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# 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.

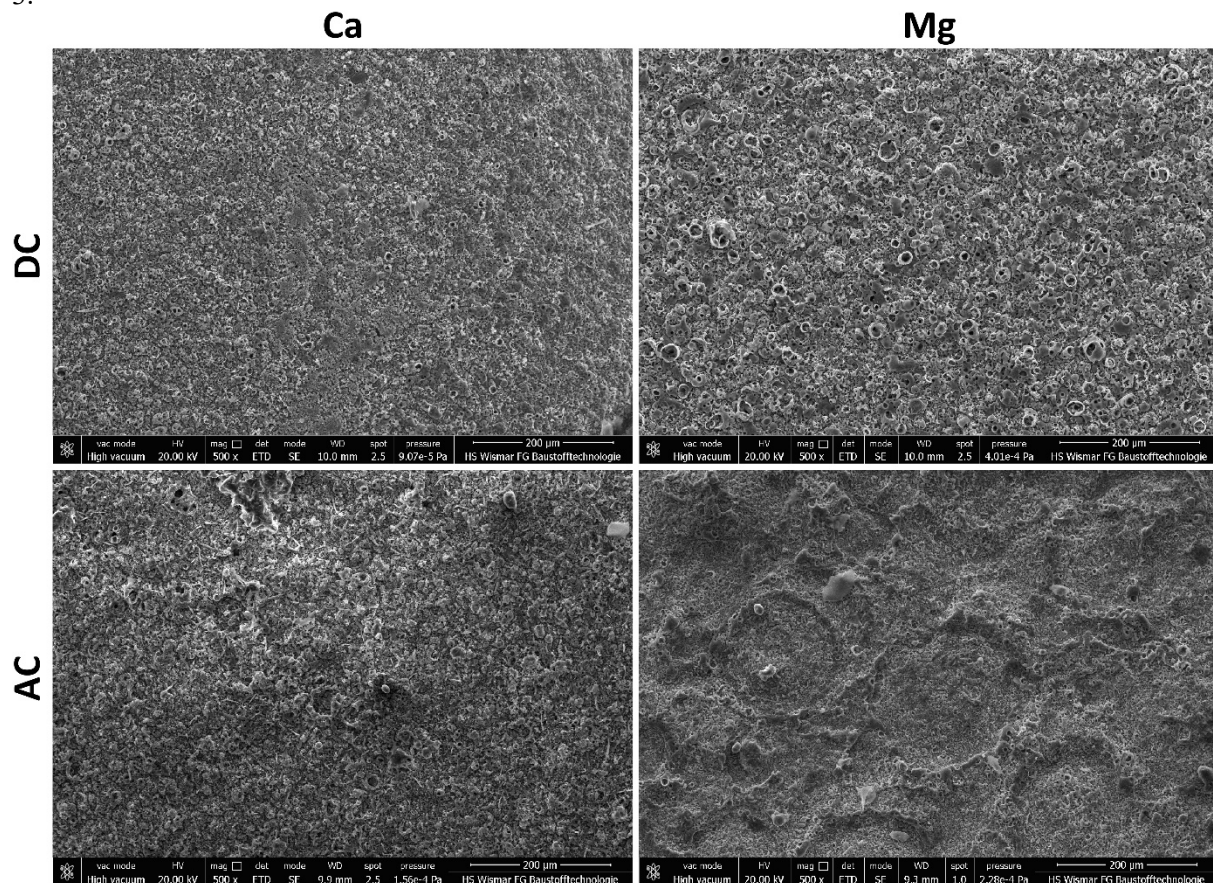


## 2. Methods

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<sub>pp</sub> and frequency of 50 Hz. 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<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O or magnesium nitrate(V) hexahydrate Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O in 1 dm<sup>3</sup> of concentrated (85 wt%) phosphoric(V) acid H<sub>3</sub>PO<sub>4</sub> 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<sub>3</sub>PO<sub>4</sub> with Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O or Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O

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

come from the titanium substrate; here also oxygen quantification should be interpreted as an approximate one. However, calcium- and/or magnesium-to-phosphorus ratios, as the reliable quantitative parameters, were calculated. EDS results revealed that under the AC PEO process with the use of the same electrolyte, the obtained coating was composed of higher amount of calcium calculated as Ca/P (0.28) than the coating obtained under DC PEO process where Ca/P was equal to 0.13; that is much less, and approximately half of the first value. In case of magnesium enriched coatings, the same trend can be observed though not in such a strength, because the Mg/P ratios for AC and DC PEO processes are equal to 0.15 and 0.19, respectively. Both morphology and metal-to-phosphorus ratios differences originate from the different voltage regimes used while both time of the process, and the electrolytes composition were kept unchanged. The AC voltage regime differs significantly from DC voltage regime if the transport of ions, both cations and anions, in the electric field is considered. According to the authors, the mentioned phenomena are most probably the main effects influencing the coating properties and will undergo further investigations. However, it should be pointed out that the PEO process is considered as very complex one and the available literature yet does not provide any adequate explanations.

