

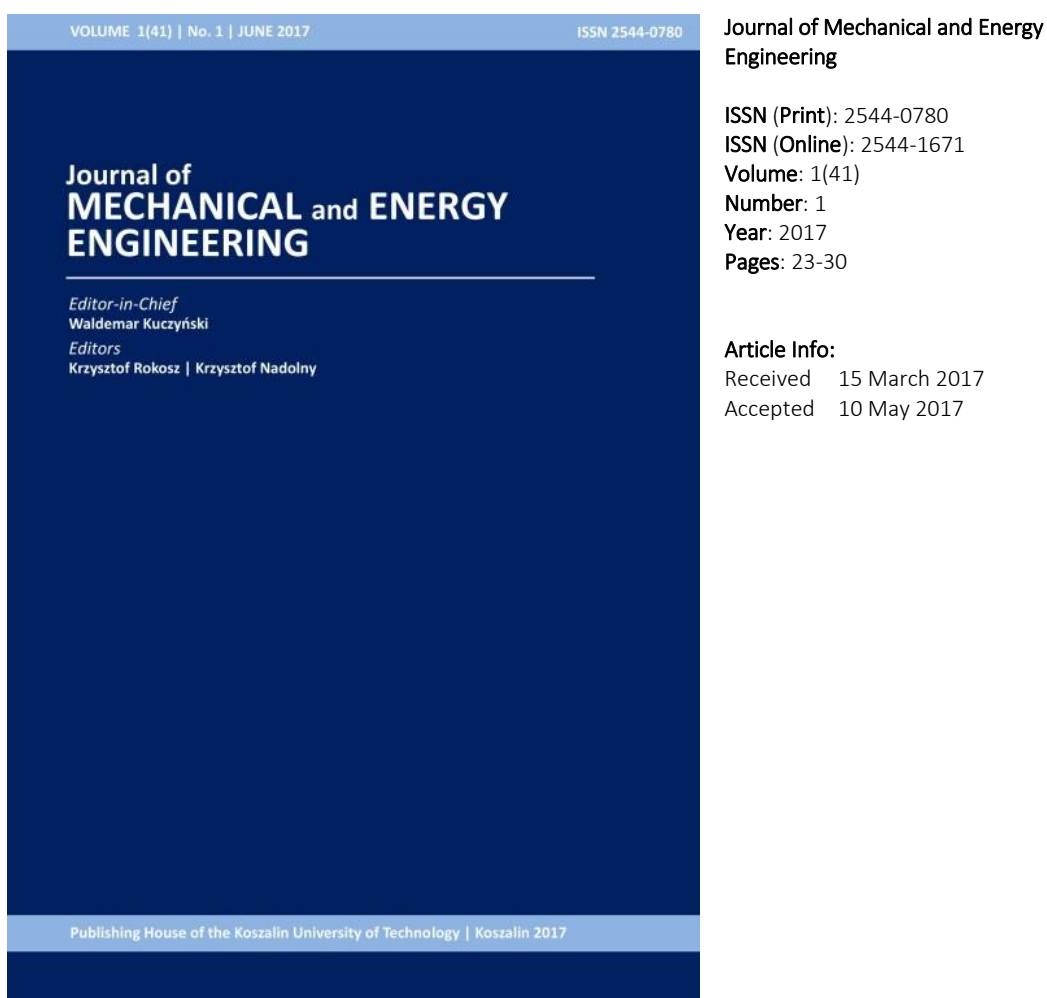
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Online: http://www.jmee.tu.koszalin.pl/download_article/jmee_2017_01_023030.pdf

Cite this article as:

Rokosz K., Hryniewicz T., Raaen S., Malorny W. Fabrication and characterisation of porous coatings obtained by plasma electrolytic oxidation. Journal of Mechanical and Energy Engineering, Vol. 1(41), No. 1, 2017, pp. 23-30.



