SEM AND EDS ANALYSIS OF NIOBIUM SURFACE AFTER PLASMA ELECTROLYTIC OXIDATION IN CONCETRATED PHOSPHORIC ACID WITHIN COPPER NITRATE

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Abstract

In the present paper, new coatings enriched in copper ions obtained on niobium by Plasma Electrolytic Oxidation in electrolyte containing concentrated phosphoric acid H_3PO_4 with copper nitrate $Cu(NO_3)_2$, are presented. It has been shown that it is possible to obtain the coatings with copper ions inside during the PEO treatment. The highest copper amount (4.05 wt. % | 1.75 at. %) was detected after oxidation at 450 V in electrolyte containing 300 g $Cu(NO_3)_2$, while the lowest copper amount (1.95 wt. % | 0.97 at. %) was detected after oxidation at 180 V in electrolyte containing 150 g $Cu(NO_3)_2$. The highest copper to phosphorus ratio (0.23 wt. % | 0.11 at. %) was detected after oxidation at 450 V in both electrolytes, *i.e.* that containing 150 g as well as 300 g $Cu(NO_3)_2$ in 500 ml H_3PO_4.The lowest copper to phosphorus ratio (0.15-0.17 wt. % | 0.07-0.09 at. %) was detected after oxidation at 180 V in both electrolytes, *i.e.* that containing 150 g as well as 300 g $Cu(NO_3)_2$ in 500 ml H_3PO_4. In addition, it was found that the higher the PEO potential used (here 450 V), the higher copper to phosphorus ratio gained.

Keywords: Niobium, plasma electrolytic oxidation, $Cu(NO_3)_2$

1. INTRODUCTION

Nowadays, more and more often the electrochemical treatments such as electropolishing EP [1-2], magnetoelectropolishing MEP [3], high-current-density electropolishing HDEP [4] as well as Plasma Electrolytic Oxidation (PEO) [5-15] to obtain desired nano- [1-4] or micro- [5-15] surface layers, are used. With the help of these electrochemical treatments it is possible to change the chemical composition of nano- [1-4] or micro-[5-15] layers as well as the mechanical properties and corrosion resistance. Specifically the Plasma Electrolytic Oxidation (PEO), known also as Micro Arc Oxidation (MAO), makes it possible to introduce copper ions into the PEO coating [14-15]. Most interesting chemical elements, due to their bactericidal action, are silver [16-19] and copper [20-26]. In the presented paper, Authors propose using Plasma Electrolytic Oxidation (PEO) with the electrolyte consisting of concentrated phosphoric acid with copper nitrate to create a micro-coating on niobium with the copper ions embedded.

2. METHOD

2.1. Material and set up

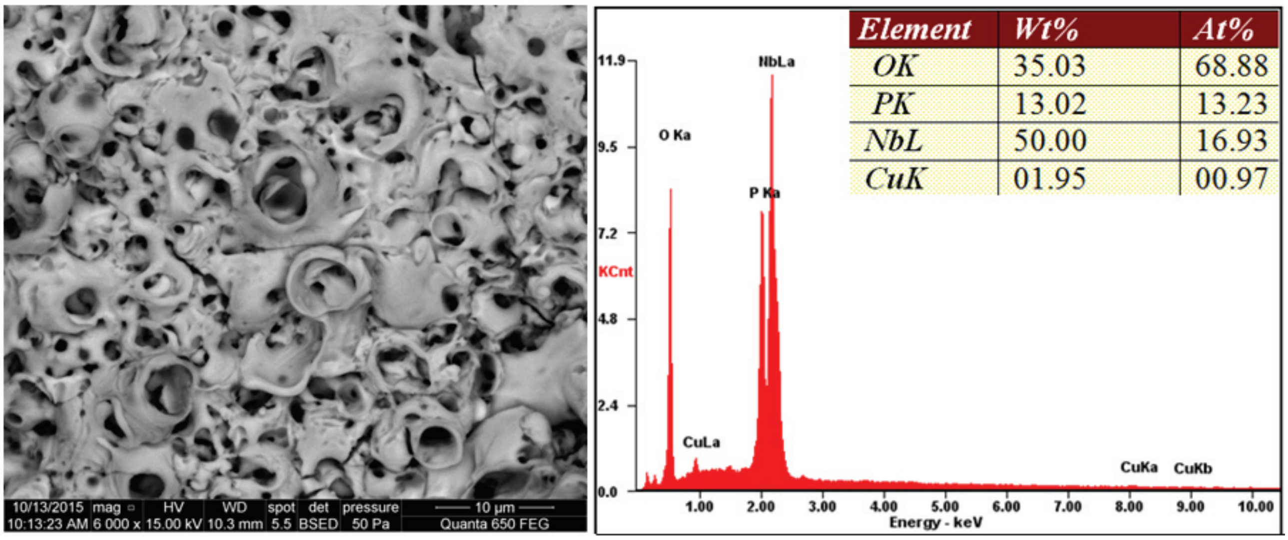
The pure as-rolled Niobium was used to prepare samples with the dimensions 35 × 10 × 1 mm. The samples were treated by Plasma Electrolytic Oxidation (PEO), known also as Micro Arc Oxidation (MAO), at the voltages of 180±10 V and 450±10 V during a 3-minute processing. The studies were carried out in the electrolyte containing of 500 ml concentrated (85 %) orthophosphoric acid with 300 g copper II nitrate.