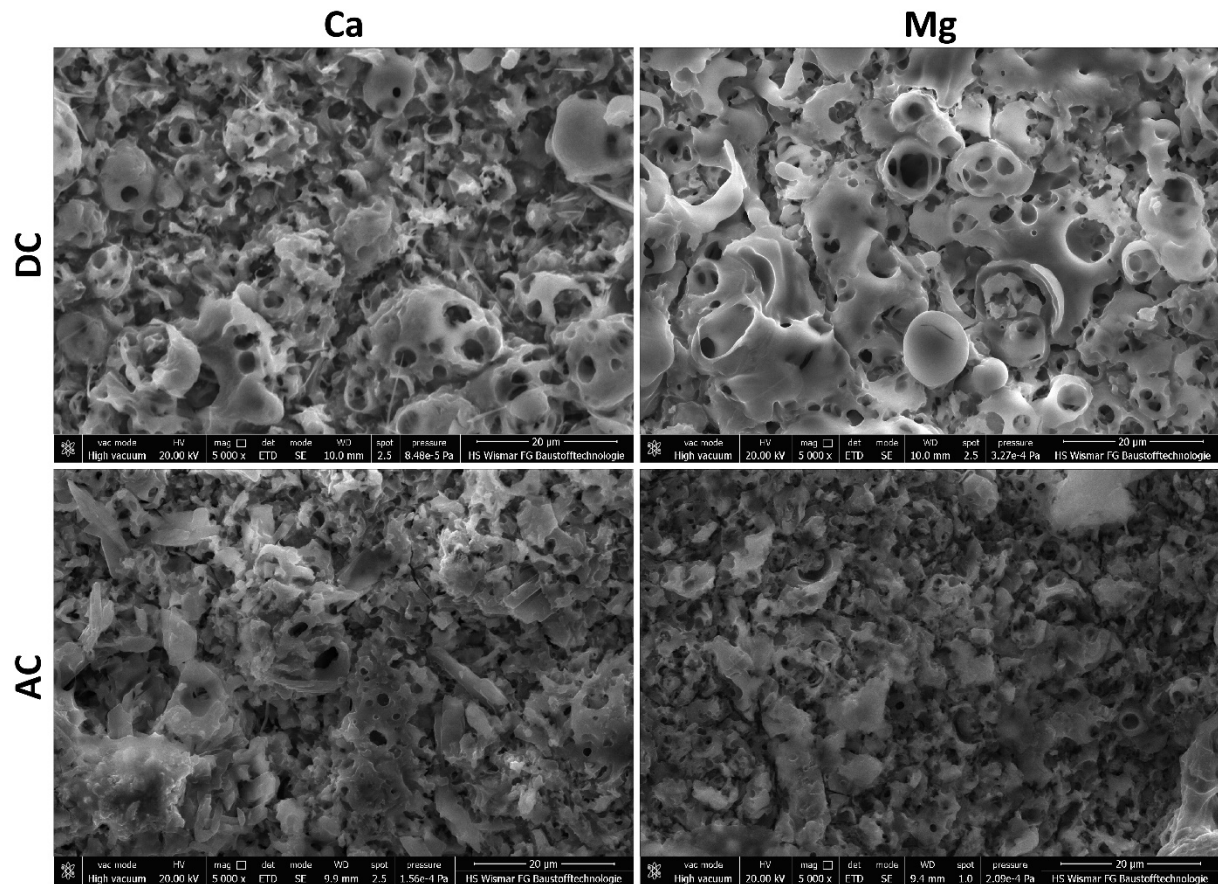
**Table 1.** EDS results of PEO coatings obtained under DC or AC PEO process in the electrolytes consisting of  $\text{H}_3\text{PO}_4$  with  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

| Voltage regime | Ca, at% | P, at% | O, at% | Ti, at% | Ca/P |
|----------------|---------|--------|--------|---------|------|
| DC             | 1.8     | 13.9   | 76.2   | 8.1     | 0.13 |
| AC             | 4.4     | 15.7   | 72.3   | 7.6     | 0.28 |

