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SEM, EDS, AND XPS CHARACTERIZATION OF COATINGS OBTAINED ON TITANIUM DURING AC PLASMA ELECTROLYTIC PROCESS ENRICHED IN MAGNESIUM

ABSTRACT

Plasma Electrolytic Oxidation (PEO) known also as Micro Arc Oxidation (MAO) process is widely used to fabricate porous coatings on titanium and its alloys mainly in water- and acid-based solutions to different applications, e.g. in biomaterials, catalysts, and sensors. In the present paper, the SEM, EDS, and XPS results of porous coatings obtained by PEO treatment on titanium in electrolytes based on concentrated phosphoric H_3PO_4 acid with calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$, or magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$, or zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ for 3 minutes at 200 Vpp (peak to peak) with frequency of 50 Hz, are presented. Based on EDS results, the Ca/P, Mg/P, and Zn/P ratios, which equal to 0.95, 0.176, and 0.231, respectively, were found out. The XPS studies of the top 10 nm of the porous layer clearly indicate that it contains mainly phosphates (PO_4^{3-} and/or HPO_4^{2-} and/or $H_2PO_4^-$, and/or $P_2O_7^{4-}$) with titanium (Ti^{4+}) and calcium (Ca^{2+}) or magnesium (Mg^{2+}), or zinc (Zn^{2+}).

Keywords: *Plasma Electrolytic Oxidation (PEO), Micro Arc Oxidation (MAO), CP Titanium Grade 2, calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$, magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$, zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$*

INTRODUCTION

Nano-passive layers may be obtained by electrochemical treatments, such as standard and high-current density electropolishing (EP) [1-2] as well as magnetoelectropolishing (MEP) [3-4], while the thicker (micrometer scale) and more biocompatible coatings may be obtained by Plasma Electrolytic Oxidation (Micro Arc Oxidation) processes, e.g. under DC [5], DC pulsed [6] and AC [7] regimes on titanium [8] and its alloys (Ti6Al4V [9-10], Ti-15Mo [11], NiTi [12], Ti-6Al-7Nb [13], Ti-Nb-Zr-Sn [14]). It should also be pointed out that the PEO coatings may be

used inter alia in biomaterials [15], sensors [16], and aerospace applications [17]. In previous works, the analysis of porous PEO coatings obtained on titanium under DC regime in electrolytes based on concentrated phosphoric acid with nitrates of copper [18], calcium [19], magnesium [20], zinc [20], were described, that may be a solid basis for further research on AC-PEO coatings, what is presented in this paper.

EXPERIMENTAL

Samples of CP Titanium Grade 2 with dimensions of 10 mm × 10 mm × 2 mm were used for treatment in plasma electrolytic oxidation (PEO) process. Voltage of 200 V_{pp} with the use of 50 Hz AC power transformer was employed for titanium treatment. Electrolytes were composed of 500 g calcium nitrate tetrahydrate Ca(NO₃)₂·4H₂O in 1 L of concentrated 85% phosphoric acid H₃PO₄ or 500 g magnesium nitrate hexahydrate Mg(NO₃)₂·6H₂O in 1 L of concentrated 85% phosphoric acid H₃PO₄ or 500 g zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O in 1 L of concentrated 85% phosphoric acid H₃PO₄. The process was performed in a glass vessel with 500 mL of electrolyte for 3 minutes. The Scanning Electron Microscope (SEM) FEI Quanta 650 FEG equipped with Energy-Dispersive X-ray Spectroscopy (EDS) for surface analysis was employed. The microscope operated under the following conditions: voltage 15 kV, current 8-10 nA, chamber pressure 10⁻⁵ Pa. The identification of spectral lines was performed by means of spectral decomposition using the holographic peak deconvolution function. The X-ray photoelectron spectroscopy (XPS) measurements on studied sample surfaces were performed by means of SCIENCE SES 2002 instrument (SCIENTA AB, ScientaOmicron, Uppsala, Sweden) using a monochromatic (Gammadata-Scienta) Al K(alpha), (h ν = 1486.6 eV) X-ray source (18.7 mA, 13.02 kV). Scan analyses were carried out with an analysis area of 1 mm × 3 mm and a pass energy of 500 eV with the energy step 0.2 eV and a step time 200 ms. The binding energy of the spectrometer was calibrated by the position of the Fermi level on a clean metallic sample. The power supplies were stable and of high accuracy. The experiments were carried out in an ultra-high vacuum system (SCIENTA AB, ScientaOmicron, Uppsala, Sweden) with a base pressure of about 6 × 10⁻⁸ Pa. The XPS spectra were recorded in normal emission. For the XPS analyses, the CasaXPS 2.3.14 software (Casa Software Ltd., Teignmouth, Devon, UK) (Shirley background type, D.A. Shirley, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, USA), were used. All the binding energy values presented in this paper were charge corrected to C 1s at 284.8 eV.

