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FABRICATION AND CHARACTERISATION OF POROUS, CALCIUM ENRICHED COATINGS ON TITANIUM AFTER PLASMA ELECTROLYTIC OXIDATION UNDER DC REGIME

ABSTRACT

The purpose of this work is to produce and characterize (chemical composition and roughness parameters) porous coatings enriched in calcium and phosphorus on the titanium (CP Titanium Grade 2) by plasma electrolytic oxidation. As an electrolyte, a mixture of phosphoric acid H_3PO_4 and calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$ was used. Based on obtained EDS and roughness results of PEO coatings, the effect of PEO voltages on the chemical composition and surface roughness of porous coatings was determined. With voltage increasing from 450 V to 650 V, the calcium in PEO coatings obtained in freshly prepared electrolyte was also found to increase. In addition, the Ca/P ratio increased linearly with voltage increasing according to the formula $Ca/P = 0.035 \cdot U + 0.176$ (by wt%) and $Ca/P = 0.03 \cdot U + 0.13$ (by at%). It was also noticed that the surface roughness increases with the voltage increasing, what is related to the change in coating porosity, *i.e.* the higher is the surface roughness, the bigger are pores sizes obtained.

Keywords: *Plasma Electrolytic Oxidation PEO, Micro Arc Oxidation MAO, SEM, titanium, porous coatings, concentrated phosphoric acid H_3PO_4, calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$*

INTRODUCTION

Titanium is used in many different ways all over the world, mostly for aerospace parts in jet engines and aircraft, but recently it has been used widely in the prosthetic industry and the artificial heart. It is used both in bioengineering, because of its biological compatibility, and for the catalysts construction. It should be also noted that titanium, despite of its higher prices than stainless steels, in many cases cannot be replaced by cheaper materials due to its mechanical and corrosive properties as well as very good biocompatibility. Fabrication of a suitable metal-based material for use in construction of implants or endoprosthesis is a huge challenge for engineer, who expected to obtain the material with appropriate strength, weight, and Young's modulus, which may have similar chemical composition and mechanical properties as a bone tissue. In addition, it should be resistant to corrosion in the environment of the living organism. It has to be also pointed that the surfaces which may be used as biomaterials should be treated additionally by several methods to improve their osseointegration. To prepare the nano-layers with expected chemical composition and mechanical properties, the electropolishing (EP) [1], magnetoelectropolishing (MEP) [2], and high-current density electropolishing (HDEP) [3] processes are employed, while for obtaining the micro scale layers, the Plasma Electrolytic Oxidation (PEO), known also as Micro Arc Oxidation (MAO) [4-6], should be used. That method may be used to oxidize inter alia the titanium [7-10], its alloys (Ti6Al4V [11-12], Ti6Al7Nb [13], NiTi [14], TiNbZr [15], TiNbZrSn [16]) as well as niobium [18] and tantalum [19]. In addition, it has to be pointed that PEO coatings may be enriched also in other elements, *i.e.* antibacterial copper [20] or zinc [21].

In the present paper, the Authors describe the porous surfaces obtained on titanium after PEO treatment under DC regime of voltage in the electrolyte containing concentrated (85%) phosphoric acid H_3PO_4 and zinc nitrate $Ca(NO_3)_2{\cdot}4H_2O$. A focus was directed on the calcium-to-phosphorus (Ca/P) ratio in the porous coatings obtained.

METHOD AND EXPERIMENTAL SET UP

Plasma Electrolytic Oxidation/Micro Arc Oxidation process was used for treating the samples of CP Titanium Grade 2 with dimensions 10 mm × 10 mm × 2 mm. The plasma electrolytic oxidation (PEO) was performed at the voltages of 450 V_{DC}, 550 V_{DC} and 650 V_{DC}. The electrolyte consisted of a concentrated 85% analytically pure H_3PO_4 (98 g/mole) acid, one liter, with 500 g of zinc nitrate $Ca(NO_3)_2{\cdot}4H_2O$ dissolved in it.

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, beam diameter 6 µm, decreased vacuum in the chamber with the pressure of 50 Pa. The identification of spectral lines was performed by means of spectral decomposition using the holographic peak deconvolution function. For graphical presentation of obtained data, the box-and-whisker plots with minimum, maximum, lower and upper quartiles and median, were used.

A computerized HOMMEL TESTER T800 system of Hommelwerke GmbH to study of surface roughness measurement was used. It was equipped with sliding measuring head Waveline 60 Basic/51808 and the sensor TKL100/17 MO435005. Measuring needle beam was equal to 3.5 µm with its angle of 87°. The tracing, evaluation and single measuring lengths, equal to 4.8, 4.0 and 0.8 mm, respectively, were used. Due to the porous surface, the non-contact methods for surface roughness [22] were not possible to be used, *inter alia* because of the uncertainties in measurement results [23]. According to the EN ISO 4287:1999 (Geometrical product specifications (GPS)—surface texture: profile method—terms, definitions and surface texture parameters) and DIN 4768 (Determination of values of surface roughness parameters Ra, Rz, Rmax using electrical contact (stylus) instruments; concepts and measuring conditions) standards, the following roughness parameters have been measured: arithmetic mean of the sum of roughness profile values (Ra), mean peak-to-valley height (Rz^{DIN}), ten-point height (Rz^{ISO}), total height of the roughness profile (Rt).

