

# Characterisation of porous coatings formed on titanium under AC plasma electrolytic oxidation

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**Abstract.** The Plasma Electrolytic Oxidation (PEO) process may be used to fabricate porous coatings on titanium. The ranges of voltages used in case of these plasma treatments are different. It has been found that for DC PEO processing the voltage must be higher than that in the case of AC PEO treatment. In addition, the shape and frequency of the voltage signal have also an influence. In the paper scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy and glow discharge optical emission spectroscopy (GDEOS) were used to characterise obtained coatings. It was found that it is possible to obtain the porous coatings enriched with phosphorus and copper by use of AC-PEO at only 200 Vpp, while increasing the PEO voltage results in non-porous and cracked coatings. Based on GDEOS for 200 Vpp three sublayers were used, with ranges of 0-400, and 400-2400, and 2400-3600 seconds of sputtering time for first, and second, and transition sublayers respectively. XPS spectra for sample processed at 200 Vpp indicate in top 10 nm layer presence of titanium as  $Ti^{4+}$  and phosphorous as phosphates (most likely  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ ,  $P_2O_7^{3-}$ ).

## 1 Introduction

Light metals such as titanium, niobium, tantalum, zirconium, and their alloys may be treated by Plasma Electrolytic Oxidation also known as Micro Arc Oxidation (MAO). Nowadays, for biomedical and industrial applications the titanium [9-11] and its alloys [12-24] are mostly used. The main advantage of use of that electrolytical method is possibility of forming the porous micro-coatings, which may be enriched with selected materials. It

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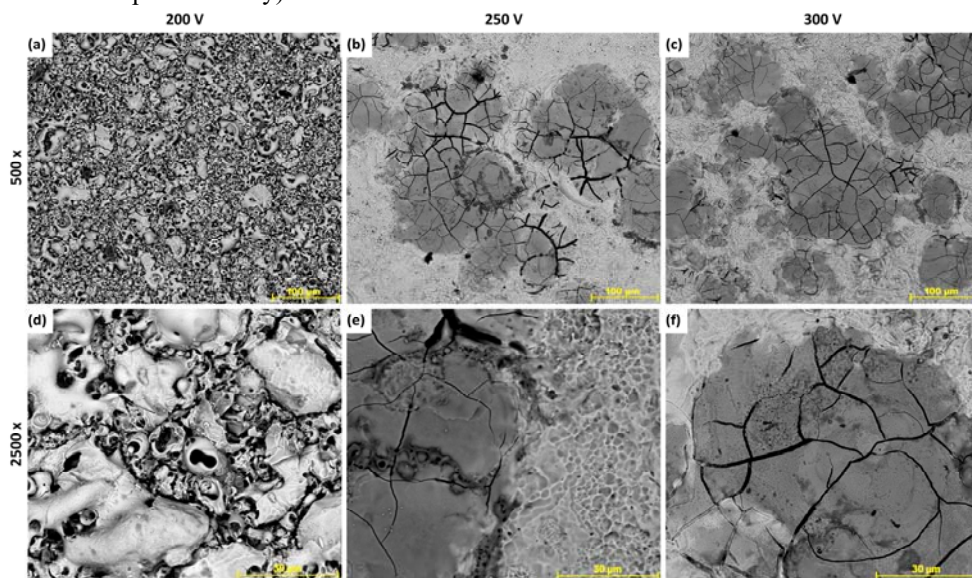
should be also pointed out that in literature there are informations about nano-layers, that may be obtained by the electropolishing techniques [1-8]. The PEO coatings used as biomaterials should have hydroxyapatite-like structure enriched with bactericidal copper [10, 25-29], what is very important in the case of surgery of human and animal bodies. The coatings are fabricated at DC or AC voltages of several hundred volts. It addition, it should be noted that errors related to the voltage instability as well as with the distortion associated with the shape of the wave are also affected [30-31]. Porous coatings obtained by DC PEO processes with the use of concentrated phosphoric acid based electrolyte were described in previous papers [32-37].

## 2 Methods

The titanium samples (10×10×2 mm) were treated by PEO treatment in electrolyte consisting of 1 L of 85% phosphoric acid  $H_3PO_4$  with 500 g copper nitrate trihydrate  $Cu(NO_3)_2 \cdot 3H_2O$  for 3 min at voltages of 200 V<sub>pp</sub>, 250 V<sub>pp</sub> and 300 V<sub>pp</sub> (volts peak-to-peak) by using 50 Hz alternating current transformer. The set ups of SEM, EDS, GDOES, XPS measuring systems were described earlier in [18, 20, 31].