2.2. SEM and EDS studies

Scanning Electron Microscope (SEM) FEI Quanta 650 FEG equipped with the Energy-Dispersive X-ray Spectroscopy (EDS) for surface analysis was used. The microscope operated under the following conditions: voltage 15 kV, current 8-10 nA, beam diameter 6 mm, decreased vacuum in the chamber with the pressure of 50 Pa. The identification of spectral lines was performed by means of a spectral decomposition using the holographic peak deconvolution function.

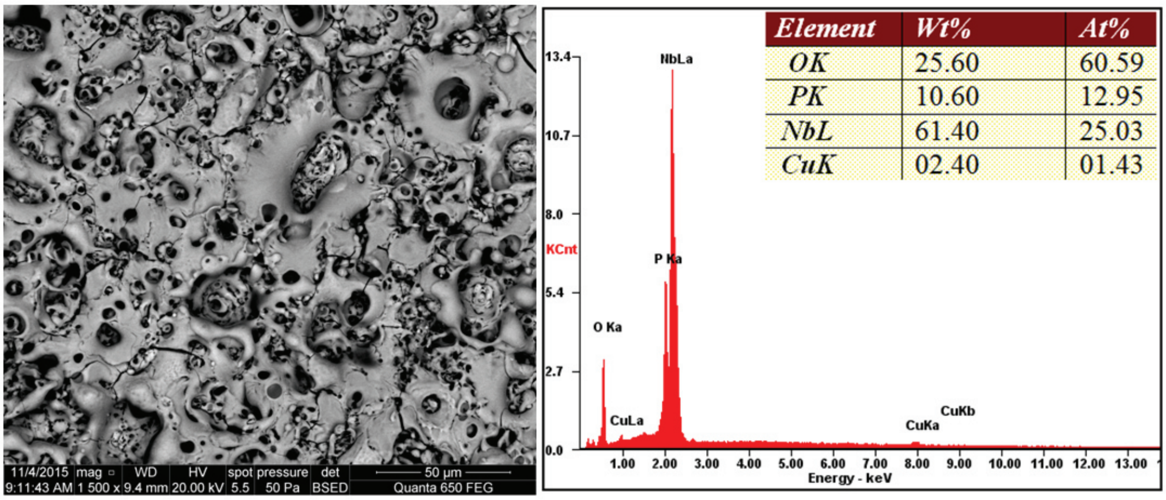
3. RESULTS AND DISCUSSION

In **Figures 1-4**, are shown the SEM images with the EDS spectra of coating formed on Niobium after PEO treatment at the voltages of 180 V and 450 V in the electrolyte containing 500 ml $H_3PO_4$with consecutively 150 g and 300 g $Cu(NO_3)_2$. All presented surfaces are porous, but the shape of each coating is different. In case of the chemical composition it should be noted that coating obtained at 180 V has smaller amount of copper inside than that one formed during the processing at 450 V. It appears that the amount of copper nitrate in the solution has the influence on the content of copper inside the coating created. The highest amount of copper in the PEO coating (4.05 wt. % | 1.75 at. %) was obtained at voltage of 450 V in the electrolyte containing 500 ml H_3PO_4 with 300 g $Cu(NO_3)_2$ and the lowest one (1.95 wt. % | 0.95 at. %) – after the PEO treatment at 180 V in the electrolyte with 150 g $Cu(NO_3)_2$.