RESULTS

In Figure 1, the SEM images with different zoom lens (500×, 1000×, 5000×) and EDS spectrum of porous surface obtained on titanium after the PEO treatment at 450 V_{DC} for 3 minutes, in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL concentrated H_3PO_4, are presented. In Figure 2, the basic statistics of obtained EDS data, are shown. The average calcium content of the porous coating obtained on titanium in a new and fresh electrolyte after PEO treatment at 450 V_{DC} is equals to 9.4 ± 1.2 wt% (8.8 ± 1.1% at%), while phosphorus and titanium are 45.4 ± 0.5 wt% (55.4 ± 0.4 at%) and 45.3 ± 1.6 wt% (35.8 ± 1.4 at%), respectively. The coating also obtained at 450 V_{DC} in 3 minutes in the same electrolyte, which was already once used, contains the following amounts of calcium 8.8 ± 0.5 wt% (8.5 ± 0.4 at%), phosphorus 51.1 ± 0.6 wt% (41.4 ± 0.6 at%) and titanium 50.2 ± 1.0 wt% (40.4 ± 0.9 at%). The third PEO processing in the same electrolyte contains the following amounts of elements: calcium 9.8 ± 0.7 wt% (9.3 ± 0.6 at%), phosphorus 44.3 ± 0.5 wt% (54.4 ± 0, %) and titanium 45.9 ± 0.8 wt% (36.4 ± 0.7 at%).

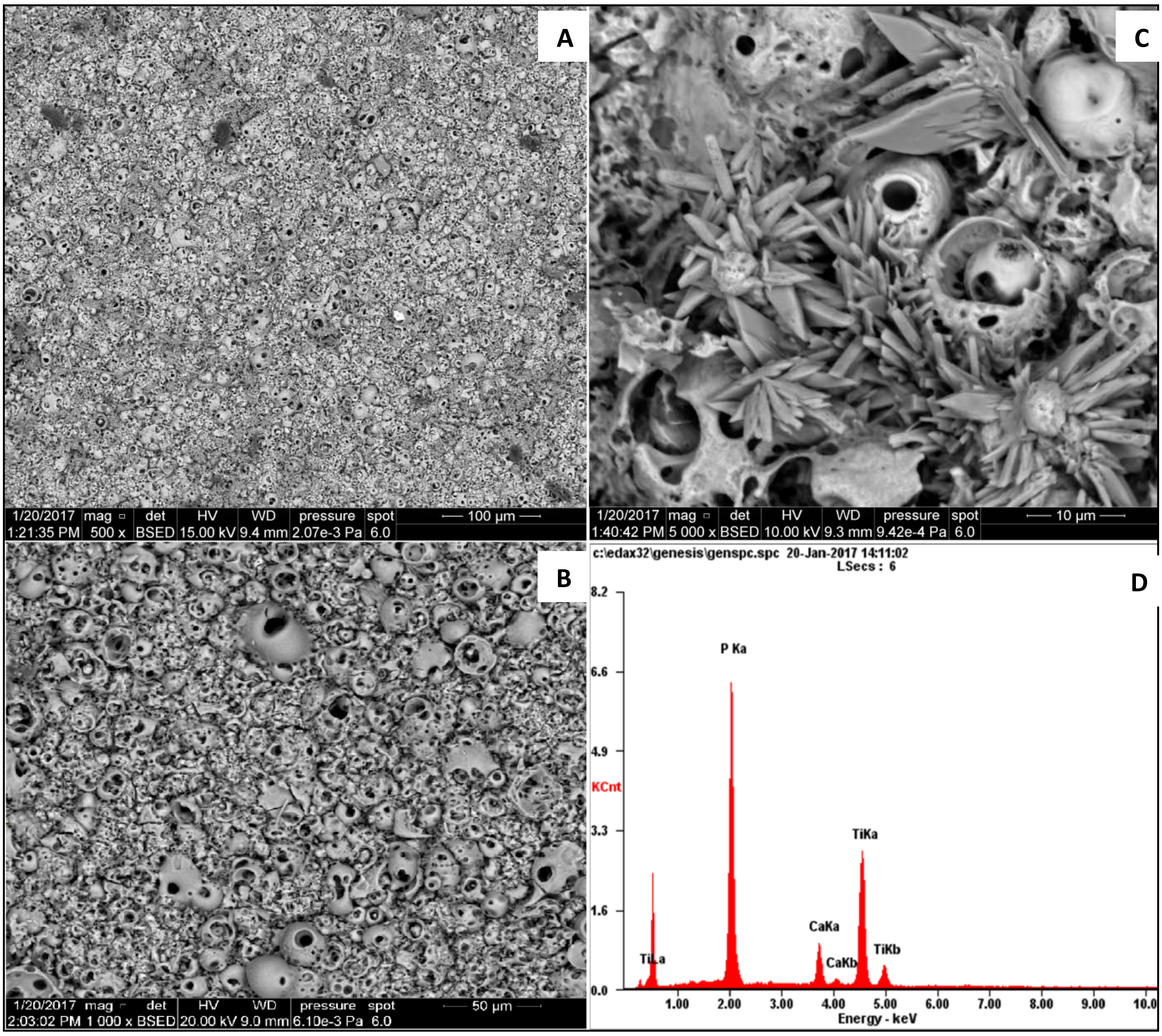

Fig. 1. SEM images (A-C) and EDS spectrum of coating obtained on Titanium after PEO treatment at 450 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL H_3PO_4; SEM magnifications: 500× (A), 1000× (B), 5000× (C); magnification for EDS analysis: 500×

