with increasing the treatment time. The PEO coating thickness also decreases after each successive PEO processing. The last layer (from the top surface), is the transition sub-layer named "C", and it has a thickness corresponding to a sputtering time equaling 450 s.

**Keywords:** copper(II) nitrate(V) trihydrate; GDOES depth profiles and derivatives; Plasma Electrolytic Oxidation (PEO); SEM/EDS; three-layer model; titanium

## 1 INTRODUCTION

Contemporary surface technology is frequently realized under electrochemical processing, effective with oxide layers of nanometric thickness or porous compounded layers of micrometric thickness. In view of obtaining nano-layers, the standard electrochemical polishing (EP) method [1-5], electropolishing in magnetic field (MEP) [6-12] or high-current density electropolishing (HDEP) [14, 15], or High-Voltage Electropolishing (HVEP) [16], are used. Micro-layers with micro- and nanopores may be obtained by Plasma Electrolytic Oxidation (PEO), which is also described in literature as Micro Arc Oxidation (MAO) on metals, e.g. titanium [17-19], niobium [20], tantalum [21, 22], zirconium [23], and alloys, such as Ti6Al4V [24], NiTi [25], and TNZ (Ti-Nb-Zr) [26], Ti-Nb-Zr-Sn [27], Ti-3Zr-2Sn-3Mo-25Nb [28]. In the present work, results of porous PEO coatings enriched with bactericidal copper [29], similar to those ones presented in references [30-32], obtained on titanium, treated by PEO in electrolyte containing  $H_3PO_4$  with  $Cu(NO_3)_2$ , are displayed. The previous works of the Authors [25, 30, 31] with XPS results have shown clearly that in top layer of 10 nm of the PEO coating, titanium is on the fourth stage of oxidation ( $Ti^{4+}$ ) while copper is on the first and second stages of oxidation ( $Cu^+$  and  $Cu^{2+}$ ). The detected phosphorus and oxygen indicated that the obtained structure of the coating is dominated by phosphates of titanium and copper. The present work is to answer the question whether the processing time affects the composition and thickness of the PEO coating obtained on titanium. Therefore, the main issue of the presented results is to show the dependence of the thickness and composition of the porous coatings with reference to the treatment time and aging of electrolyte used. The surface characterizations of the porous coatings obtained by PEO treatment were mainly performed by SEM with EDS and by GDOES. These two techniques are also used in the present paper to describe the chemical composition of these coatings.

## 2 METHODS

CP Titanium Grade 2 samples under Plasma Electrolytic Oxidation (PEO)/Micro Arc Oxidation (MAO) were treated for the study. They were in the form of rectangular specimens of size  $30 \times 10$  mm cut off from a metal sheet 2 mm thick. In order to maintain normalized starting conditions of the specimens, surface samples were ground by abrasive mechanical treatment using 240 grit size.

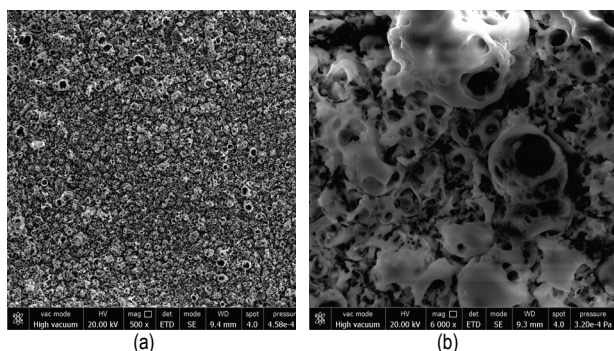
The PEO during the preliminary studies was performed at the average voltage of  $450 \pm 46$  V with pulsation at frequency of 300 Hz during 3 minutes of treatment by using the three-phase transformer with six diodes of Greatz Bridge as well as at 450 V<sub>DC</sub> voltage without any pulsation with the use of commercial PWR 1600H, Multi Range DC Power Supply 1600W, 0-650 V/0-8A.