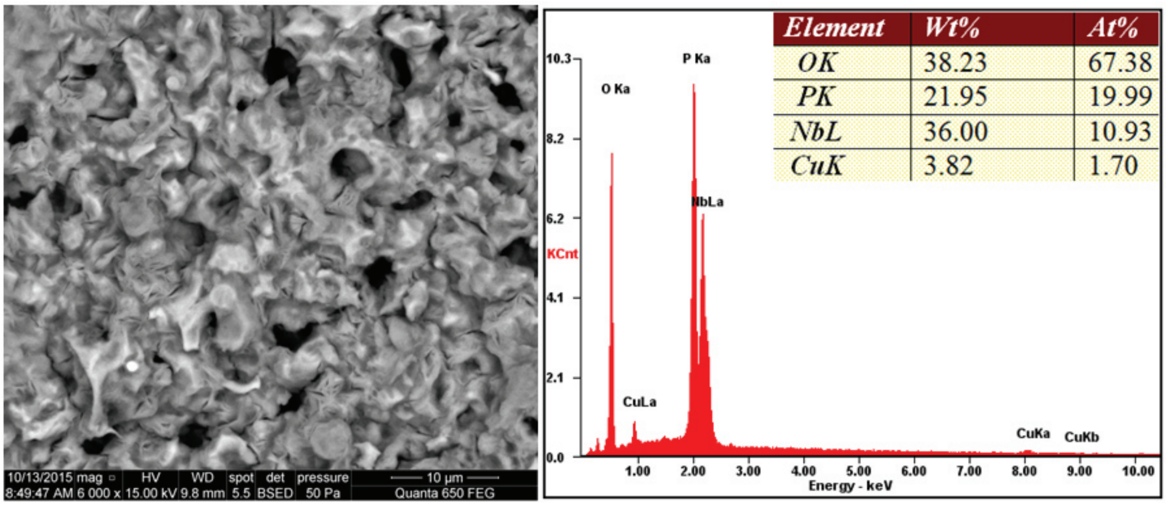
Element	Wt%	At%
OK	35.03	68.88
PK	13.02	13.23
NbL	50.00	16.93
CuK	01.95	00.97

Figure 1 SEM picture of coating formed on Niobium after the PEO treatment at the voltage of 180 V in electrolyte containing 500 ml H_3PO_4 with 150 g $Cu(NO_3)_2$



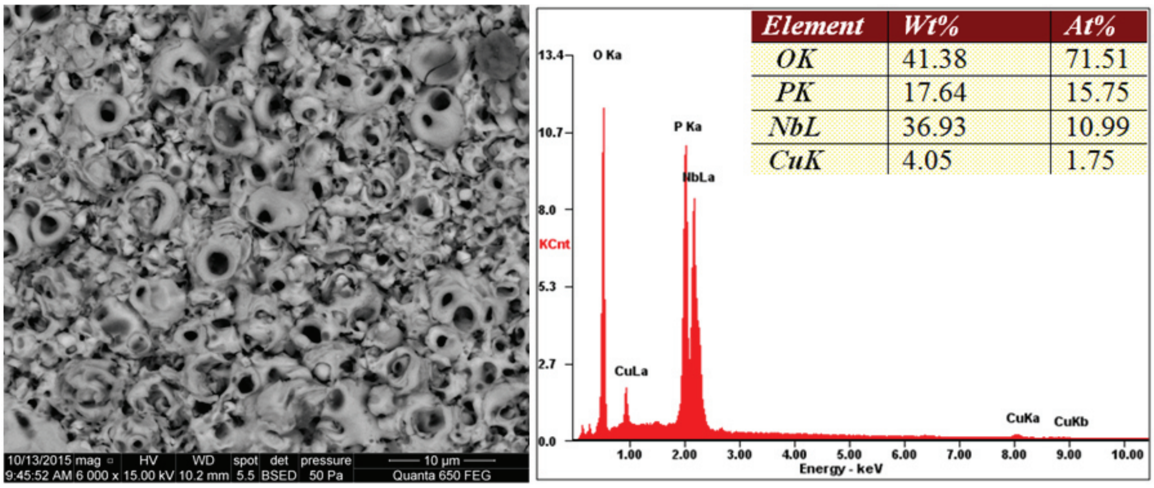
Element	Wt%	At%
OK	25.60	60.59
PK	10.60	12.95
NbL	61.40	25.03
CuK	02.40	01.43

Figure 2 SEM picture of coating formed on Niobium after the PEO treatment at the voltage of 450 V in electrolyte containing 500 ml H_3PO_4 with 150 g $Cu(NO_3)_2$



Element	Wt%	At%
OK	38.23	67.38
PK	21.95	19.99
NbL	36.00	10.93
CuK	3.82	1.70

Figure 3 SEM picture of coating formed on Niobium after the PEO treatment at the voltage of 180 V in electrolyte containing 500 ml H_3PO_4 with 300 g $Cu(NO_3)_2$