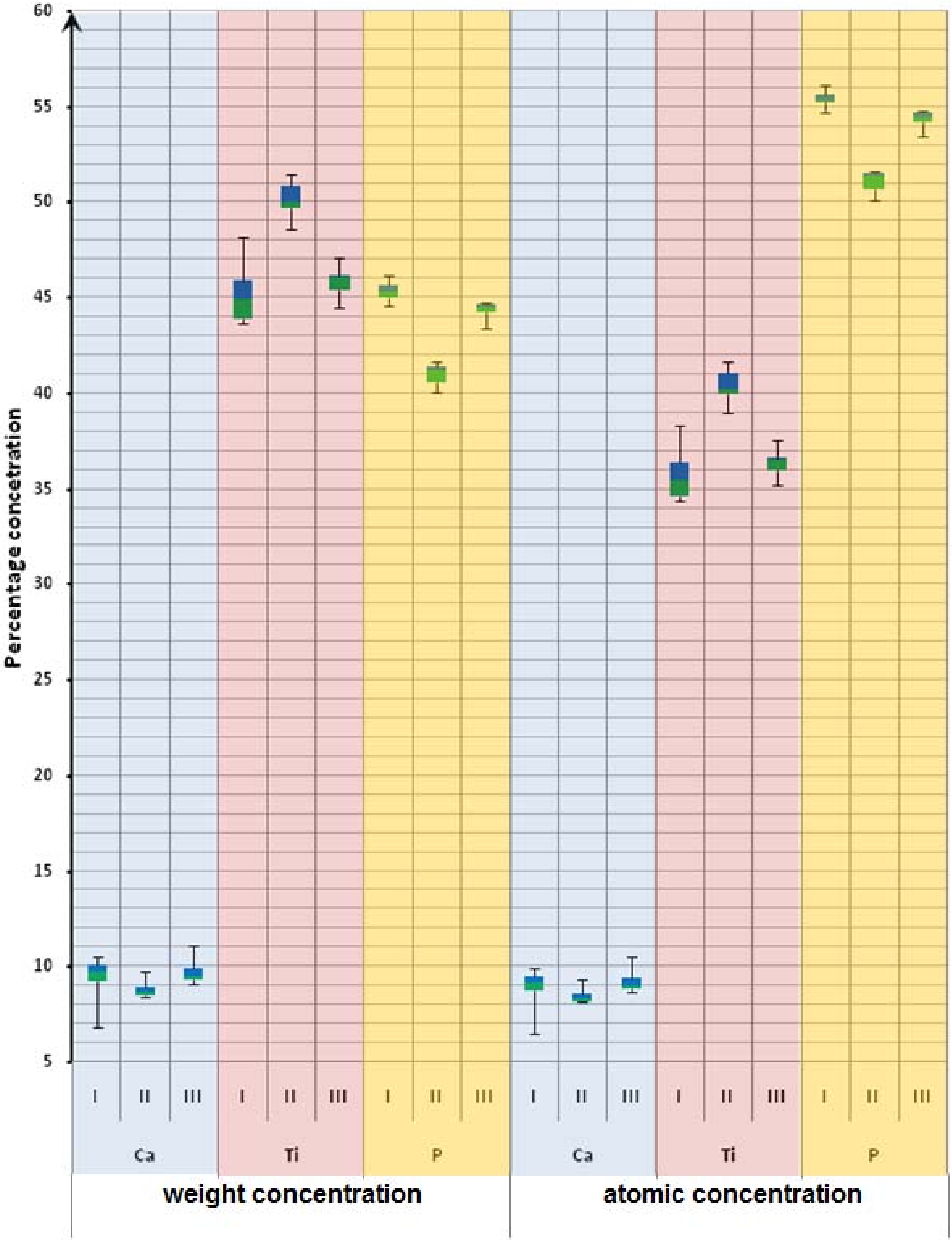

Fig. 2. Basic statistics of EDS results of coating obtained on Titanium after PEO treatment at 450 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL H_3PO_4

In Figure 3, the SEM images with different zoom lens (500×, 1000×, 5000×) and EDS spectrum of porous surface obtained on titanium after the PEO treatment at 550 V_{DC} in 3 minutes, in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL concentrated H_3PO_4, are presented. In Figure 4, the basic statistics of obtained EDS data, are shown. The average content of calcium in the coating obtained on titanium in a new electrolyte after PEO treatment at 550 V_{DC} is equals to 10.1 ± 0.2 wt% (9.7 ± 0.2%), while the contents of phosphorus and titanium are 40.6 ± 0.3 wt% (50.6 ± 0.3 at%) and 49.3 ± 0.2 wt% (39.7 ± 0.2 at%), respectively. The coating also obtained at 550 V_{DC} in 3 minutes in the electrolyte only once used contains the following amounts of calcium 9.9 ± 0.5 wt% (9.5 ± 0.4 at%), phosphorus 42.7 ± 0.3 wt% (52.7 ± 0.3 at%) and titanium 47.3 ± 0.5% (37.8 ± 0.5 at%). The third PEO processing in the same electrolyte contains the following amounts of calcium 8.9 ± 0.1 wt% (8.6 ± 0.1 at%), phosphorus 39.7 ± 0.5 wt% (49.8 ± 0,5 %) and titanium 51.3 ± 0.6 wt% (41.6 ± 0.5 at%).