RESULTS

In Figure 1, the SEM images (Fig. 1 a-e) and EDS results (Fig. 1 f) of titanium samples obtained by PEO treatment at 200 V_{pp} in electrolyte with concentration of 500 g Ca(NO₃)₂·4H₂O per 1 L of 85% H₃PO₄ during 3 min plasma electrolytic oxidation process, are displayed. Based on the obtained SEM images, the morphology of obtained samples may be described as porous and well developed, where the sharp edges are present. In Figure 1f, the example of EDS spectrum is shown, where the peaks of phosphorus, calcium and titanium, are recorded. Whereas

there is no doubt that the calcium and phosphorus peaks origin from coatings obtained during the PEO process, the titanium peak may origin from both, obtained coatings and metallic matrix. Therefore, as an independent measure parameter of the mentioned phenomena, metal-to-phosphorus ratio (here: calcium-to-phosphorus Ca/P ratio), is additionally presented.

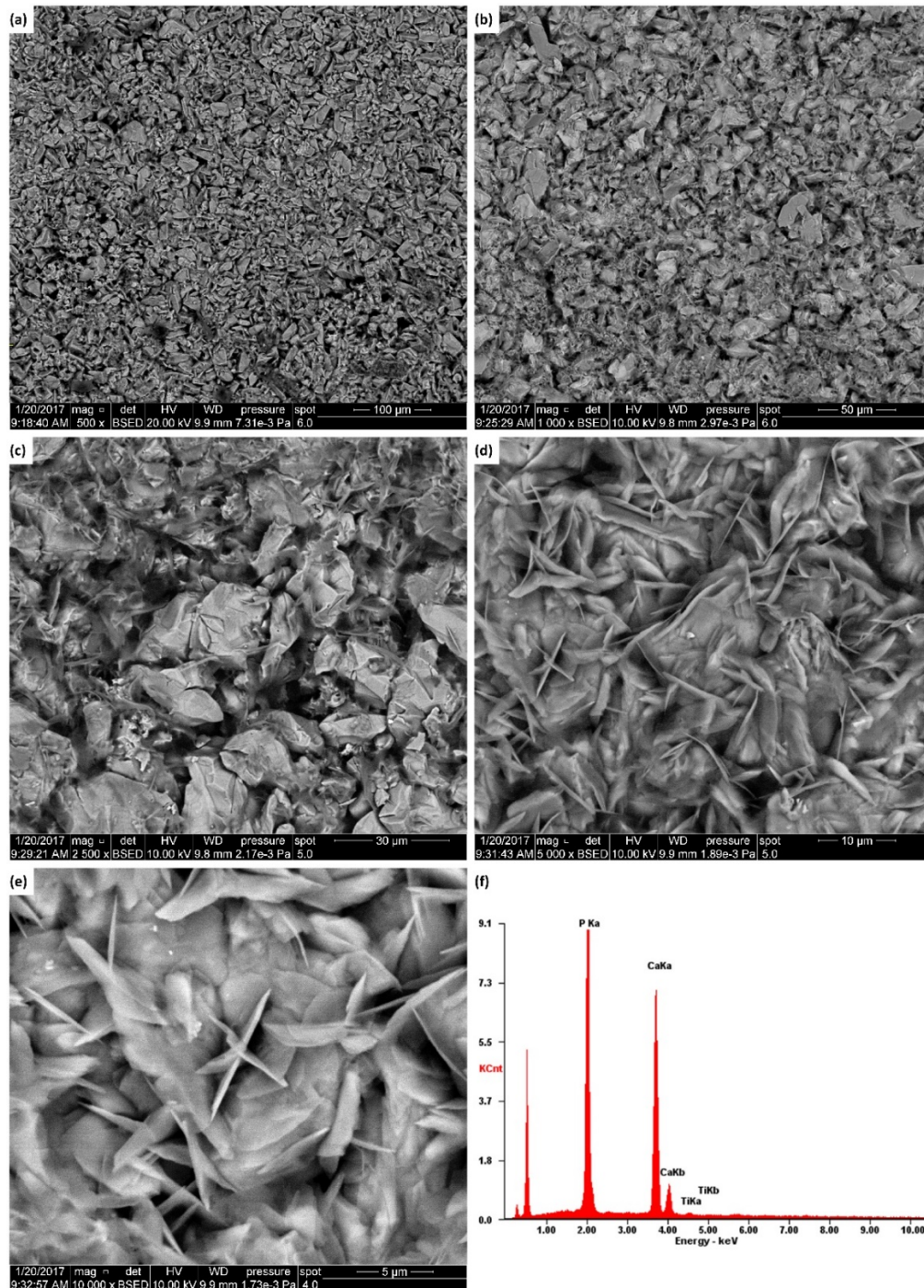


Fig. 1. SEM micrographs with magnifications: 500 times (a), 1000 times (b), 2500 times (c), 5000 times (d), 10000 times (e), and EDS spectrum (f) for samples obtained in AC PEO process in electrolyte consisting of 500 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 V_{pp} for 3 min

The EDS measurements results (Table 1) for samples obtained at 200 Vpp in electrolyte with concentration of 500 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per 1 L of 85% H_3PO_4 during 3 min of plasma electrolytic oxidation process as (mean \pm standard deviation) for calcium, phosphorus, and titanium, equaling to (48.3 ± 0.5) at%, (50.9 ± 0.3) at%, (0.8 ± 0.2) at%, respectively, and the Ca/P ratio equaling to 0.950 ± 0.015 , were calculated. In our previous paper [19] it has been reported that Ca/P ratio (0.08 ± 0.01) of coatings obtained at 450 ± 46 V with pulsation of 300 Hz was over ten times lower than Ca/P value (0.950 ± 0.015) presented in this paper. It may be explained by differences in coatings' structural composition. In Figure 2, the XPS spectra for the samples obtained at 200 Vpp in electrolyte with concentration of 500 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per 1 L of 85% H_3PO_4 during 3 min of plasma electrolytic oxidation, are presented. The obtained data prove the presence of calcium as Ca^{2+} (Ca2s, 439.1 eV), titanium as Ti^{4+} (Ti2p, 347.5 eV), phosphates/polyphosphates as PO_4^{3-} and/or HPO_4^{2-} and/or H_2PO_4^- , and/or $\text{P}_2\text{O}_7^{4-}$ (P2s, 191.2 eV; P2p, 134.0 eV; O1s, 531.5 eV). Based on XPS studies, the top 10 nm surface layer of the obtained coatings was containing most likely calcium and/or titanium(IV) phosphates, what was also reported in reference [19].

Table 1. EDS results for samples obtained in AC PEO process in electrolyte consisting of 500 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 Vpp for 3 min

Ca [at%]	P [at%]	Ti [at%]	Ca/P
48.3 ± 0.5	50.9 ± 0.3	0.8 ± 0.2	0.950 ± 0.015

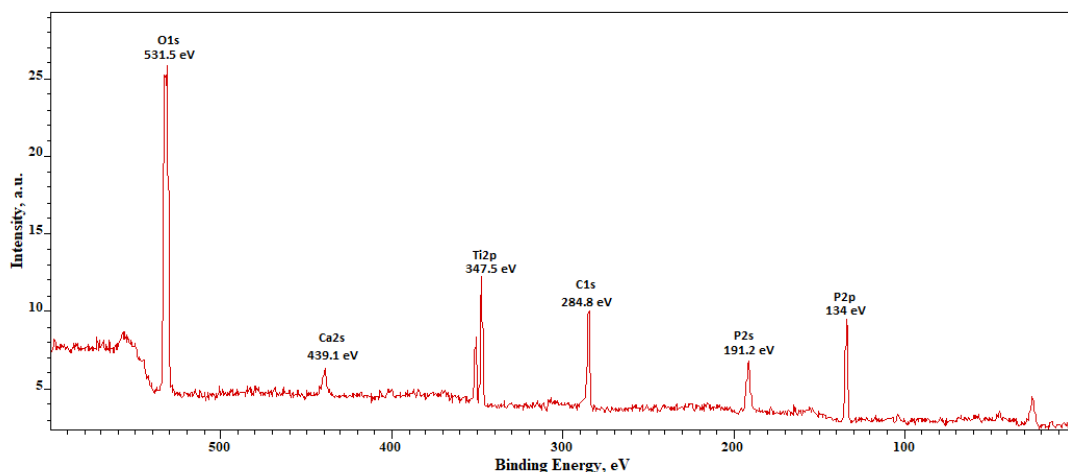


Fig. 2. X-ray Photoelectron Spectroscopy (XPS) spectrum of coating obtained in AC-PEO process in electrolyte containing 500 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 Vpp