Element	Wt%	At%
OK	41.38	71.51
PK	17.64	15.75
NbL	36.93	10.99
CuK	4.05	1.75

Figure 4 SEM picture of coating formed on Niobium after the PEO treatment at the voltage of 450 V in electrolyte containing 500 ml H_3PO_4 within 300 g $Cu(NO_3)_2$

In **Figure 5**, is presented the bar graph showing the amount of copper inside the PEO coating as well as copper to phosphorus ratio. On the basis of these data it is possible to conclude that using the electrolyte with a higher amount of copper nitrate inside, the satisfactory results are obtained even at lower potential (180 V) applied. This is really important because of the energy costs of producing such a coating. On the other hand, when analyzing the chart showing copper to phosphorus ratio, the other tendency is visible, *i.e.* the oxidation at higher potential (450 V) in two electrolytes results in the same ratio. In case of the PEO treatments at 180V the ratios are very similar. The differences in the two graphs can be explained by the effect of a signal from matrix, which is partly also taken into account during the EDS analysis. The signals from phosphorus and copper originate only from the PEO coatings.

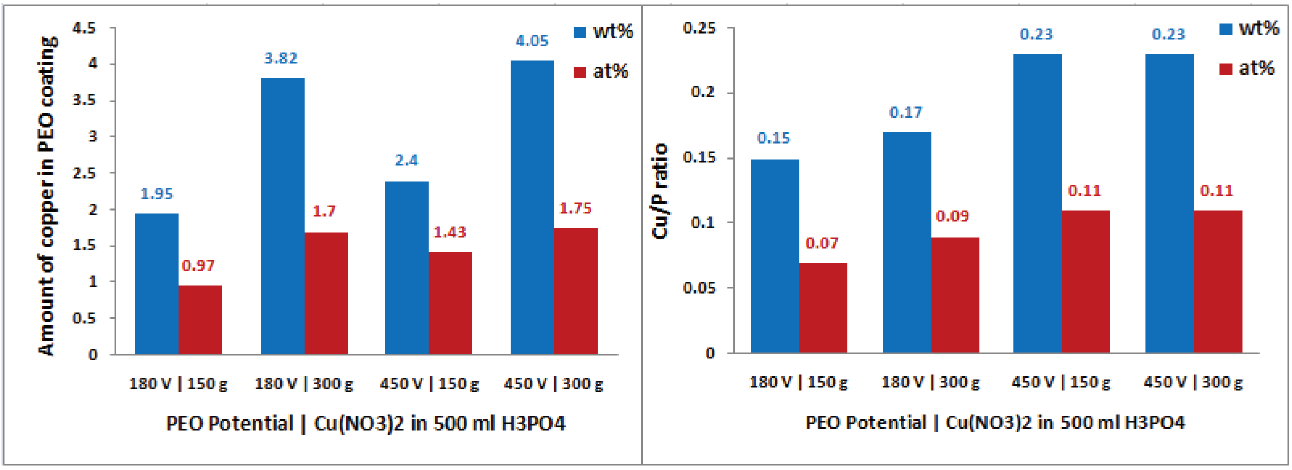


Figure 5 The amount of copper in the PEO coating and Cu/P ratio as the function of PEO potential and the amount of copper nitrate in concentrated phosphoric acid

4. CONCLUSION

- It is possible to obtain the coating with copper ions inside during the PEO treatment.
- The use of concentrated phosphoric acid with copper nitrate can be successfully employed to form the PEO coating enriched in copper ions.
- The PEO potential has a significant influence on the amount of copper ions inside the PEO coating.
- The highest copper amount (4.05 wt/% | 1.75 at%) was detected after oxidation at 450 V in the electrolyte containing 300 g $Cu (NO_3)_2$in 500 ml H_3PO_4.
- The smallest copper amount (1.95 wt/% | 0.97 at%) was detected after oxidation at 180 V in the electrolyte containing 150 g $Cu (NO_3)_2$.
- The highest copper to phosphorus ratio (0.23 wt/% | 0.11 at%) was detected after oxidation at 450 V in both electrolytes, *i.e.* that containing 150 g as well as 300 g $Cu(NO_3)_2$ in 500 ml H_3PO_4.
- The smallest copper to phosphorus ratio (0.15-0.17 wt/% | 0.07-0.09 at%) was detected after oxidation at 180 V in both electrolytes, *i.e.* that containing 150 g as well as 300 g $Cu(NO_3)_2$ in 500 ml H_3PO_4.
- The higher the PEO potential (here 450 V), the higher copper to phosphorus ratio was obtained.

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