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Porous coatings obtained on titanium after IMPULSE – PEO processes

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Abstract. The surface stereometry and chemical compositions of porous coatings obtained during Plasma Electrolytic Oxidation, PEO/ (Micro Arc Oxidation, MAO) processes with use of impulse regime with different frequencies were the main goal of discussions presented in that paper. All the coatings were characterized by Scanning Electron Microscope (SEM), Energy-dispersive X-ray Spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS). It was found out that the frequencies of voltage signals used in PEO process as well as their duty ratios have a big influence on porosity, roughness and chemical composition of fabricated layers. In addition, it was noted that all the coatings' compounds contained Ti^{4+} and Ca^{2+} or Mg^{2+} as well as PO_4^{3-}, and/or HPO_4^{2-}, and/or $H_2PO_4^{-}$, and/or $P_2O_7^{4-}$.

1. Introduction
The electrolytes consisting of sulfuric(VI) and phosphoric(V) acids are typically used for electropolishing, high-density electropolishing and electropolishing in the magnetic field to obtain passive nanolayers [1-7] but they can be also used for plasma electrolytic oxidation (PEO). Fabrication of much thicker PEO coatings, in the range of micrometers, was proved to be feasible under current or voltage control with DC, pulsed and AC processes. Light metals such as titanium, niobium, tantalum, magnesium, aluminium, and their alloys can be processed [8-9]. Our previous papers characterized porous coatings enriched with calcium, magnesium, zinc and copper obtained under constant voltage conditions [9-16]. The purpose of this work is to compare two shapes of pulsed voltage controlled PEO treatments for coatings enriched with calcium or magnesium, obtained in electrolytes based on concentrated phosphoric acid.

2. Methods
All PEO processes were performed under two shapes of voltages, i.e. 50 Hz and 100 Hz. The results were recorded by oscilloscope with the shape characteristics, which are presented in Figure 1. In both

cases the same peak-to-peak voltages with the value 500 V_{pp} with different frequency and duty ratio were applied. Titanium samples (CP Grade 2) of sizes 10 × 10 × 2 mm were treated in electrolyte containing 500 g of calcium nitrate(V) tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$ or magnesium nitrate(V) hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$ in 1 dm^3 of concentrated (85 wt%) phosphoric(V) acid H_3PO_4 in time of 3 minutes. The methodic related to SEM, EDS and XPS equipment's was described in detail in our previous article [18].

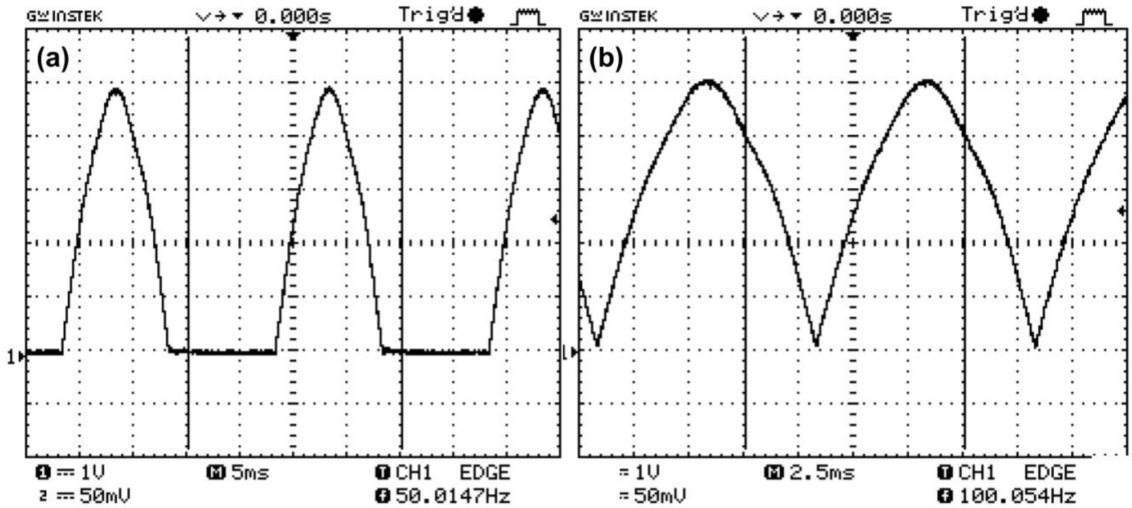

Figure 1. Shape of PEO voltage used for IMPULSE-PEO treatment a) 50 Hz, b) 100 Hz (during measurements the voltage divider 100 times was used)

3. Results and discussion

Two magnifications of porous PEO coatings obtained in IMPULSE PEO process, in order to show differences between two voltage frequencies, and they are presented in Figures 2 and 3. The most noticeable difference is the pore size of surfaces obtained at two regimes (IMPULSE-PEO 50 Hz and IMPULSE-PEO 100 Hz). Pores obtained at frequency of 50 Hz have visibly bigger diameters than those once obtained at the frequency of 100 Hz. The differences between coatings enriched in calcium and magnesium are not so obvious and are to be described with roughness parameters elsewhere. However, a possible explanation of the that phenomena may be the different plasma nature during PEO treatment, what corresponds with the applied frequency, duty ratio, as well as with a complex nature of ions transport in changing electric field. In figure 4, EDS spectra of coatings obtained with IMPULSE-PEO enriched in calcium and magnesium at 50 Hz and 100 Hz are presented. Signals of oxygen, titanium, phosphorus and calcium or magnesium were recorded.

Quantification of the obtained results, presented in tables 1 and 2, has to be interpreted with the consideration of porosity and the layer finite thickness, what in this case. Here also oxygen quantification should be interpreted as an approximate one. However, calcium- or magnesium-to-phosphorus (Ca/P, Mg/P) ratios, as the reliable quantitative parameters were calculated. According to the recorded results, coatings obtained at frequency of 100 Hz showed higher titanium peak, lower phosphorus, oxygen and magnesium or calcium once, than for treatment at 50 Hz. In case of calcium enriched coatings, the higher Ca/P ratio for coatings obtained at 50 Hz (Ca/P = 0.13) was recorded, then at 100 Hz (Ca/P = 0.10). Magnesium enriched coatings most likely do not show significant differences in Mg/P value, which is in the range of 0.15-0.16. It is also worthy noticing that in the same mass concentration of nitric salts in phosphoric(V) acid, with the use of any presented voltage regime, magnesium enriched coatings would have higher Mg/P ratio than calcium enriched coatings Ca/P ratio.it practically means that titanium signal may partially come from the titanium substrate.