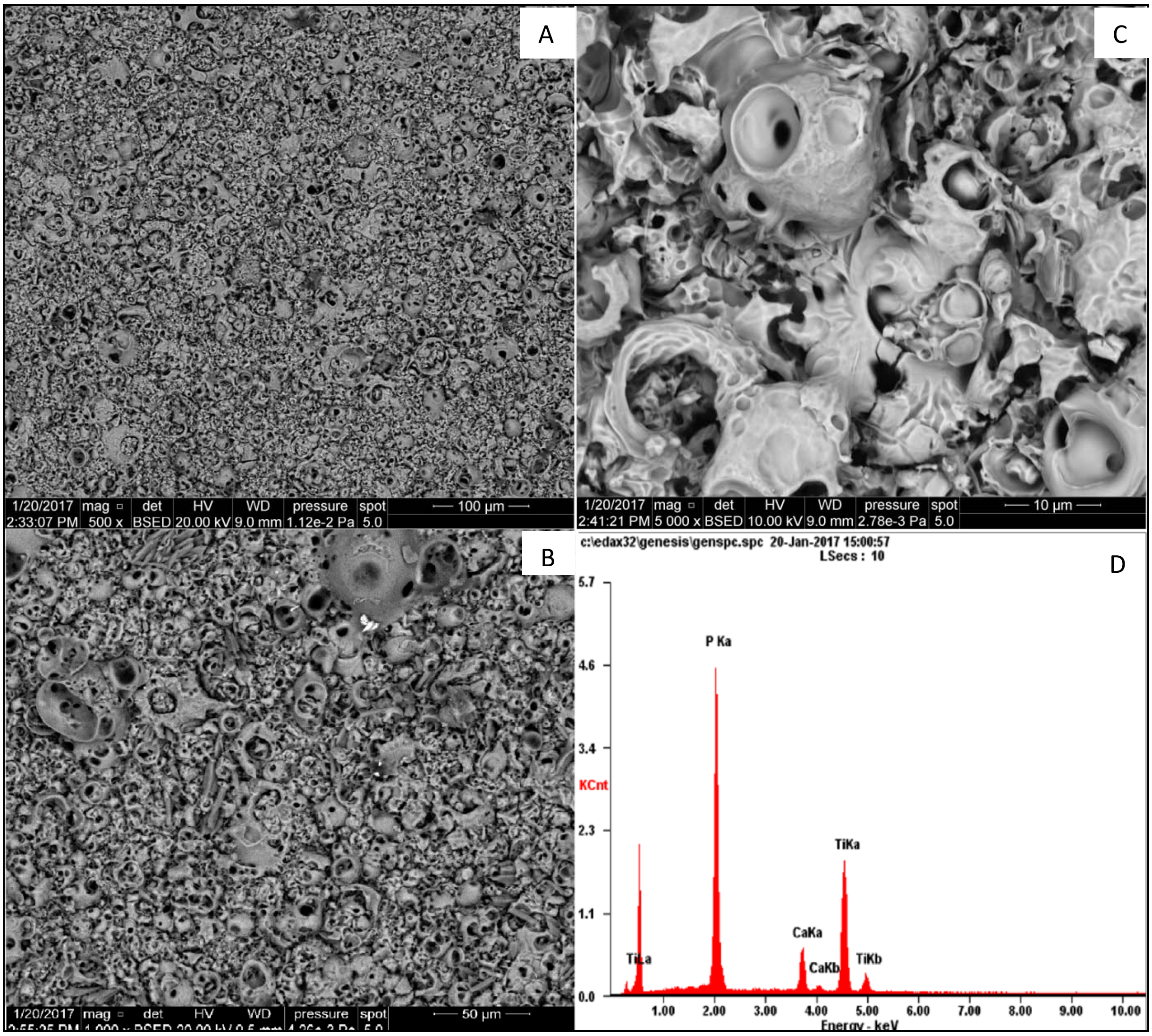

Fig. 3. SEM images (A-C) and EDS spectrum of coating obtained on Titanium after PEO treatment at 550 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL H_3PO_4; SEM magnifications: 500× (A), 1000× (B), 5000× (C); magnification for EDS analysis: 500×