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FABRICATION AND CHARACTERISATION OF POROUS COATINGS OBTAINED BY PLASMA ELECTROLYTIC OXIDATION

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(Received 15 March 2017, Accepted 10 May 2017)

Abstract: In the paper, characteristics of porous coatings enriched in copper on pure Titanium and its alloys (NiTi, Ti6Al4V, TNZ, Ti2448) as well as on niobium obtained by Plasma Electrolytic Oxidation (PEO) in electrolyte containing H_3PO_4 within $Cu(NO_3)_2$, are presented. All obtained surfaces of PEO coatings have different shapes and diameters of pores. The binding energies of main peaks for titanium $Ti2p_{3/2}$, niobium $Nb3d_{5/2}$, zirconium $Zr3d_{5/2}$, phosphorus (P2p) and oxygen (O1s) suggest the presence of titanium Ti^{4+} , niobium Nb^{5+} and zirconium Zr^{x+} ($x \leq 2$) as well as PO_4^{3-} .

Keywords: Plasma Electrolytic Oxidation (PEO), Micro Arc Oxidation (MAO), CP Titanium Grade 2, Niobium, Ti2448, Ti6Al4V, TNZ

1. INTRODUCTION

To prepare the porous surfaces for automotive and industrial catalysts as well as for metallic biomaterials it is necessary to use electrochemical methods. Bright, smooth and pore-free surfaces in nanometric scale are received after standard electropolishing [1-6], magneto-electropolishing [6-27], high-current density electropolishing [28-30], whereas for obtaining micro-layers the Plasma Electrolytic Oxidation known also as Micro Arc Oxidation [31-53], may be used.

2. MATERIALS AND METHODS

The plasma electrolytic oxidation (PEO) was performed at the average voltage of 450 ± 46 V with pulsation at frequency of 300 Hz as well as at $450V_{DC}$ without any pulsation. The main elements of the set-up are: processing cell, DC power supply, the electrodes and connecting wiring. For the studies, the electrolyte composed of orthophosphoric acid H_3PO_4 , with an addition of copper II nitrate, was used. For each run,

the electrolytic cell made of glass was used, containing up to 500 ml of the electrolyte.

The scanning electron microscope Quanta 250 FEI with Low Vacuum and ESEM mode and a field emission cathode as well as the energy dispersive EDX system in a Noran System Six with nitrogen-free silicon drift detector, were employed. The magnifications of 500 and 6000 times for SEM images were used. The EDS analyses were performed from the whole frame for magnification of 500 times.

The X-ray photoelectron spectroscopy (XPS) measurements on titanium samples were performed employing SCIENCE SES 2002 instrument using a monochromatic (Gammadata-Scienta) Al K(alpha) ($h\nu = 1486.6$ eV) X-ray source (18.7 mA, 13.02 kV). Scans analyses were carried out with an analysis area of $1 \text{ mm} \times 3 \text{ mm}$ and a pass energy of 500 eV with the energy step 0.2 eV and step time 200 ms. The binding energy of the spectrometer has been 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 with a base pressure of about $6 \cdot 10^{-8}$ Pa. The XPS spectra were recorded in normal emission. For the XPS analyses the CasaXPS 2.3.14 software (Shirley background type) [23] with the help of XPS tables [24-25] was used. All the binding energy values presented in that paper were charge corrected to C1s at 284.8 eV.

3. RESULTS AND DISCUSSION

In Figures 1 and 2 the SEM images of Titanium after PEO treatment at 450 V for 3 minutes in the electrolytes consisting of 300 g and 600 g of copper nitrate $\text{Cu}(\text{NO}_3)_2$ in 1000 mL of orthophosphoric acid H_3PO_4 are presented. The surfaces formed during PEO process are porous, however the shapes and diameters of pores are different for the two studied electrolytes.