## 3 Results and discussion

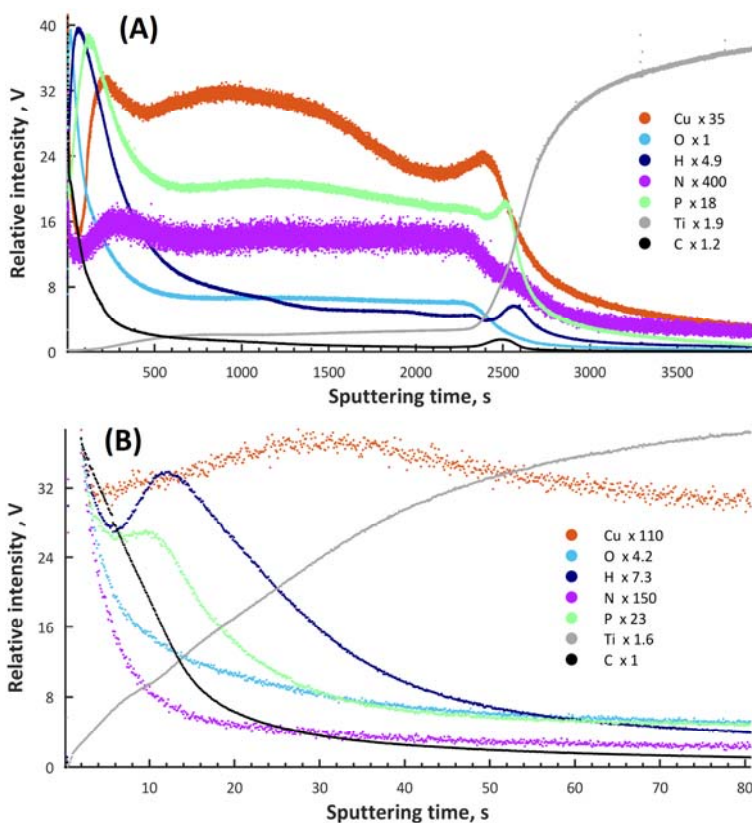
In Figure 1, SEM micrographs of coatings formed on titanium after AC PEO treatment at voltages 200, 250, and 300 V<sub>pp</sub>, are presented. The coating obtained at the voltage of 200 V<sub>pp</sub> may be characterized as porous with well-developed surface. The developed morphology type can be used for different applications (biomaterials, catalysts, as well as for air and space industry).



**Fig. 1.** SEM pictures of coatings formed on Titanium Grade 2 after AC PEO treatment at voltages of 200 V<sub>pp</sub>, 250 V<sub>pp</sub>, 300 V<sub>pp</sub>. Magnifications 500 and 2500 times.

The surfaces obtained at voltages of 250 and 300 V<sub>pp</sub> look not so well developed as that one obtained at 200 V<sub>pp</sub>. Higher voltage correlates with more energy delivered to create plasma on the material surface during the process. Under these conditions, the increasing voltage seems to have a negative influence on building porous, well developed surfaces.

Based on the EDS data from 5 records for each sample generated at magnification of 500 times the Cu/P atomic ratios were equal to  $0.18 \pm 0.01$  (first quartile 0.18; third quartile 0.19),  $0.15 \pm 0.04$  (first quartile 0.12; third quartile 0.19), and  $0.07 \pm 0.02$  (first quartile 0.05; third quartile 0.09). The Cu/P ratio has negative correlation with voltage of the AC PEO process. Based on the presented SEM and EDS results, where the porous coating was obtained at 200 V<sub>pp</sub>, the authors decided to continue studies (GDOES and XPS) on that coating only. In Figure 2A, the GDEOS results of the analysis of coating obtained on CP Titanium Grade 2 after AC PEO treatment at the voltage of 200 V<sub>pp</sub>, are presented. The presence of copper and phosphorus as the basic elements of coating, and titanium as a matrix was described and proved by the higher given EDS data. The obtained coating can be divided into three sub-layers, i.e. the first one with open and organic contaminated from the atmosphere pores; the second one, semi-porous with lower concentrations of phosphorus, hydrogen, oxygen and carbon, and the third transition sub-layer in which decreasing phosphorus, oxygen signals, and increasing titanium signal can be observed.