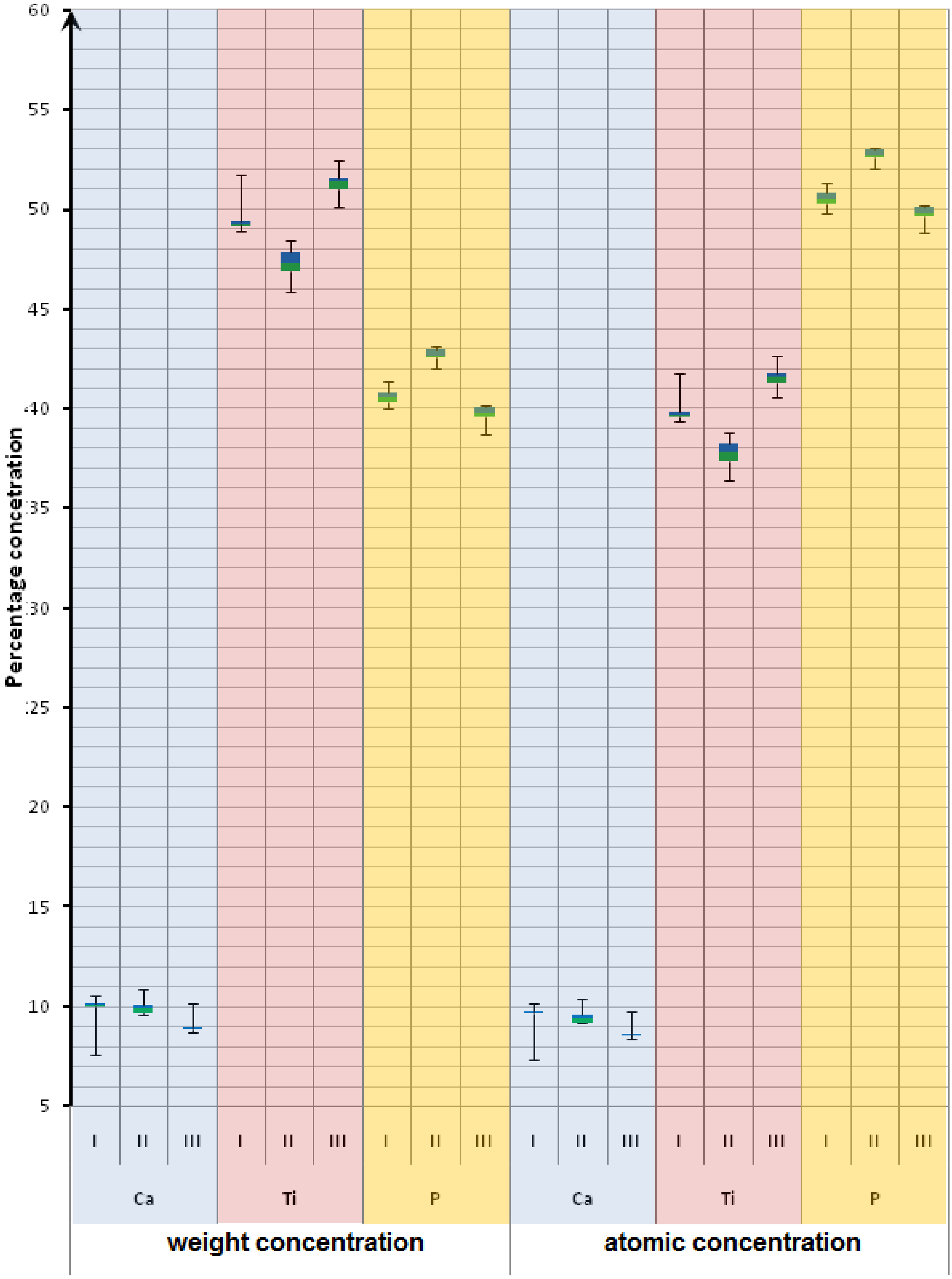

Fig. 4. Basic statistic of EDS results of coating obtained on Titanium after PEO treatment at 550 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL H_3PO_4

In Figure 5, the SEM images with different zoom lens (500×, 1000×, 5000×) and EDS spectrum of porous surface obtained on titanium after the PEO treatment at 650 V_{DC} in 3 minutes, in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL concentrated

H_3PO_4, are presented. In Figure 6, the basic statistics of obtained EDS data, are shown. The average content of calcium in the coating obtained on titanium in a new electrolyte after PEO treatment at 650 V_{DC} is 10.7 ± 0.1 wt% (10.4 ± 0.1 at%), while the contents of phosphorus and titanium are 37.6 ± 0.4 wt% (47.5 ± 0.5 at%) and 51.7 ± 0.4 wt% (42.1 ± 0.4 at%), respectively. The coating obtained at 650 V_{DC} in the electrolyte only once used contains calcium 10.1 ± 0.2 wt% (9.8 ± 0.2 at%), phosphorus 38.8 ± 0.4 wt% (48.7 ± 0.5 at%) and titanium 51.1 ± 0.3% (41.5 ± 0.3 at%). The third sample processed in the same electrolyte contains calcium 10.2 ± 0.6 wt% (9.9 ± 0.6 at%), phosphorus 39.8 ± 1.0 wt% (49.8 ±1 at%) and titanium 49.9 ± 1.4 wt% (40.3 ± 1.4 at%).