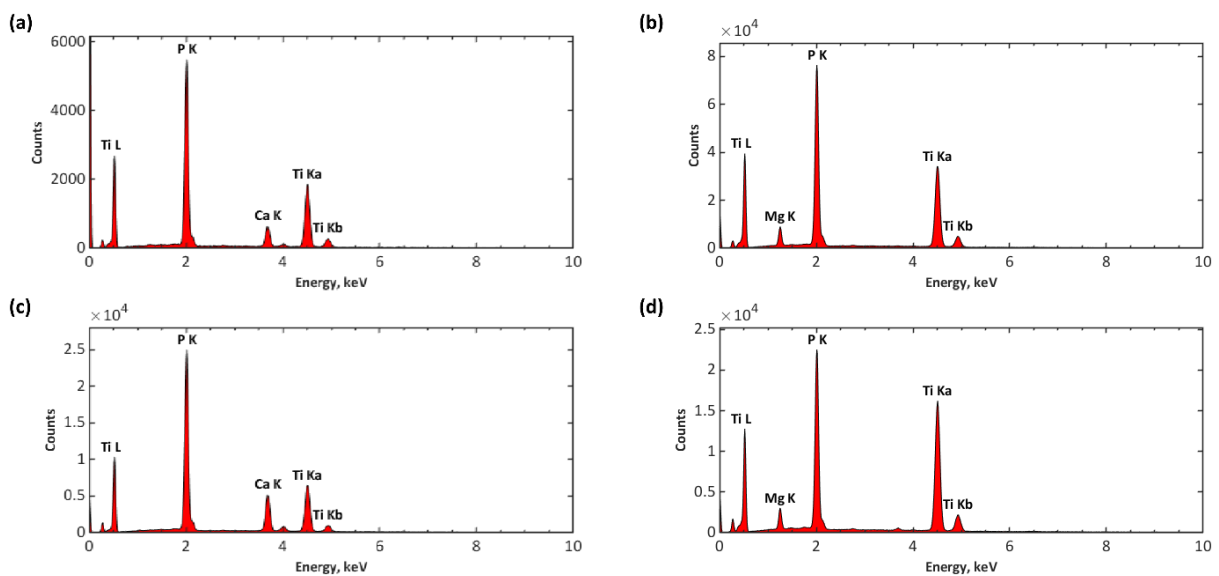
**Table 2.** EDS results of PEO coatings obtained under DC or AC PEO process in the electrolytes consisting of  $\text{H}_3\text{PO}_4$  with  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

| Voltage regime | Mg, at% | P, at% | O, at% | Ti, at% | Mg/P |
|----------------|---------|--------|--------|---------|------|
| DC             | 2.1     | 14.0   | 73.0   | 10.9    | 0.15 |
| AC             | 2.3     | 11.9   | 72.9   | 12.9    | 0.19 |