The electrolyte was composed of orthophosphoric acid  $H_3PO_4$  (85% w/w) and copper (II) nitrate (V) trihydrate  $Cu(NO_3)_2 \cdot 3H_2O$ . During the preliminary studies (experiments performed on homemade power supply with three phase transformer and Greatz Bridge) for each run, the electrolyte volume was equal to 0.25 L, while for main research, which was done by using the commercial power supply, in the cell containing 0.5 L volume of electrolyte. The SEM, EDS, XPS, GDOES, and roughness measurement instruments with operating conditions were described in our previous papers [26, 27]. Characterization of porous surfaces was done with/using non-contact methods [33, 34]. According to the EN ISO 4287:1999 (Geometrical product specifications (GPS)—surface texture: profile method—terms, definitions and surface texture parameters) and DIN 4768 (Determination of values of surface roughness parameters  $R_a$ ,  $R_z$ ,  $R_{max}$  using electrical contact (stylus) instruments; concepts and measuring conditions) standards, the following roughness parameters have been measured: arithmetic average of the absolute values of the profile heights over the evaluation length/roughness average ( $R_a$ ), average peak-to-valley

height when there are five sampling lengths ( $Rz^{DIN}$ ), ten-point height of irregularities ( $Rz^{ISO}$ ), root mean square average of the profile heights ( $Rq$ ), maximum height of the profile/vertical distance between the highest and the lowest points of the profile ( $Rt$ ), mean spacing of the profile irregularities ( $RSm$ ), the ratio of the developed profile length to the evaluation length ( $l_0$ ) and profile peak density ( $D$ ).

### 3 RESULTS AND DISCUSSION

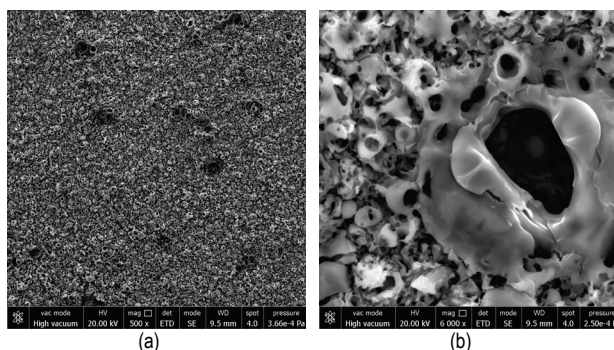
In Fig. 1 and Tab. 1, the SEM pictures (Fig. 1) and EDS spectrum analysis (Table 1) of porous coating formed on titanium after PEO process at voltage of 450 V after 1 minute in 600 g (preliminary studies) and 500 g (main studies) of copper nitrate  $Cu(NO_3)_2 \cdot 3H_2O$  in 1 L  $H_3PO_4$  electrolyte, with 500 $\times$  and 6000 $\times$  magnifications, are presented. The obtained surface is porous with a copper-to-phosphorus ratio (Cu/P) equaling 0.26 by weight concentration and 0.12 by atomic concentration, as shown in Fig. 2. The pores are partly opened on the top of the PEO coating and closed inside the obtained coating.



**Figure 1** SEM images of coating formed on Titanium after PEO process at voltage of 450 V after 1 min in 600 g/L of  $Cu(NO_3)_2 \cdot 3H_2O$  in  $H_3PO_4$  electrolyte. Magnifications: 500 $\times$  (a) and 5000 $\times$  (b)

**Table 1** Quantitative results of weight and atomic concentrations of selected elements and Cu/P ratio based on the EDS of surface presented in Fig. 1

Elementlines	wt%	at%
P K	36.9	48.5
Ti K	53.6	45.5
Cu K	9.5	6.0
Cu/P	<b>0.26</b>	<b>0.12</b>



**Figure 2** SEM images of coating formed on titanium after PEO process at voltage of 450 V after 3 min; in 600 g/L of  $Cu(NO_3)_2 \cdot 3H_2O$  in  $H_3PO_4$  electrolyte. Magnifications: 500 $\times$  (a) and 6000 $\times$  (b)

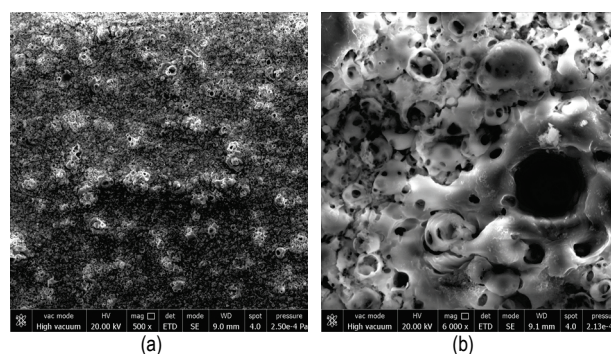
In Fig. 2 and Tab. 2, the SEM image and quantitative results of EDS of porous coating formed on Titanium after PEO process at voltage of 450 V after 3 minutes in 600 g/L of  $Cu(NO_3)_2$  in 1 L  $H_3PO_4$  electrolyte with 500 $\times$  and 6000 $\times$

magnifications, are presented. The obtained surface is porous and with copper-to-phosphorus ratio (Cu/P) equaling to 0.26 by weight concentration and 0.12 by atomic concentration.