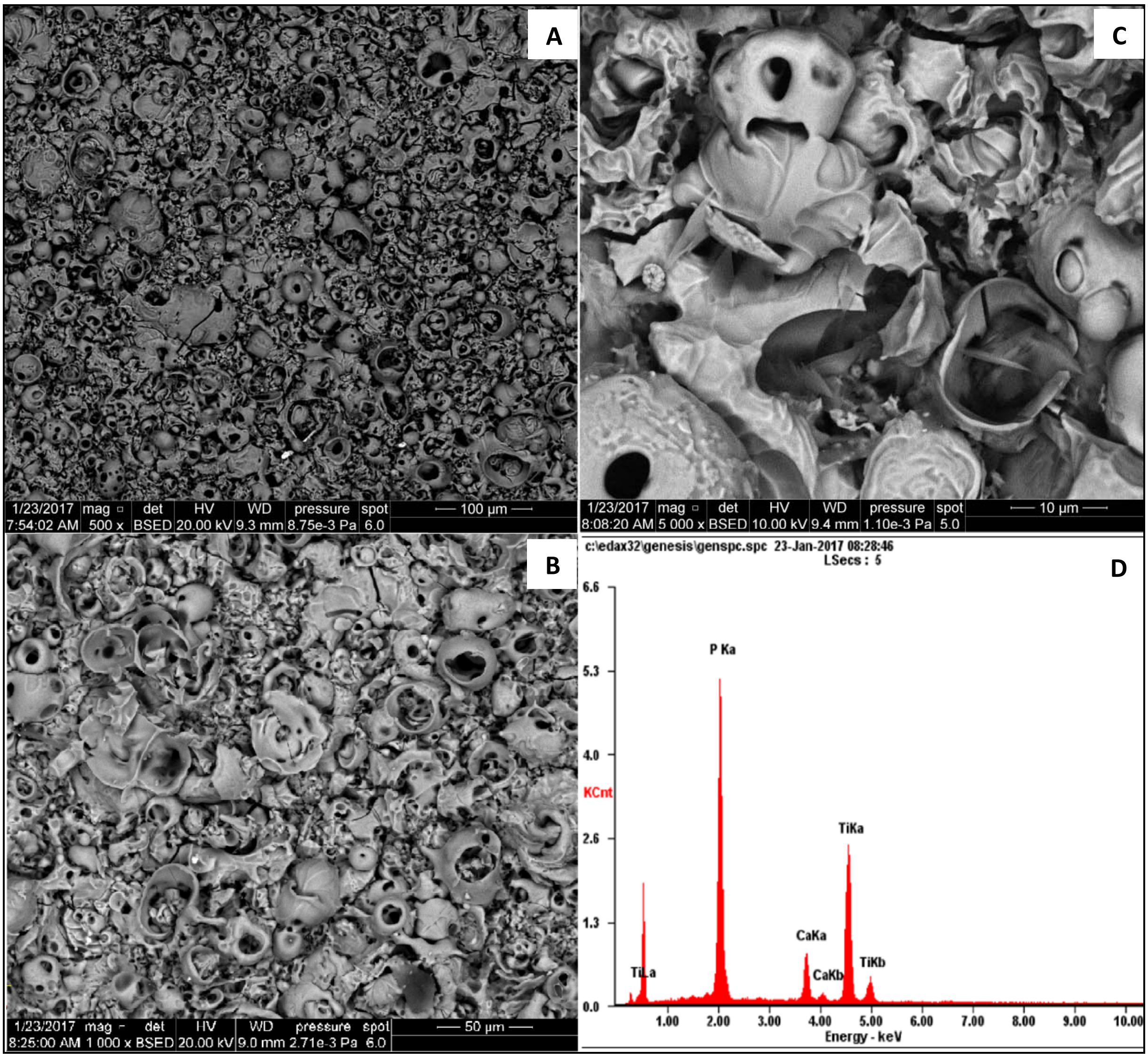

Fig. 5. SEM images (A-C) and EDS spectrum of coating obtained on Titanium after PEO treatment at 650 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2 \cdot 4H_2O$ in 1000 mL H_3PO_4; SEM magnifications: 500× (A), 1000× (B), 5000× (C); magnification for EDS analysis: 500×

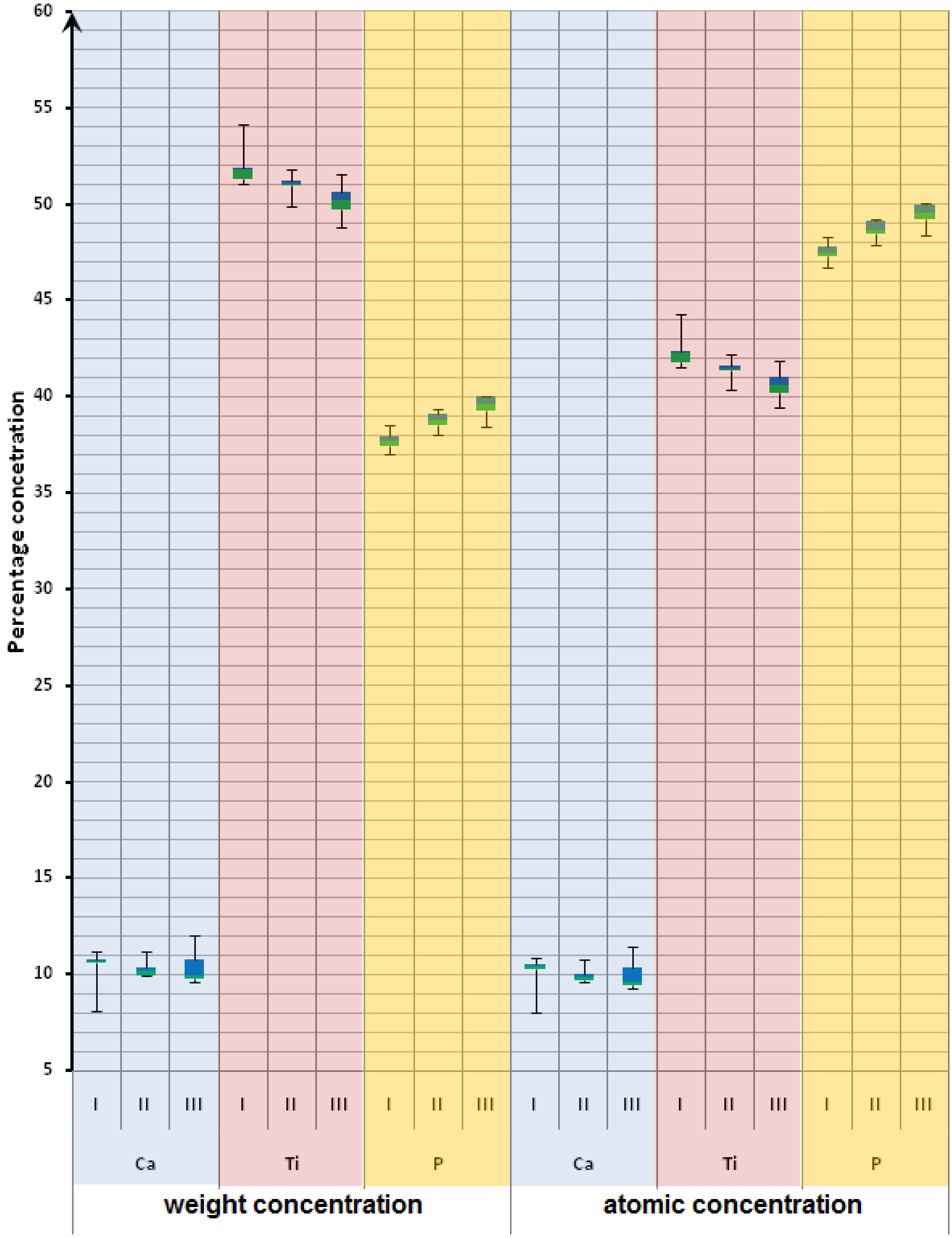

Fig. 6. Basic statistic of EDS results of coating obtained on Titanium after PEO treatment at 650 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2·4H_2O$ in 1000 mL H_3PO_4

In Figure 7, the Ca/P ratios of coatings obtained on Titanium after PEO treatment at 650 V_{DC} in 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2·4H_2O$ in 1000 mL

H_3PO_4, are presented. Based on these results, it should be stated that both the chemical composition and the porosity of these coatings depend both on the PEO voltage and on the "electrolyte aging". In order to enable any comparison of the obtained PEO coatings, it was decided to calculate the Ca/P ratios (Figure 7), which clearly indicates the differences between the obtained coatings. The results show that the increasing of PEO voltage causes a linear increasing of the calcium-to-phosphorus ratio, what may be mathematically described by the following equations: Ca/P = 0.035 · U + 0.176 (based on wt%) and Ca/P = 0.03 · U + 0.13 (based on at%).