The coatings enriched in magnesium, which SEM micrographs are presented in Figure 3 (a-e), were obtained at 200 Vpp in electrolyte containing 500 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per 1 L of 85% H_3PO_4 during 3 min of plasma electrolytic oxidation process. Their structures are porous with well-developed surface, but the external pore shapes are different than those ones enriched in calcium, i.e. they have more round-like shapes. The example of EDS spectrum, in which magnesium, phosphorus and titanium are present, is displayed in Figure 3 (f). The EDS results (Table 2) revealing magnesium, phosphorus, and titanium with elemental concentrations equaling to 8.8 ± 0.5 at%, 49.9 ± 0.6 at% and 41.3 ± 1.1 at%, respectively, and Mg/P ratio equaling to 0.176 ± 0.008 , were designated. In our previous paper [20], in which the EDS results of porous

coatings obtained in the same electrolyte composition, but under DC voltages, i.e. 500 V and 650 V, the Mg/P ratios equaled to 0.16 ± 0.01 and 0.17 ± 0.01 , respectively. Based on those data, a similarity may be noticed between the coatings formed under DC and AC conditions.

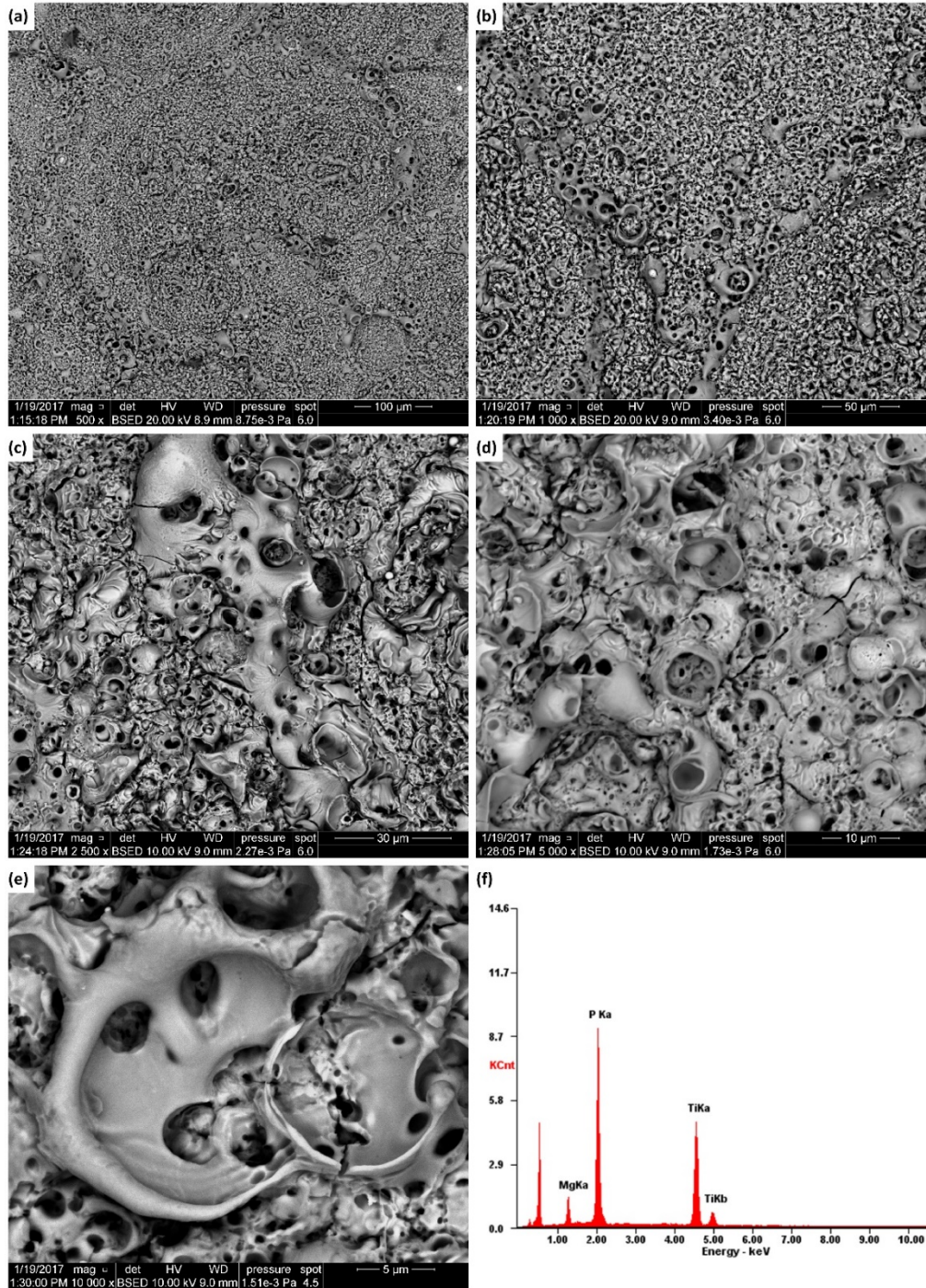