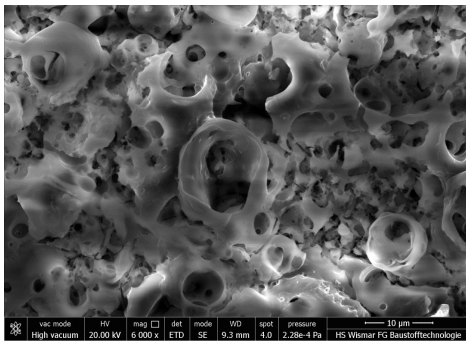


Fig. 1. SEM image of Titanium after PEO treatment at 450 ± 46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 300 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [50]

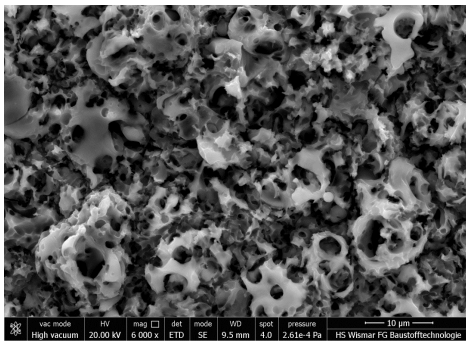


Fig. 2. SEM image of Titanium after PEO treatment at 450 ± 46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 600 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [50]

Figure 3 shows the XPS spectra with binding energies of peaks of Titanium (Ti2p), phosphorus (P2p), carbon (C1s), oxygen (O1s), copper (Cu2p) and nitrogen (N1s). Based on these spectra, it is possible to state that in studied top 10 nanometers of PEO

coatings, the titanium (Ti^{4+}), copper (Cu^+ & Cu^{2+}), phosphorus and oxygen (PO_4^{3-}) were found. The signals of carbon and nitrogen with some oxygen may be interpreted as contamination nano-layer. It was found that the copper to phosphorus (Cu/P) ratios of surfaces obtained during PEO treatment in electrolytes containing 300 g and 600 g $\text{Cu}(\text{NO}_3)_2$ were equal to 0.12 by atomic concentration, respectively. More details regarding these surfaces may be found under the Authors' reference [50].

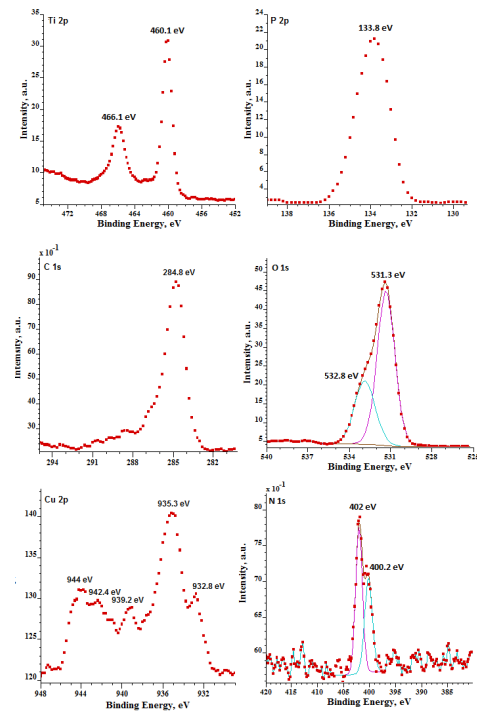


Fig. 3. XPS results of coating formed on Titanium after PEO treatment at voltage of 450 ± 46 V with pulsation at frequency of 300 Hz in the electrolyte consisting of 600 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4

Figure 4 shows the XPS spectra with binding energies of peaks of titanium (Ti2p), niobium (Nb3d), zirconium (Zr3d), phosphorus (P2p), carbon (C1s), oxygen (O1s) and nitrogen (N1s) of porous Titanium-Zirconium-Niobium (TNZ) alloy surface (Fig. 5) after PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 300 g and 600 g of copper nitrate $\text{Cu}(\text{NO}_3)_2$ in 1000 mL of orthophosphoric acid H_3PO_4 . Based on these spectra, it is possible to state that in studied top 10 nanometers of PEO coatings, the titanium (Ti^{4+}), niobium (Nb^{5+}), zirconium (Zr^{x+} , where: $x \leq 2$), copper (Cu^+ & Cu^{2+}), phosphorus and oxygen (PO_4^{3-}) were found. The signals of carbon and nitrogen with some oxygen may

be interpreted as contamination nano-layer. It was found that the copper to phosphorus (Cu/P) ratio of surface obtained during PEO treatment in electrolytes containing 600 g $\text{Cu}(\text{NO}_3)_2$ were equal to 0.13 (by atomic concentration).