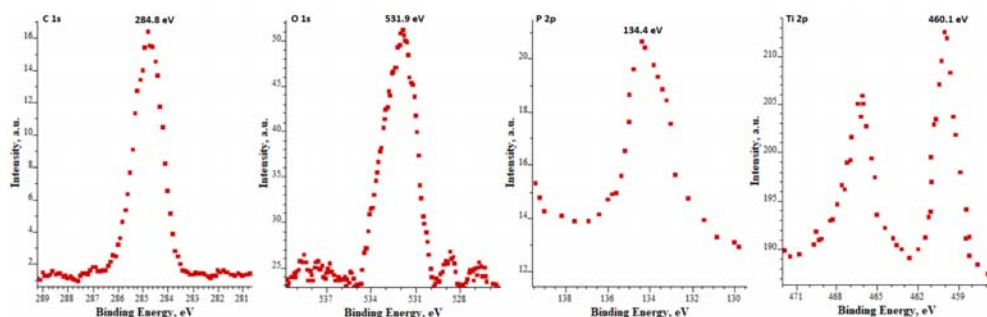


**Fig. 2.** GDEOS results for copper (a), phosphorus (b), oxygen (c), titanium (d), hydrogen (e), carbon (f), nitrogen (g), and summary (h) of coatings formed on Titanium Grade 2 after AC PEO treatment at voltages of 200 V<sub>pp</sub> (A), and 300 V<sub>pp</sub> (B).

The first sub-layer thickness corresponds with approximately 400 s of sputtering time. The second sub-layer is thicker than the first one and refers to approximately 400 up to 2400 s resulting in thickness corresponding with 2000 s of sputtering time. The third sub-layer, with the thickness corresponding with the sputtering time of 1100 s, should be treated as the transition one. Local maxima in case of hydrogen and carbon can be considered as organic contaminations coming from the air that can prove the existence of pore-in-pore structures.

In Figure 2B, the GDEOS results of coating obtained on CP Titanium Grade 2 after AC PEO treatment at voltage of 300 V<sub>pp</sub>, are presented. Based on the GDEOS data one can conclude that the coating obtained at 300 V<sub>pp</sub> is enriched in copper, phosphorus, oxygen and titanium. The obtained results indicate that much thinner single layer is formed, referred to approximately 40 s of sputtering time, with the reference to coating obtained at 200 V<sub>pp</sub> (at approximately 3500 s of sputtering time).

In Figure 3, XPS spectra of coatings formed on CP Titanium Grade 2 after AC PEO treatment at the voltage of 200 V<sub>pp</sub>, are presented. The obtained XPS results show that the top 10 nm layer is constituted from titanium (most likely Ti<sup>4+</sup>) and phosphates (most likely PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, P<sub>2</sub>O<sub>7</sub><sup>3-</sup>) presence, which are confirmed by the binding energies, i.e. Ti 2p<sub>3/2</sub> (460.1 eV), O 1s (531.9 eV), P 2p (134.4 eV).



**Fig. 3.** XPS results for coatings formed on Titanium Grade 2 after AC PEO treatment at voltages of 200 V<sub>pp</sub>.

## 4 Conclusions

- It is possible to obtain the porous coatings enriched with phosphorus and copper by use of AC-PEO at only 200 V<sub>pp</sub>.
- The use of voltages higher than 200 V<sub>pp</sub> results in non-porous and cracked PEO coatings
- Three-sublayer model was proposed based on GDEOS data, where porosity was confirmed by detection of organic contamination.
- Considering GDEOS results total thickness of coatings obtained at voltage of 200 V<sub>pp</sub> was ca. more than 80 times thicker than the ones obtained at 300 V<sub>pp</sub>.
- The top 10 nm layer is composed of titanium (most likely Ti<sup>4+</sup>) and phosphates (most likely PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, P<sub>2</sub>O<sub>7</sub><sup>2-</sup>), which are confirmed by the binding energies, i.e. Ti 2p<sub>3/2</sub> (460.1 eV), O 1s (531.9 eV), P 2p (134.4 eV).

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