Fig. 3. SEM micrographs with magnifications: 500 times (a), 1000 times (b), 2500 times (c), 5000 times (d), 10000 times (e), and EDS spectrum (f) for samples obtained in AC PEO process in electrolyte consisting of 500 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 Vpp for 3 min

The XPS spectrum of coating obtained on titanium sample at 200 Vpp in electrolyte with 500 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per 1 L of 85% H_3PO_4 during 3 min of plasma electrolytic oxidation process is presented in Figure 4. Based on these XPS data, it is possible to state that in the top-nano-sublayer there are compounds containing mainly magnesium Mg^{2+} (Mg KLL, 306.7 eV; Mg 2s, 89.3 eV), titanium Ti^{4+} (Ti2p, 459.5 eV), and phosphates and/or polyphosphates PO_4^{3-} and/or HPO_4^{2-} and/or H_2PO_4^- , $\text{P}_2\text{O}_7^{4-}$ (P2s, 190.8 eV; P2p, 133.7 eV; O1s, 531.9 eV), what is consistent with the results presented in reference [20].

Table 2. EDS results for samples obtained in AC PEO process in electrolyte consisting of 500 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 Vpp for 3 min

Mg [at%]	P [at%]	Ti [at%]	Mg/P
8.8 ± 0.5	49.9 ± 0.6	41.3 ± 1.1	0.176 ± 0.008

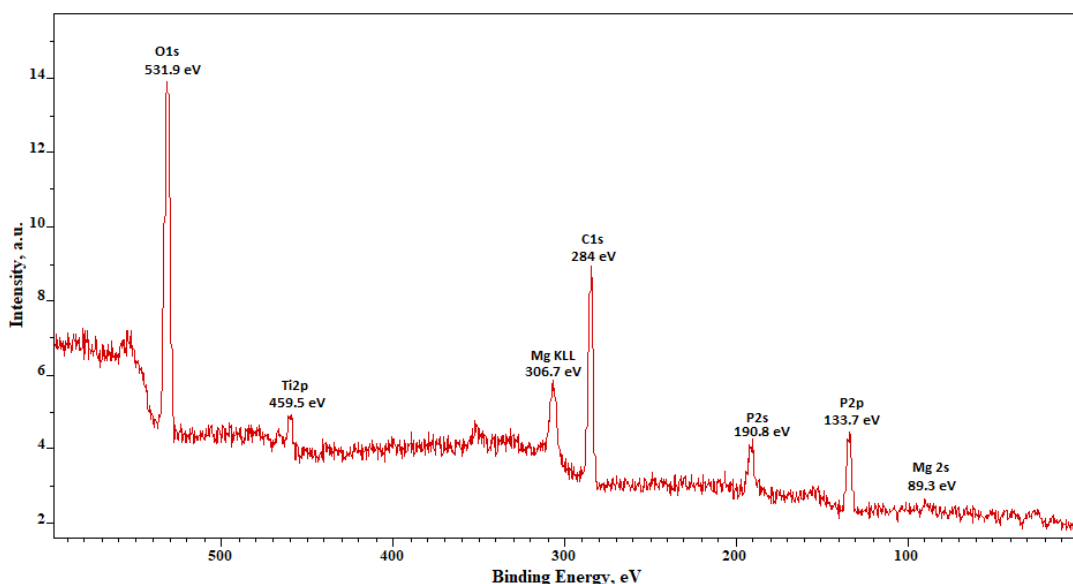


Fig. 4. X-ray Photoelectron Spectroscopy (XPS) spectra of samples obtained in AC PEO process in electrolyte consisting of 500 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 Vpp for 3 min