and 600 g of copper nitrate $\text{Cu}(\text{NO}_3)_2$ in 1000 mL of orthophosphoric acid H_3PO_4 are presented. It has to be pointed that formed pores have different shapes and diameters. The chemical compositions of these surfaces were presented in Authors' references [53].

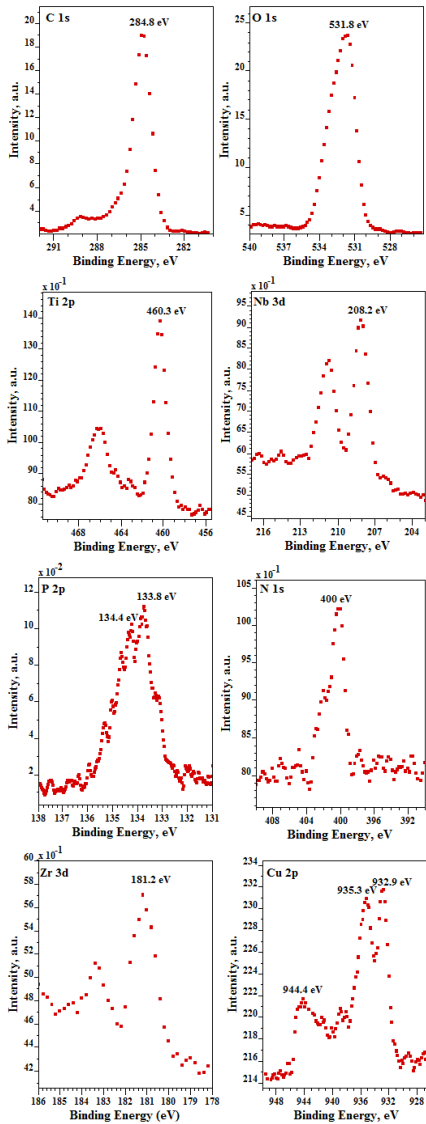


Fig. 4. High resolution XPS spectra/results of coating formed on Ti-Nb-Zr alloy after 3 minutes of PEO treatment at voltage of 450 ± 46 V with pulsation at frequency of 300 Hz in electrolyte containing of H_3PO_4 within $\text{Cu}(\text{NO}_3)_2$ [42]

In Figures 6-7 and 8-9 the SEM images of Nickel-Titanium (Ni-Ti) alloy known also as Nitinol, and Niobium, respectively, after PEO treatment at 450 V for 3 minutes in the electrolytes consisting of 300 g

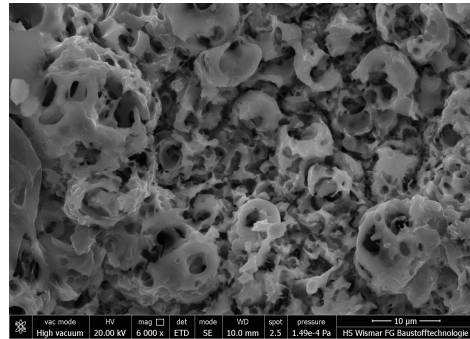


Fig. 5. SEM picture of surface layer formed on TNZ alloy after the PEO treatment at voltage of 450 V the electrolyte consisting of 600 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [44]