**Table 2** Quantitative results of weight and atomic concentrations of selected elements and Cu/P ratio based on the EDS of surface presented in Fig. 2

Elementlines	wt%	at%
P K	38.4	50.1
Ti K	51.2	43.3
Cu K	10.4	6.6
Cu/P	<b>0.27</b>	<b>0.13</b>

In Fig. 3 and Tab. 3, the SEM image and quantitative results of EDS of porous coating formed on Titanium after PEO process at voltage of 450 V after 5 minutes in 600 g/L of  $Cu(NO_3)_2$  in 1 L  $H_3PO_4$  electrolyte with 500 $\times$  and 6000 $\times$  magnifications, are presented. The obtained surface is porous with mostly closed pores and with copper-to-phosphorus ratio (Cu/P) equaling 0.14 by weight concentration and 0.07 by atomic concentration. The amount of copper inside the PEO coating after 5 minutes of oxidization is about twice smaller than the one found after one- or three-minute PEO treatment, i.e. in fact it equals 4.8 wt% (3.1 at%).



**Figure 3** SEM images of coating formed on Titanium after PEO process at voltage of 450 V after 5 min; in 600 g/L of  $Cu(NO_3)_2 \cdot 3H_2O$  in  $H_3PO_4$  electrolyte. Magnifications: 500 $\times$  (a) and 6000 $\times$  (b)

**Table 3** Quantitative results of weight and atomic concentrations of selected elements and Cu/P ratio based on the EDS of surface presented in Fig. 3

Elementlines	wt%	at%
P K	33.2	44.0
Ti K	62.0	52.9
Cu K	4.8	3.1
Cu/P	<b>0.14</b>	<b>0.07</b>

In Fig. 4, the GDOES spectra of copper (325 nm), phosphorus (178 nm), oxygen (130 nm), hydrogen (122 nm), nitrogen (149 nm) and titanium (365 nm), are presented, respectively. The results displayed in that Figure demonstrate that there is a high influence of the plasma electrolytic oxidation time on the chemical composition of PEO coating as a function of depth.

The longer time of PEO treatment, the thinner is the porous coating and the lower are the amounts of copper, phosphorus and oxygen inside it. To compare all the spectra, Authors have used the first and second derivatives of the GD signals (Fig. 4) and propose a model presenting sub-layers (Fig. 5), for which thicknesses are dependent on the PEO treatment time. Based on data presented in Fig. 4, it is possible to conclude that the top sub-layers "A", which are presented in Fig. 5a, have thicknesses corresponding to a sputtering time of about 100 s. They are very porous and

contaminated by organic substances down to a sputtering time of about 50 s because of the contact with surrounding environment/air and with cleaning liquids (alcohols). The thickness of the second, semi-porous sub-layer "B", which

is displayed in Fig. 5b, is dependent on the PEO treatment time, i.e. the thickest one is gained after one-minute of PEO treatment and it gradually decreases with increasing processing time.