In Figure 5 (a-f), the SEM images of PEO coatings obtained at 200 Vpp in electrolyte with concentration of 500 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per 1 L of 85% H_3PO_4 during 3 min of plasma electrolytic oxidation process, are presented. Morphologies of these samples are similar to those ones obtained at 200 Vpp in electrolyte with concentration of 500 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per 1 L of 85% H_3PO_4 during 3 min of PEO process.

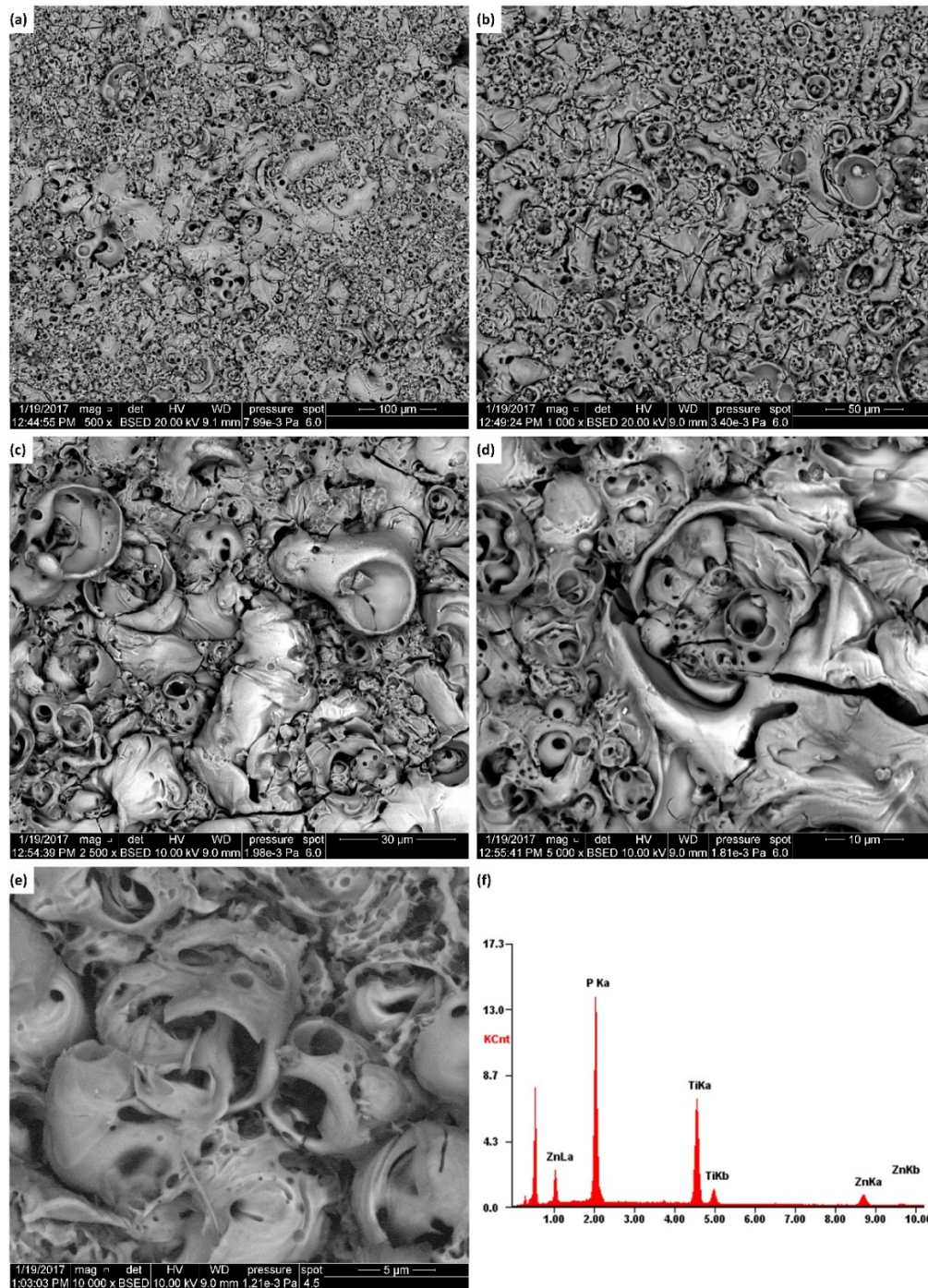


Fig. 5. SEM micrographs with magnifications: 500 times (a), 1000 times (b), 2500 times (c), 5000 times (d), 10000 times (e) and EDS spectrum (f) for samples obtained in AC PEO process in electrolyte consisting of 500 g $Zn(NO_3)_2 \cdot 6H_2O$ in 1 L of H_3PO_4 at 200 Vpp for 3 min

Based on EDS results of zinc enriched coatings (Table 3), the presence of zinc, phosphorus and titanium elements, was confirmed. The atomic concentrations of zinc, phosphorus and titanium in these coatings are equaling to 11.7 ± 0.7 , 50.6 ± 0.3 , 37.7 ± 0.7 , respectively. The

Zn/P ratio equals to 0.231 ± 0.014 and it is close to the value from the reference [20], i.e. 0.12 - 0.20 (500 V- 650 V).