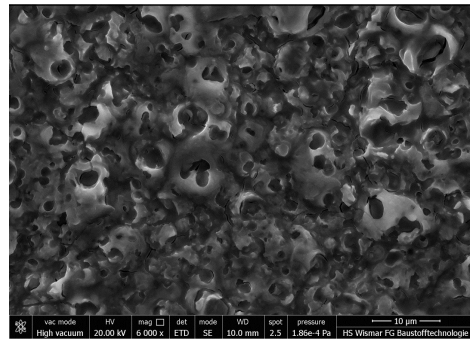


Fig. 6. SEM image of NiTi alloy after PEO treatment at 450 ± 46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 300 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4

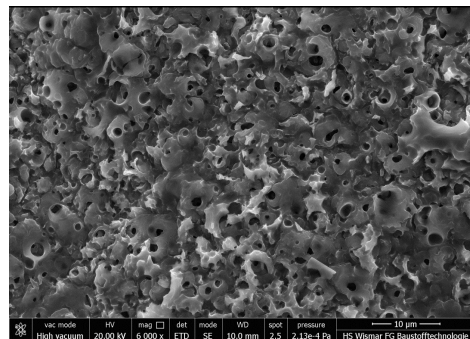


Fig. 7. SEM image of NiTi alloy after PEO treatment at 450 ± 46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 600 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [50]

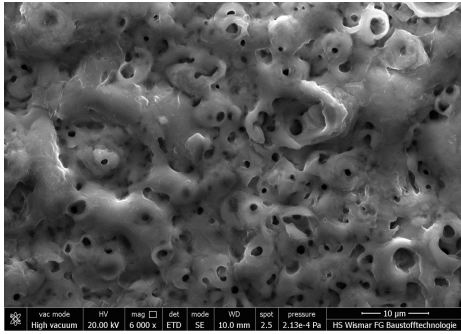


Fig. 8. SEM image of Niobium after PEO treatment at 450 ± 46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 300 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [50]

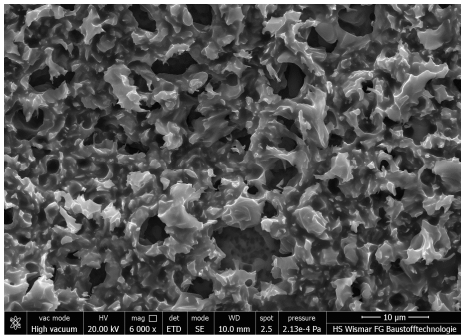


Fig. 9. SEM picture of surface layer formed on Niobium after the PEO treatment at voltage of 450 ± 46 V with pulsation at frequency of 300 Hz the electrolyte consisting of 600 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [44]

In Figures 10-11, the SEM images of porous surface of Ti6Al4V titanium alloy after PEO treatment at 450 V for 3 minutes in the electrolytes consisting of 600 g of copper nitrate $\text{Cu}(\text{NO}_3)_2$ in 1000 mL of orthophosphoric acid H_3PO_4 are presented.

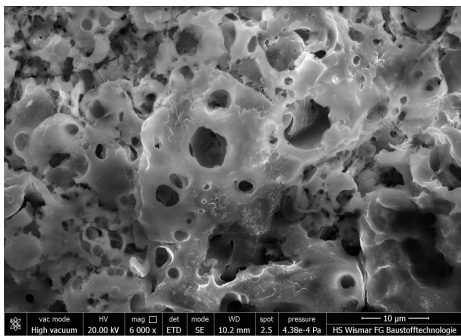


Fig. 10. SEM image of Ti6Al4V alloy after PEO treatment at 450 ± 46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 300 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [50]

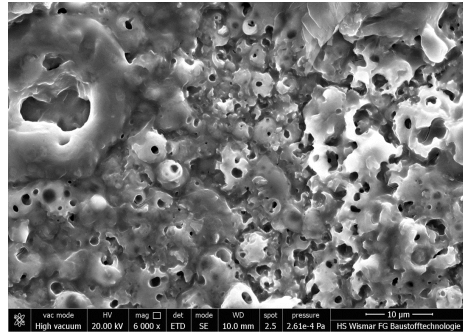


Fig. 11. SEM image of Ti6Al4V alloy after PEO treatment at 450 ± 46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 600 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [50]

Figure 12 shows the XPS spectra with binding energies of peaks of titanium (Ti2p), aluminum (Al2p), vanadium (V2p), phosphorus (P2p), copper (Cu2p), oxygen (O1s) and carbon (C1s). Based on these spectra it should be noted that the surface layer consists mainly of titanium (Ti^{4+}), aluminum (Al^{3+}), copper (Cu^+ & Cu^{2+}), phosphorus (PO_4^{3-}). More details regarding that surface may be found under the Authors' reference [41].