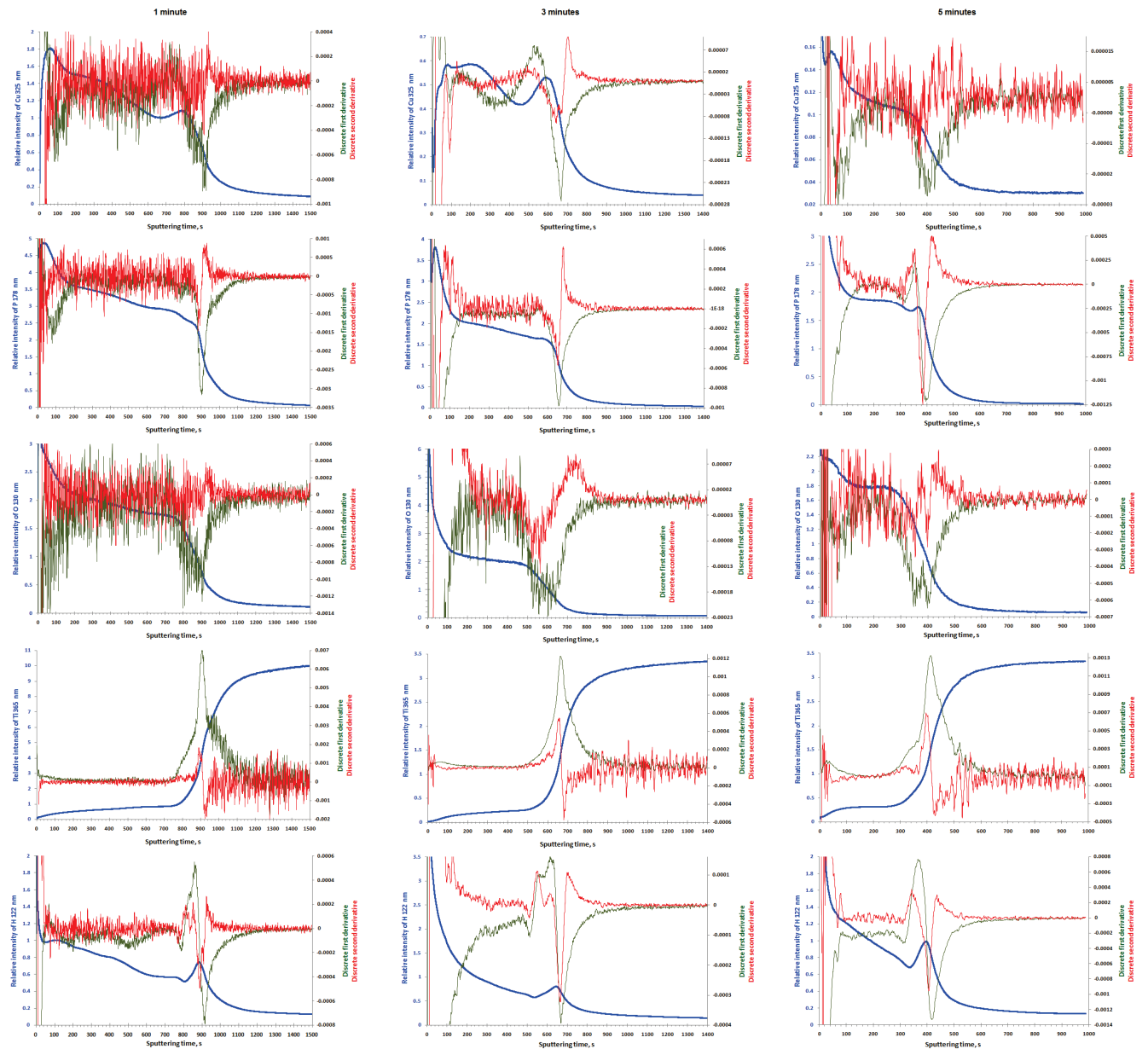


Figure 4 GDOES signals with the first and second derivatives of copper, phosphorus, oxygen, titanium and hydrogen of coatings formed on titanium; influence of PEO oxidation time on PEO coating formation

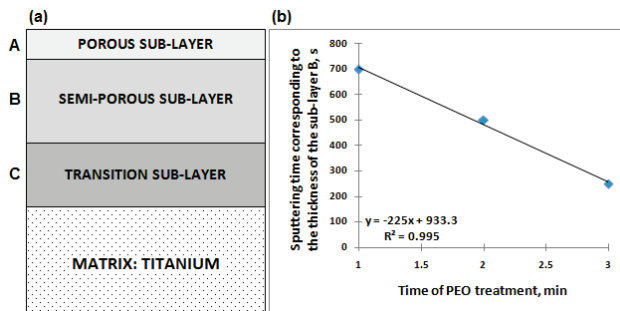
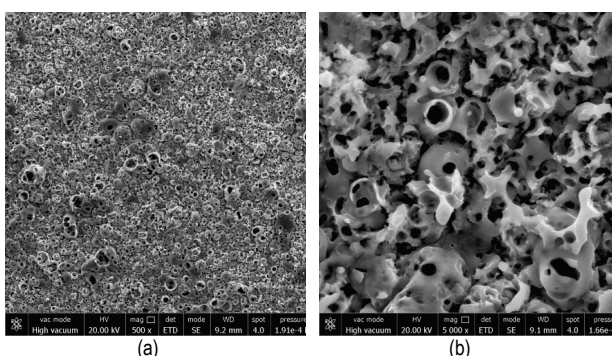


Figure 5 Model (a) describing PEO coatings formed on Titanium with the thicknesses of the sub-layers A and C equalling sputtering times of 100 s and 450 s, respectively, sputtering time corresponding to the thickness of the sub-layer B as a function of PEO treatment time (b)