The XPS spectra of sample obtained at 200 Vpp in electrolyte with concentration of 500 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per 1 L of 85% concentrated H_3PO_4 during 3 min of plasma electrolytic oxidation process are presented in Figure 6. Based on these results, it may be stated that external, top part of coatings consists mainly of zinc Zn^{2+} (Zn2s, 1021.3 eV), titanium Ti^{4+} (Ti2p, 459.6 eV), and phosphates PO_4^{3-} and/or HPO_4^{2-} and/or H_2PO_4^- , and/or $\text{P}_2\text{O}_7^{4-}$ (P2s, 191.0 eV; P2p, 133.6 eV; O1s, 531.0 eV; O KLL 976.2 eV).

Table 3. EDS results for samples obtained in AC PEO process in electrolyte consisting of 500 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 Vpp

Zn [at%]	P [at%]	Ti [at%]	Zn/P
11.7 ± 0.7	50.6 ± 0.3	37.7 ± 0.7	0.231 ± 0.014

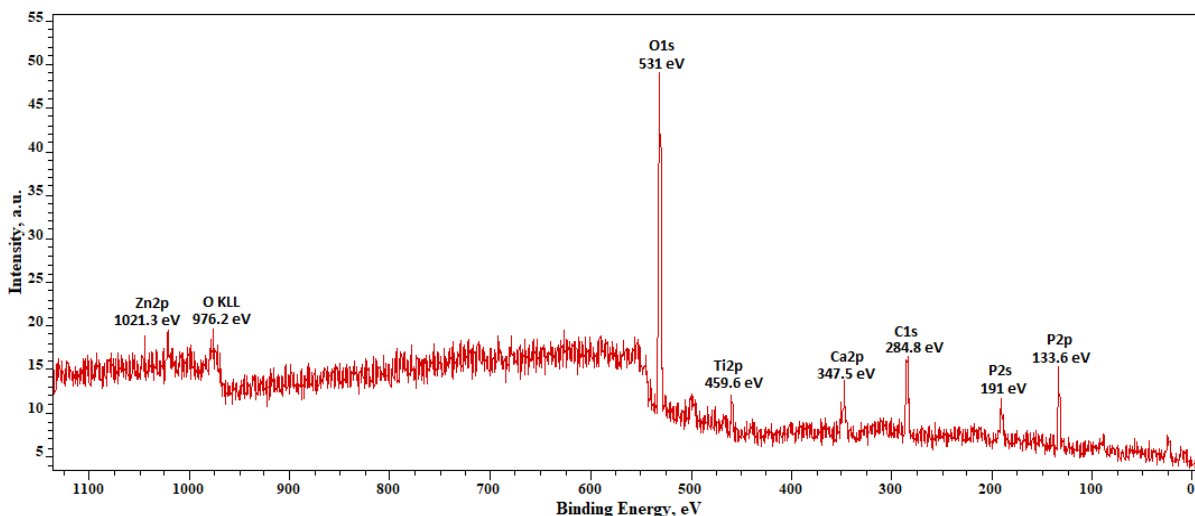


Fig. 6. X-ray Photoelectron Spectroscopy (XPS) spectra of samples obtained in AC PEO process in electrolyte consisting of 500 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1 L of H_3PO_4 at 200 Vpp for 3 min

To summarize, the EDS results of calcium, magnesium, zinc, phosphorus, and titanium atomic concentrations (a) and metal-to-phosphorus ratios (b) in Figure 7, are presented. Concentrations of calcium in the obtained coatings is significantly higher (more than four times) than concentrations of magnesium and zinc at the same voltage conditions, what is confirmed by differences between Ca/P, Mg/P, and Zn/P ratios.