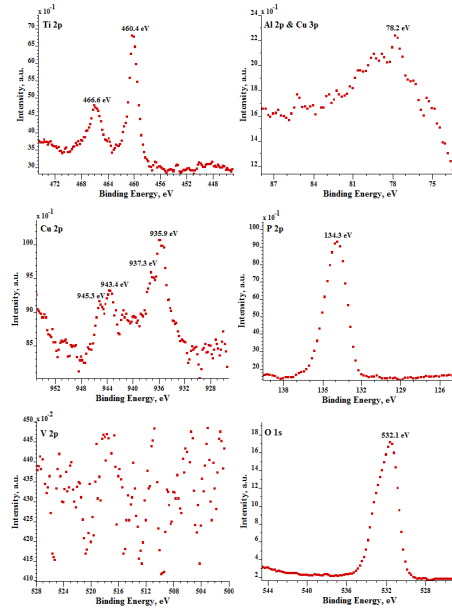


Fig. 12. XPS results of coating formed on Ti6Al4V after PEO treatment at voltage of 450 ± 46 V with pulsation at frequency of 300 Hz in the electrolyte consisting of 600 g $\text{Cu}(\text{NO}_3)_2$ in 1000 mL H_3PO_4 [41]

Figures 13 and 14 show the XPS spectra and SEM image, respectively, of porous surface obtained on

Ti2448 (Ti-Nb-Zr-Sn) titanium alloy in the electrolyte consisting of 600 g Cu(NO₃)₂ in 1000 mL H₃PO₄.

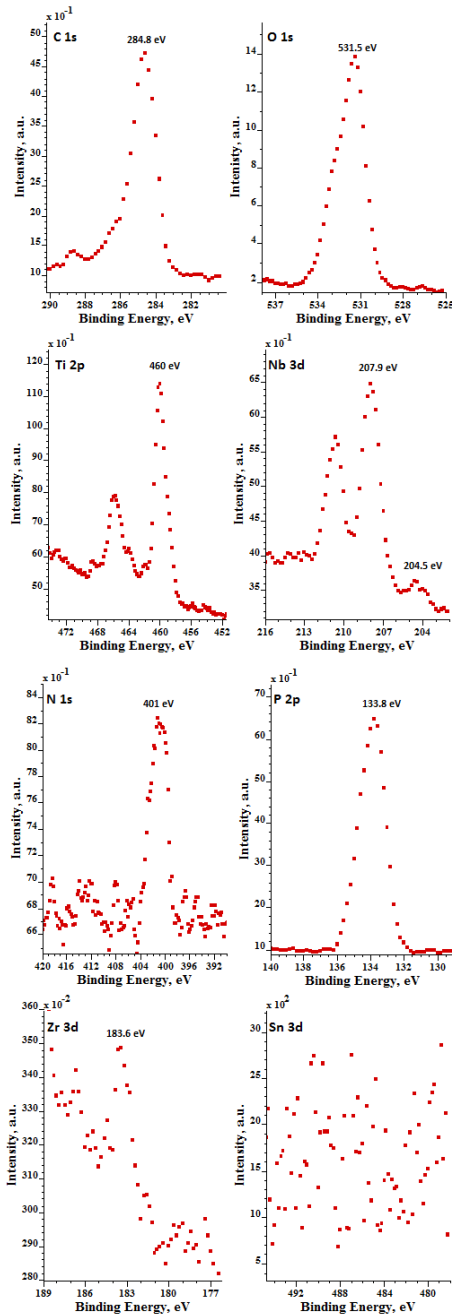


Fig. 13. XPS results of coating formed on Ti2448 after PEO treatment at voltage of 450±46 V with pulsation at frequency of 300 Hz in the electrolyte consisting of 600 g Cu(NO₃)₂ in 1000 mL H₃PO₄ [42]