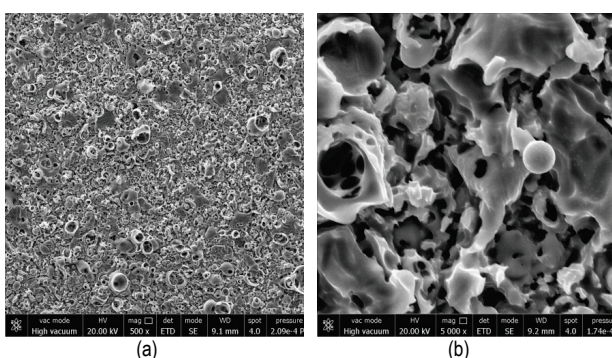
Based on results, which were obtained using voltage with sinusoidal pulsation and which are shown in Figs. 1-4, the new experiments based on three-level statistical plan with using the commercial DC power supply without any pulsation, were performed. For these experiments, three DC voltages, i.e. 450 V<sub>DC</sub>, 550 V<sub>DC</sub>, and 650 V<sub>DC</sub>, were chosen. In Fig. 6, the SEM pictures with two magnifications (500×, 5000×) of coating formed on Titanium after PEO process at voltage of 450 V<sub>DC</sub> after 3 min in 500 g/L of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in 1 L H<sub>3</sub>PO<sub>4</sub> electrolyte, are presented. The obtained surface is porous as it was observed in Fig. 3. Based on seven EDS results the basic statistics were done. For PEO treatment at 450 V<sub>DC</sub> in the obtained coating were found: copper (9.9±0.6 wt% | 6.3±0.4 at%), phosphorus (37.3±0.7 wt% | 48.9±0.7



at%), and titanium ( $52.8 \pm 1.0$  wt% |  $44.8 \pm 0.9$  at%). The maxima and minima of copper (max: 10.6 wt% | 6.8 at%; min: 9 wt% | 5.8 at%), phosphorus (max: 37.8 wt% | 49.4 at%; min: 35.8 wt% | 47.3 at%), and titanium (max: 54.9 wt% | 46.8 at%; min: 52.2 wt% | 44.2 at%) show that the results may be classified to the same statistical population. Hence, the decreasing of copper nitrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  amounts from 600 g/L down to 500 g/L in 1000 mL of concentrated phosphoric acid  $\text{H}_3\text{PO}_4$ , and using the stable DC voltage without pulsation allows to obtain the same chemical composition of PEO coatings under the PEO treatment. In addition, the copper-to-phosphorus ratios were found. They were equal to  $0.3 \pm 0.01$  (max: 0.28; min: 0.25) and  $0.13 \pm 0.01$  (max: 0.14; min: 0.12) by weight and atomic concentrations, respectively.



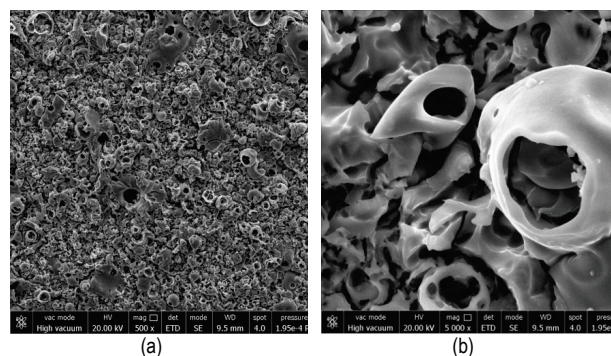
**Figure 6** SEM images of coating formed on Titanium after PEO process at voltage of  $450 \text{ V}_{\text{DC}}$  after 3 min, in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in  $\text{H}_3\text{PO}_4$  electrolyte. Magnifications:  $500\times$  (a) and  $5000\times$  (b)



**Figure 7** SEM images of coating formed on Titanium after PEO process at voltage of  $550 \text{ V}_{\text{DC}}$  after 3 min, in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in  $\text{H}_3\text{PO}_4$  electrolyte. Magnifications:  $500\times$  (a) and  $5000\times$  (b)

