SEM, EDS and XPS studies of AC & DC PEO coatings obtained on titanium substrate

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Abstract. The porous coatings may be fabricated on titanium substrate by Plasma Electrolytic Oxidation (PEO), known also as Micro Arc Oxidation (MAO), under AC or DC regimes. The obtained surfaces were characterized by Scanning Electron Microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS), and X-ray Photoelectron Spectroscopy (XPS). This work has discussed the influence of electrolyte composition and of PEO type (AC-PEO or DC-PEO) on chemical composition of fabricated porous coatings as well as on their surface stereometry. The recorded results show clearly that the external porosity and roughness of obtained surfaces as well as metal-to-phosphorus ratios are different for different solutions and PEO processes, but for all PEO surfaces the bindings energies of titanium (Ti 2p), oxygen (O 1s), phosphorus (P 2p) may suggest that all the top nano-layers consist of Ti^{4+} and groups PO_4^{3-}, and/or HPO_4^{2-}, and/or $H_2PO_4^-$, and/or $P_2O_7^{2-}$.

1. Introduction

Electrolyte consisting of sulfuric(VI) acid and phosphoric(V) acids are generally used for electropolishing, high-density electropolishing and electropolishing in the magnetic field to obtain passive nanolayers [1-7]. On the other hand, to produce coatings of much higher thickness, in the range of micrometers, plasma electrolytic oxidation (PEO) is used. DC, pulsed, and AC processes, with current or voltage control, are applied to obtain the porous coatings on light metals, such as titanium, niobium, tantalum, magnesium, aluminium, and their alloys can be processed [8-9]. Our previous papers characterize porous coatings enriched with calcium, magnesium, zinc and copper obtained under constant voltage conditions [10-18]. The aim of this work is to compare coatings obtained under DC and AC voltage regimes. Moreover, they are enriched in calcium or magnesium gained in the electrolytes based on concentrated phosphoric acid.

2. Methods
PEO process was conducted with the use of DC and AC voltages under controlled conditions. The DC process was performed under constant voltage of 450 V while the AC process was conducted with sinusoidal shape of voltage, with voltage control, and peak-to-peak voltage value of 200 V_{pp} and frequency of 50 Hz. Titanium samples (CP Grade 2) of sizes $10 \times 10 \times 2$ 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. SEM, EDS and XPS methodology was described in detail in our previous article [18].

3. Results and discussion
In figures 1 and 2, SEM images of PEO coatings obtained with DC or AC, enriched with calcium or magnesium, at two magnifications, are presented. Coatings obtained at 450 V DC, enriched with magnesium, have visually rougher structures than those enriched with calcium. In case of AC PEO process, the coatings enriched with magnesium have, beside a standard microporosity (up to approximately 15 µm) present in all of the displayed SEM images here, visible round macro structures of approximate sizes in the range of 100-200 µm. More in depth morphology analysis with the use of CLSM will be shown elsewhere. EDS spectra of PEO processed titanium samples are shown in figure 3.
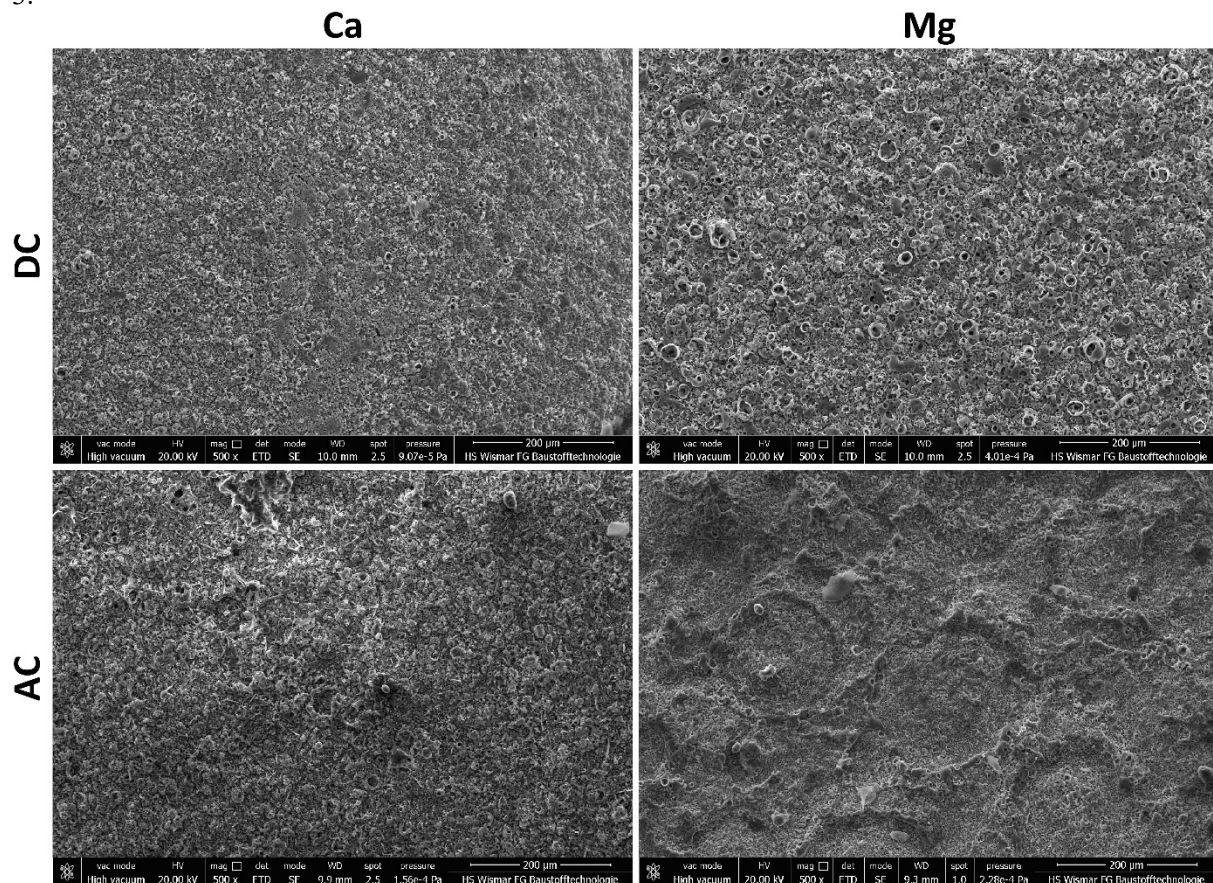
Figure 1. SEM images of PEO coatings obtained under DC or AC PEO process, with magnification of 500×, in electrolytes consisting of H_3PO_4 with $Ca(NO_3)_2 \cdot 4H_2O$ or $Mg(NO_3)_2 \cdot 6H_2O$

Based on the presented data for calcium or magnesium, the enriched coatings indicating 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 by taking into consideration the porosity of coatings and their finite thickness. In this case it practically means that titanium signal may partially