The XPS spectra of titanium (Ti2p), niobium (Nb3d), zirconium (Zr3d), tin (Sn3d), phosphorus (P2p), carbon (C1s), oxygen (O1s), copper (Cu2p) and nitrogen (N1s) of porous Titanium-Zirconium-Niobium (TNZ) alloy surface after PEO treatment have been studied. Based on these spectra, it is possible to state that the copper inside the PEO coating appears as Cu₀ and Cu²⁺ ions whereas titanium, niobium and zirconium occur as Ti⁴⁺, Nb⁵⁺ and Zr⁴⁺, respectively. More details regarding that surface may be found under the Authors' reference [42].

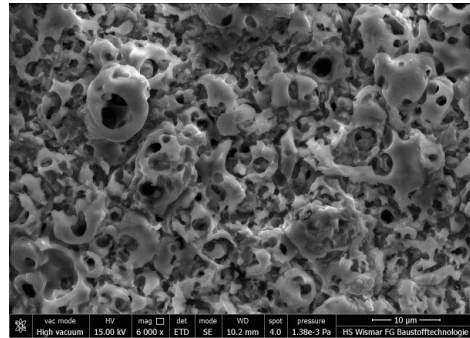


Fig. 14. SEM picture of coating formed on Ti2448 after PEO treatment at voltage of 450±46 V with pulsation at frequency of 300 Hz in the electrolyte consisting of 600 g Cu(NO₃)₂ in 1000 mL H₃PO₄ [42]

In addition, some new characteristics of PEO coating obtained at DC voltage of 450 V without any pulsation on titanium have been performed, with SEM image shown in Figure 15. The copper to phosphorus ratio is equal to 0.12 by atomic concentration, which is the same as was found for PEO treatment of titanium at voltage of 450±46 V with pulsation at frequency of 300 Hz for 3 minutes in the electrolyte consisting of 600 g Cu(NO₃)₂ in 1000 mL H₃PO₄.

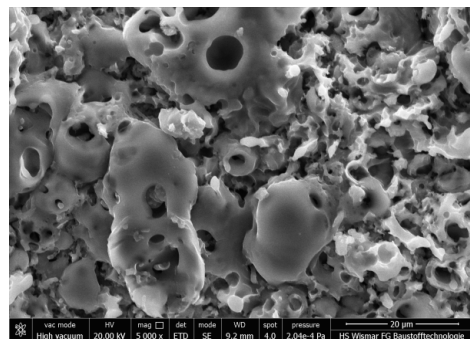


Fig. 15. SEM picture of coating formed on Titanium after PEO treatment at DC voltage of 450V without any pulsation in the electrolyte consisting of 500 g Cu(NO₃)₂ in 1000 mL H₃PO₄ (magnification: 5 000×)

4. CONCLUSIONS

1. Porous coatings enriched in copper on titanium and its alloys (NiTi, Ti6Al4V, TNZ, Ti2448) as well as on Niobium were obtained with using DC voltage of average value equal to 450 V with and without pulsation.
2. The shapes of pores depend on voltage and electrochemically treated metal or alloy
3. By using of DC voltage without any pulsation, the amount of copper nitrate in electrolyte may be smaller than that used for DC voltage with pulsation, to obtain the same amount of copper in coating.

Acknowledgements

This work was partly subsidized by Grant OPUS 11 of National Science Centre, Poland, with registration number 2016/21/B/ST8/01952, titled "Development of models of new porous coatings obtained on titanium by Plasma Electrolytic Oxidation in electrolytes containing phosphoric acid with addition of calcium, magnesium, copper and zinc nitrates".

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