In Fig. 7, the SEM pictures with two magnifications ( $500\times$ ,  $5000\times$ ) of coating formed on Titanium after PEO process at voltage of  $550 \text{ V}_{\text{DC}}$  after 3 min in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 1000 mL  $\text{H}_3\text{PO}_4$  electrolyte, are presented. The obtained surface is porous as it was observed in Fig. 6. For PEO treatment at  $550 \text{ V}_{\text{DC}}$  in the obtained coating, copper ( $13.4 \pm 0.4$  wt% |  $8.6 \pm 0.3$  at%), phosphorus ( $38.3 \pm 0.4$  wt% |  $50.4 \pm 0.4$  at%), and titanium ( $48.2 \pm 0.5$  wt% |  $41.0 \pm 0.4$  at%), were detected. The maxima and minima of copper (max: 14.3 wt% | 9.2 at%; min: 13.1 wt% | 8.4 at%), phosphorus (max: 38.9 wt% | 51.0 at%; min: 37.8 wt% | 49.8 at%), and titanium (max: 48.9 wt% | 41.6 at%; min: 47.7 wt% | 40.5 at%) show clearly that with PEO treatment at  $550 \text{ V}_{\text{DC}}$ , the obtained coating contains more copper than that one obtained at  $450 \text{ V}_{\text{DC}}$ . This trend is also confirmed by copper-to-phosphorus ratio, which was equal to  $0.35 \pm 0.01$  (max:

0.38; min: 0.34) and  $0.17 \pm 0.004$  (max: 0.18; min: 0.17) by weight and atomic concentrations, respectively.



**Figure 8** SEM images of coating formed on Titanium after PEO process at voltage of  $650 \text{ V}_{\text{DC}}$  after 3 min, in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in  $\text{H}_3\text{PO}_4$  electrolyte. Magnifications:  $500\times$  (a) and  $5000\times$  (b)

In Fig. 8, the SEM pictures with two magnifications ( $500\times$ ,  $5000\times$ ) of porous coating formed on Titanium after PEO process at voltage of  $650 \text{ V}_{\text{DC}}$  after 3 min in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 1 L  $\text{H}_3\text{PO}_4$  electrolyte, are presented. For PEO treatment at  $650 \text{ V}_{\text{DC}}$  in the obtained coating, copper ( $12.2 \pm 0.5$  wt% |  $7.9 \pm 0.3$  at%), phosphorus ( $35.1 \pm 0.6$  wt% |  $46.7 \pm 0.7$  at%), and titanium ( $52.7 \pm 0.8$  wt% |  $45.4 \pm 0.8$  at%), were found.

The maxima and minima of copper (max: 12.8 wt% | 8.3 at%; min: 11.4 wt% | 7.4 at%), phosphorus (max: 35.9 wt% | 47.4 at%; min: 34.2 wt% | 45.8 at%), and titanium (max: 54.0 wt% | 46.5 at%; min: 51.4 wt% | 44.1 at%) show clearly that with PEO treatment at  $650 \text{ V}$ , the obtained coating contains more copper than that one obtained at  $450 \text{ V}_{\text{DC}}$  (aver. 6.3 at%). It is also confirmed by copper-to-phosphorus ratios, which were equal to  $0.35 \pm 0.01$  (max: 0.37; min: 0.33) and  $0.17 \pm 0.01$  (max: 0.18; min: 0.16) by weight and atomic concentrations, respectively.

For better characterization of the obtained PEO surfaces, i.e. roughness/porosity, some 2D roughness parameters ( $R_a$ ,  $R_z$ ,  $R_z \text{ ISO}$ ,  $R_q$ ,  $R_t$ ,  $R_{Sm}$ ,  $l_0$ ,  $D$ ), as described in the point 2 (Method), were selected. It is clearly visible in Fig. 9 that to distinguish the PEO surfaces obtained with using of different voltages ( $450 \text{ V}_{\text{DC}}$ ,  $550 \text{ V}_{\text{DC}}$ ,  $650 \text{ V}_{\text{DC}}$ ),  $R_a$ ,  $R_q$ ,  $l_0$  roughness parameters are the best ones, which may be used to describe the coatings. The interpretation of these parameters should be as follows: the biggest roughness should be identified as surface with opened and big pores, while the small roughness points to the porous surface with small pores or closed ones. The results presented in Fig. 6 show that the voltage of PEO treatment has a significant impact on surface roughness/porosity. For PEO surfaces obtained at  $450 \text{ V}$ , the  $R_a$ ,  $R_q$ ,  $l_0$  parameters were equal to  $1.36 \pm 0.10 \mu\text{m}$ ,  $1.8 \pm 0.13 \mu\text{m}$ ,  $1.0102 \pm 0.0011$ , while for  $650 \text{ V}$  they were  $3.97 \pm 0.19 \mu\text{m}$ ,  $5.04 \pm 0.20 \mu\text{m}$ ,  $0.8442 \pm 0.003$ , respectively.