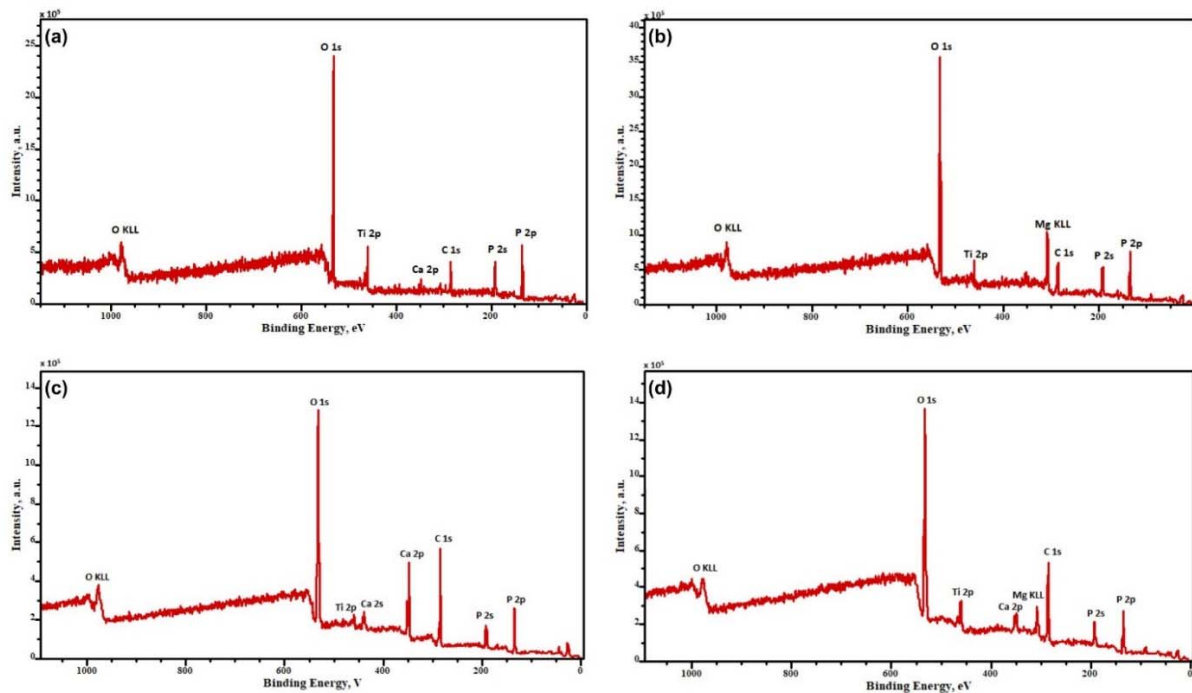
Chemical composition of 10 nm surface layer of the obtained coatings was characterized by means of XPS and is presented in Figure 4. The recorded XPS spectra for porous coatings obtained under DC or AC PEO processes in the electrolytes consisting of magnesium or calcium indicate, on the base of P 2s and P 2p, on the presence of phosphates in the forms of  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ , or  $\text{P}_2\text{O}_7^{4-}$ , on the base of Ti 2p, the presence of  $\text{Ti}^{4+}$ . In calcium or magnesium enriched coatings,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  are present, respectively. Detailed information is as follows: for calcium enriched, the obtained at 450 V DC coatings, the peaks are C1 s 284.8 eV, O1 s 531.6 eV, Ti 2p<sub>3/2</sub> 460.5 eV, Ca p<sub>2/3/2</sub> 347.8 eV, P 2s 191.3 eV, P 2p 134.4 eV, for magnesium enriched, the obtained at 450 V DC coatings, the peaks are C1 s 284.8 eV, O1 s 532.7 eV, Ti 2p<sub>3/2</sub> 459.9 eV, Mg KLL 306.8 eV, P 2s 191.2 eV, P 2p 133.7 eV, for calcium enriched, the obtained at 200 V<sub>pp</sub> AC 50 Hz coatings, the peaks are C1 s 284.8 eV, O1 s 531.9 eV, Ti 2p<sub>3/2</sub> 460.0 eV, Ca p<sub>2/3/2</sub> 347.9 eV, P 2s 191.6 eV, P 2p 134.2 eV, for magnesium enriched, the obtained at 200 V<sub>pp</sub> AC 50 Hz coatings, the peaks are C1 s 284.8 eV, O1 s 532.0 eV, Ti 2p<sub>3/2</sub> 460.2 eV, Mg KLL 306.9 eV, P 2s 191.8 eV, P 2p 134.6 eV.



**Figure 2.** SEM images of PEO coatings obtained under DC or AC PEO process, with magnification of 5000×, in the electrolytes consisting of H<sub>3</sub>PO<sub>4</sub> with Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O or Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O



**Figure 3.** EDS spectra of coatings obtained with: a) DC-PEO enriched in calcium at 450 V, b) DC-PEO enriched in magnesium at 450 V, c) AC-PEO enriched in calcium at 200 V<sub>pp</sub> 50 Hz, d) AC-PEO enriched in magnesium at 200 V<sub>pp</sub> 50 Hz



**Figure 4.** XPS spectra of coatings obtained with: a) DC-PEO enriched in calcium at 450 V, b) DC-PEO enriched in magnesium at 450 V, c) AC-PEO enriched in calcium at 200 V<sub>pp</sub> 50 Hz, and d) AC-PEO enriched in magnesium at 200 V<sub>pp</sub> 50 Hz

#### 4. Conclusions

- Used DC or AC voltage regimes are appropriate to produce porous coatings on CP Titanium Grade 2 with use of electrolytes based on concentrated phosphoric(V) acid with calcium or magnesium nitrates.
- Different morphologies can be obtained when the applied voltage regimes are changed. In case of the use of 450 V DC, a coarser morphology is obtained in comparison with 200 V<sub>pp</sub> AC when calcium or magnesium enriched coatings are produced.
- When AC PEO process is used it is more likely to produce coatings with higher calcium or magnesium-to-phosphorus ratios measured by EDS, and this trend is stronger for calcium enriched coatings.
- Both morphology, chemical composition, and other coatings characteristics are influenced by the process parameters in a complex way, so it can be described only as a black box system where exact physicochemical mechanisms are not fully explained by constitution equations. However, systematic research can be analyzed and the black box models may be created with the use of neural networks [19-22].
- Top 10 nm of coatings, what in case of biomedical and catalysis application is in direct contact with the environment, contain different possible phosphates(V) in the form of anions as well as cations of titanium(IV) and calcium or magnesium which is important for possible biomedical or catalysis applications.

#### Acknowledgments

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