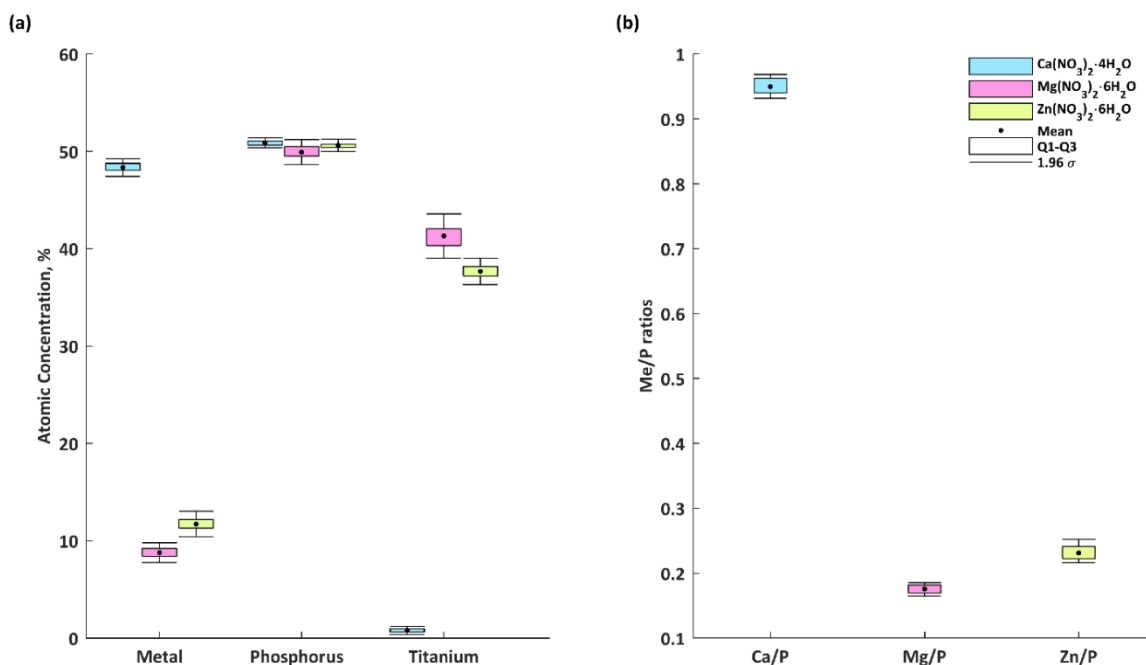


Fig. 7. EDS results for samples obtained in three electrolytes: Ca(NO₃)₂·4H₂O in 1 L of H₃PO₄; 500 g Mg(NO₃)₂·6H₂O in 1 L of H₃PO₄; 500 g Zn(NO₃)₂·6H₂O in 1 L of H₃PO₄ at 200 V_{pp} for 3 min

CONCLUSIONS

During the PEO processes performed for 3 minutes at the voltage of 200 V_{pp} with the use of 50 Hz AC power transformer it was possible to obtain porous coatings enriched in calcium, or magnesium, or zinc with visible differences in morphology. Based on EDS data analysis it is possible to state that the ratios are as follows: Ca/P >> Zn/P > Mg/P, that cannot be explained by differences in molar masses of salts used to prepare electrolytes, and most likely the mechanism of plasma electrolytic oxidation process, in these particular AC conditions, may play a main role. In all three obtained coatings, i.e. enriched with calcium, or magnesium, or zinc, beside the mentioned elements specific for type of the electrolyte, titanium as four-valent cations and phosphorus in the chemical form of phosphates/polyphosphates in the top 10 nm layer are present. This finding is in common with the previous publications [18-20]. The presence of phosphates of calcium, or magnesium, or zinc in the porous PEO coatings stands a very good forecast for application in the field of biomedicine.

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