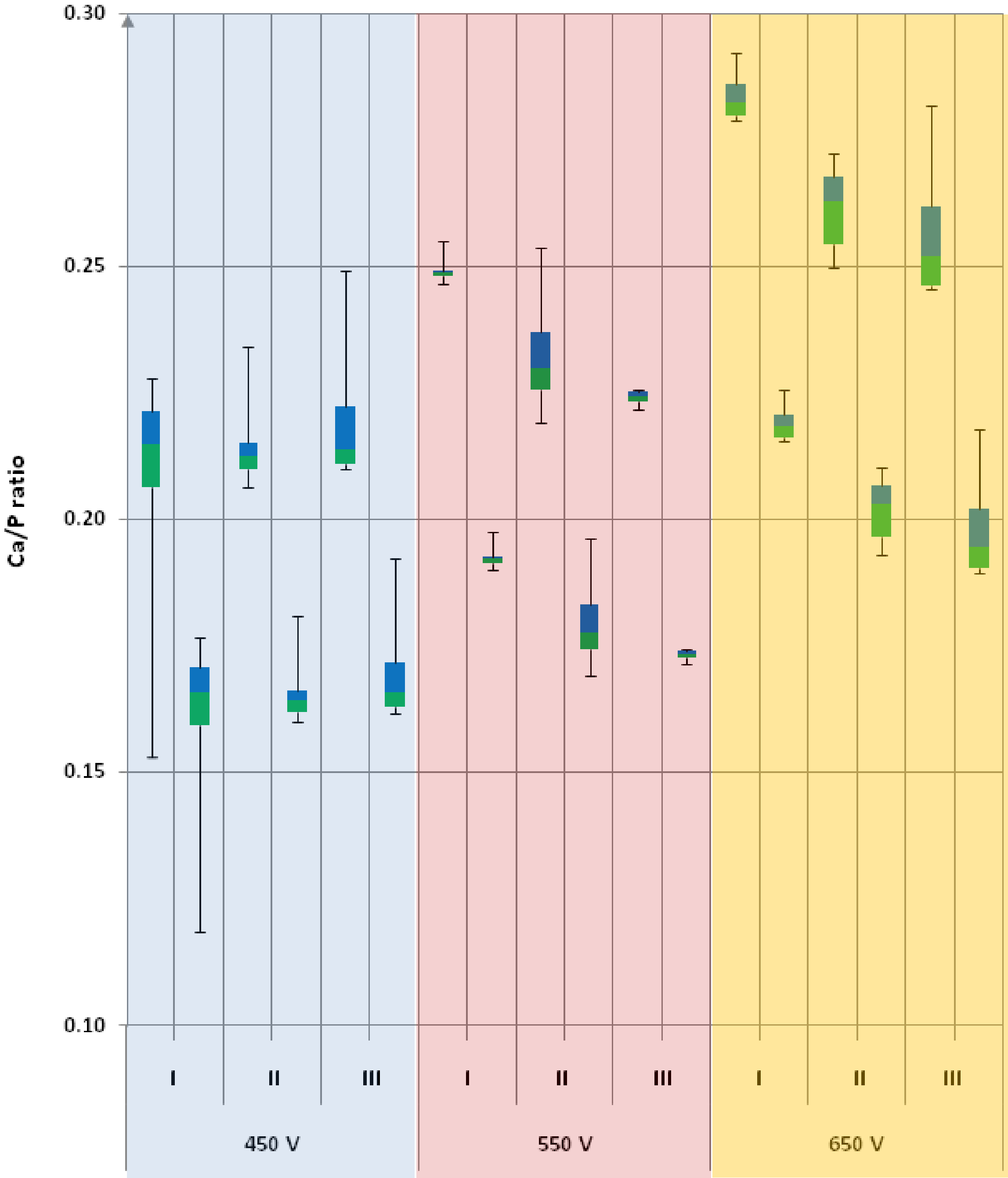

Fig. 7. Ca/P ratios of coating obtained on Titanium after PEO treatment at 650 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2 \cdot 4H_2O$ in 1000 mL H_3PO_4