In Fig. 10, XPS spectra of coating formed on titanium after PEO process at voltages of  $450 \text{ V}_{\text{DC}}$  and  $650 \text{ V}_{\text{DC}}$  after 3 min in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 1 L  $\text{H}_3\text{PO}_4$  electrolyte, are presented. The results clearly show that in the upper layer (10 nm) there are titanium ( $\text{Ti}^{4+}$ ), copper ( $\text{Cu}^{2+}$  and  $\text{Cu}^+$ ) as well as phosphorus and oxygen mostly as  $\text{PO}_4^{3-}$  present, what is confirmed by the binding energies, i.e.  $\text{Ti}2p_{3/2}$  (460.2 eV),  $\text{Cu}2p$  (92.8 eV, 935.8 eV, 942.3 eV, 944.6 eV),  $\text{P}2p$  (134 eV),  $\text{O}1s$  (531.5 eV). It may suggest

that the obtained coating may be considered as a hydroxyapatite-like structure, in which in places where normally are  $\text{Ca}^{2+}$  and  $\text{OH}^-$ , here most likely are  $\text{Cu}^{2+}$  and

$\text{Cu}^+$  (the signal of  $\text{Cu}2p$  was noised and the analysis was performed based on maximum peaks).

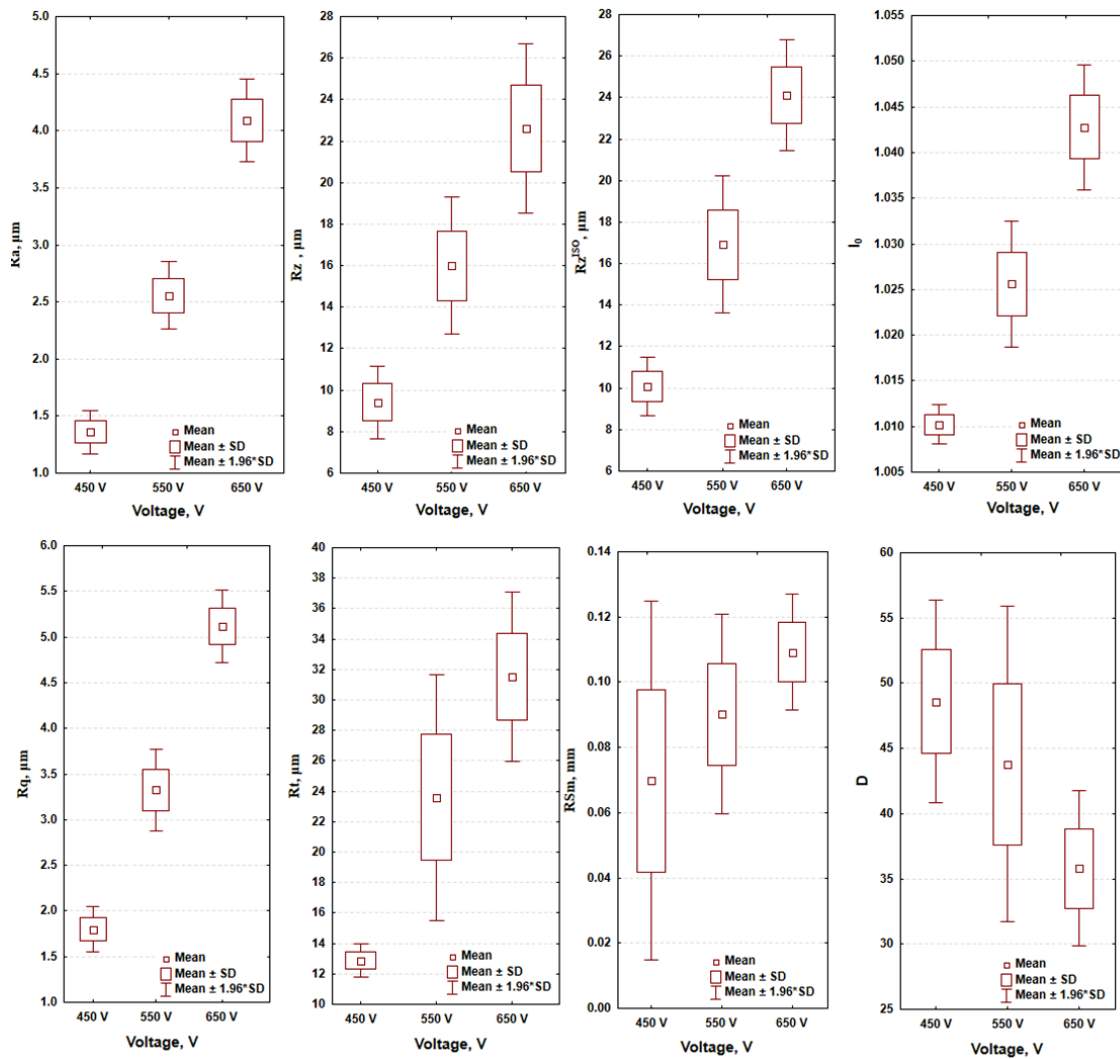


Figure 9 Roughness parameters of coatings formed on Titanium after PEO process at voltages of 450 V<sub>DC</sub>, 550 V<sub>DC</sub> and 650 V<sub>DC</sub> after 3 min in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 1 L  $\text{H}_3\text{PO}_4$  electrolyte

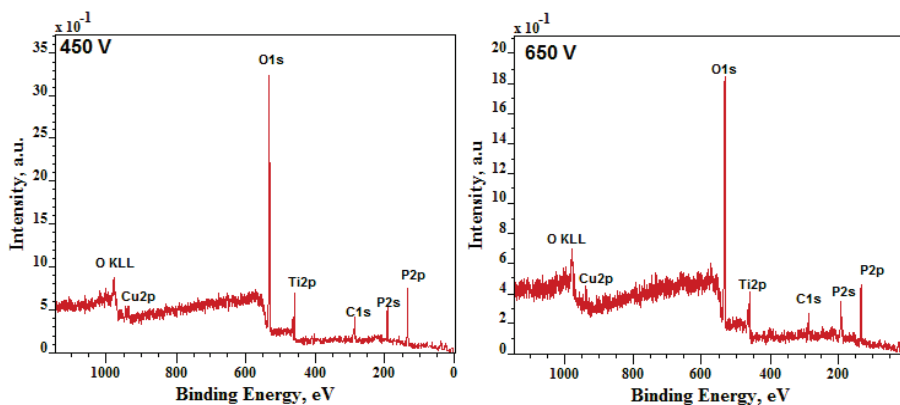


Figure 10 XPS spectra of coating obtained on titanium at voltages of 450 V<sub>DC</sub> and 650 V<sub>DC</sub> after 3 min treatment in 500 g/L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 1 L  $\text{H}_3\text{PO}_4$  electrolyte.

### 3 CONCLUSIONS

Performed complex characterization of the phenomena of electrolyte aging and influence of PEO processing time on creation of porous coatings enriched with copper on the

CP Titanium Grade 2 resulted in developing the series of conclusions:

- Time of process surely has an influence on the chemical composition and thickness of the obtained porous coatings.

- The longer time of PEO treatment, the thinner is the porous coating and the lower amounts of copper, phosphorus and oxygen are detected inside it.
- The top sub-layers ("A" in Fig. 5a), having a thickness corresponding with the sputtering time equaling 100 s are very porous and contaminated by organic substances down to about 50 s by sputtering time, because of the contact with surrounding air and with cleaning liquids (alcohols).
- The thickness of semi-porous sub-layer ("B" in Fig. 5b) depends on the treatment time; the thickest sub-layer appears to be after one-minute PEO treatment and it decreases with increasing time of processing.
- The thickness of semi-porous sub-layer ("B" in Fig. 5c) also depends on electrolyte aging: the thickest coating is obtained after first PEO treatment; after each successive PEO treatment, the coating thickness decreases.
- The transition sub-layers ("C" in Fig. 5a) have thickness corresponding with a sputtering time equaling 450 s; for the third sample successively treated during three minutes of oxidation, only two sub-layers, namely "A" and "C", are present.
- The PEO potential has an impact on the roughness/porosity of the PEO coatings: the higher is the potential, the bigger are the roughnesses, i.e. the obtained pores are opened and/or have bigger diameters; the lower is the potential, the smaller are the roughnesses, i.e. the obtained pores are closed and/or have small diameters.
- In all likelihood the upper layer of 10 nm of described coatings is constructed of titanium ( $Ti^{4+}$ ), copper ( $Cu^{2+}$  and  $Cu^+$ ), and phosphates ( $PO_4^{3-}$ ).

#### Acknowledgements

This work was supported by a subsidy from 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".

Many thanks are directed to Professor Czesław Łukianowicz, DSc PhD, head of Metrology and Quality Division, former Dean of the Faculty of Mechanical Engineering of KUT, for making available a computerized HOM-MELTESTER T800 system of Hommelwerke GmbH.

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