In Figure 8, 2D roughness parameters (Ra, Rz, Rz^{ISO}, Rt) for PEO surfaces, are presented. It is visible that with PEO voltage increasing, the increasing of roughness parameters values is observed. In case of the first samples treated at 450 V_{DC} in a fresh electrolyte, the following Ra (1.86±0.46 µm), Rz (11.01±2.13 µm), Rz^{ISO} (12.82±4.02 µm) and Rt (16.78±4.71 µm) were found. The roughness parameters for the second samples in the same electrolyte after PEO treatment also at 450 V were equal: Ra (1.88±0.08 µm), Rz (12.11±1.24 µm), Rz^{ISO} (12.78±0.90 µm), Rt (17.45±2.81 µm); and for the third one, the Ra (1.45±0.14 µm), Rz (10.50±1.91 µm), Rz^{ISO} (11.31±1.80 µm) and Rt (16.46±2.76 µm) were found. The PEO coating, which was obtained at 550 V_{DC} as the first sample in new electrolyte, may be characterized by Ra (2.17±0.17 µm), Rz (13.83±1.74 µm), Rz^{ISO} (14.48±0.90 µm) and Rt (20.11±3.51 µm). The roughness parameters of second one in the solution only once used at 450 V is higher, *i.e.* Ra (2.43±0.15 µm), Rz (15.42±2.49 µm), Rz^{ISO} (15.69±1.92 µm) and Rt (19.17±3.41 µm). In case of the third one, processed in the same electrolyte, the roughness parameters were as follows: Ra (2.04±0.18 µm), Rz (13.28±0.92 µm), Rz^{ISO} (14.77±0.82 µm) and Rt (19.07±2.13 µm). After the PEO treatment at 650V_{DC} of titanium sample in a new electrolyte its surface has the following roughness parameters: Ra (4.86±0.52 µm), Rz (27.88±3.08 µm), Rz^{ISO} (30.17±3.10 µm), Rq (6.27±0.72 µm) and Rt (37.08±3.74 µm). Next sample in the same electrolyte has a higher roughness, characterized by the following parameters: Ra (3.53±0.29 µm), Rz (20.56±2.27 µm), Rz^{ISO} (21.54±2.29 µm) and Rt (27.28±5.09 µm). In case of the third one, the obtained results were as follows: Ra (4.33±0.46 µm), Rz (25.76±2.10 µm), Rz^{ISO} (26.94±2.61 µm), Rq (5.59±0.64 µm) and Rt (33.85±5.88 µm).

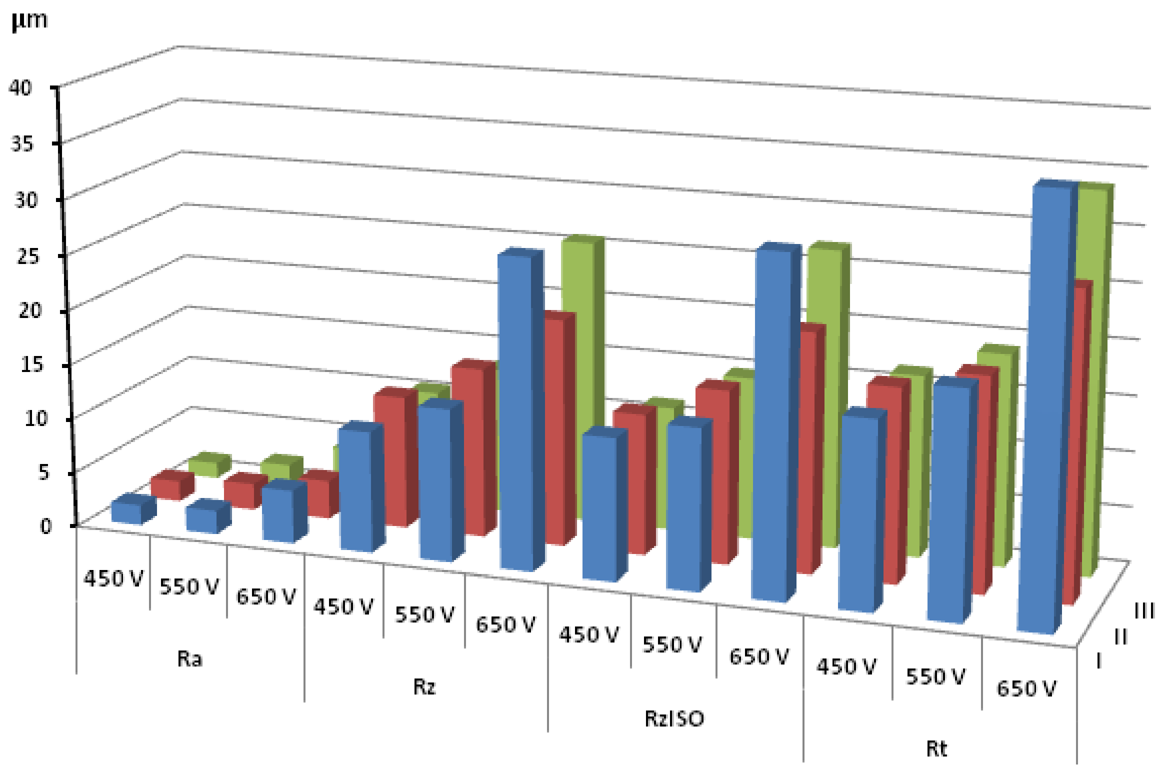

Fig. 8. Roughness parameters of porous coating obtained on Titanium after PEO treatment at 650 V_{DC} for 3 minutes in the electrolyte consisting of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1000 mL H_3PO_4

CONCLUSIONS

In this paper, the results of the porous coatings obtained by PEO treatment on titanium, with using of electrolytes containing of 500 g $Ca(NO_3)_2{\cdot}4H_2O$ in 1 L H_3PO_4, are described. Based on the results obtained, one may conclude that:

- it is possible to obtain porous coatings containing calcium and phosphorus on titanium substrate by plasma electrolytic oxidation at voltages of 450 V to 650 V in an electrolyte based on concentrated phosphoric acid H_3PO_4 and calcium nitrate $Ca(NO_3)_2{\cdot}4H_2O$
- the chemical composition of the PEO porous coatings depends on the PEO voltage; the higher voltage, the more calcium in the PEO coating is obtained
- Ca/P ratio increases linearly with increasing voltage from 450 V to 650 V
- the surface roughness of the porous coatings depends on the PEO voltage; with PEO voltage increasing, the surface roughness increases, too
- PEO treatment with potential of 650 V results in obtaining the surface roughness which is approximately twice as high in comparison with that one recorded for the coating obtained at 450 V.

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