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## SEM AND EDS ANALYSIS OF NITINOL SURFACES TREATED BY PLASMA ELECTROLYTIC OXIDATION

### ABSTRACT

In the paper, the surface layers formed on nickel-titanium alloy during Plasma Electrolytic Oxidation (PEO), known also as Micro Arc Oxidation (MAO), are described. The mixture of phosphoric acid and copper nitrate as the electrolyte for all plasma electrochemical processes was used. Nitinol biomaterial was used for the studies. All the experiments were performed under the voltage of 450 V and current density of 0.3 A/dm<sup>2</sup>. The main purpose of the studies was to achieve the highest amount of copper in the surface layer versus amount of the copper nitrate in phosphoric acid. The highest copper concentration was found in the surface layer after the PEO treatment in the electrolyte consisting of 150g Cu(NO<sub>3</sub>)<sub>2</sub> in 0.5 dm<sup>3</sup> H<sub>3</sub>PO<sub>4</sub>. The worst results, in case of the amount of copper in the NiTi surface layer, were recorded after oxidizing in the solution with 5 g Cu(NO<sub>3</sub>)<sub>2</sub>.

**Keywords:** Plasma Electrolytic Oxidation; PEO; Micro Arc Oxidation; MAO; SEM; Titanium alloy; NiTi

### INTRODUCTION

Nickel-Titanium alloy, also known as Nitinol, after a plasma electrolytic oxidation (micro arc oxidation) can be used in medicine as a biomaterial because of its very good biocompatibility. The other electrochemical treatments such as a standard electropolishing [1-3] as well as magnetoelectropolishing [3-7] can change the chemical composition of passive layers formed after those electrochemical treatments, improve their corrosion resistance, roughness and shine [1-7], but they do not form any porous layer; that layer is formed and visible after the plasma electrolytic oxidation (PEO) [8-11]. In the paper, the Authors present the SEM and EDS analysis of the porous layers formed after the PEO at 450 V for 3 minutes in the electrolyte consisting of Cu(NO<sub>3</sub>)<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>.

Plasma electrolytic oxidation (PEO) is a surface finishing technique applied to obtain a range of hard and dense oxide coatings, produced on a variety of metals, such as aluminium, magnesium, titanium and other lightweight alloy substrates [8-13]. Most of the reported PEO techniques applies an alternative voltage of 220-300 V to reach the goal. The up-to-date publications indicate that a suitable control of electrolyte and the process conditions can realise

a novel range of coatings having technologically attractive physical and chemical properties [13]. One of the recent papers underlines that the reducing of the osseointegration time for biomedical titanium implants in surgical patients is an important goal [14]. The aim of this work is to show the preliminary results of the PEO treatment performed on Nitinol.

### METHOD AND EXPERIMENTAL SET UP

The experiment of the Plasma Electrolytic Oxidation (PEO) was carried out on a set-up (Fig. 1) built in a cooperation with the Division of Applied Electronics and Electrotechnology, Koszalin University of Technology (KUT). The PEO process was performed with the use of a constant voltage of 450 V. The electrolyte solution consisted of 500 ml of a concentrated 85% pure p.a.  $\text{H}_3\text{PO}_4$  (98 g/mol) acid and dissolved therein 5 up to 300 g of  $\text{Cu}(\text{NO}_3)_2$  with some amount of casually dissolved iron ions. The nickel-titanium samples of dimensions  $100 \times 20 \times 5$  mm, were prepared at the Faculty of Mechanical Engineering, KUT.

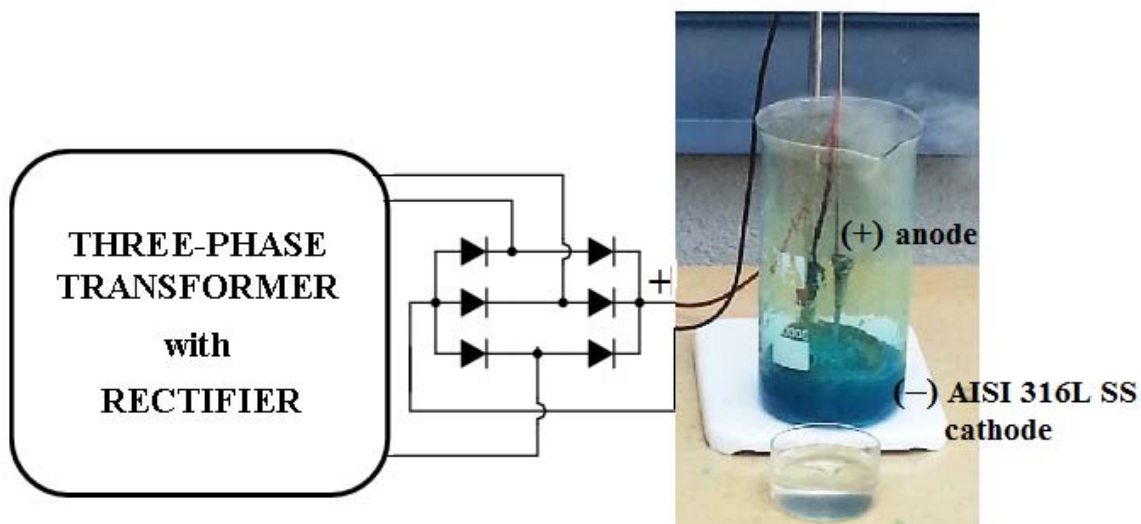
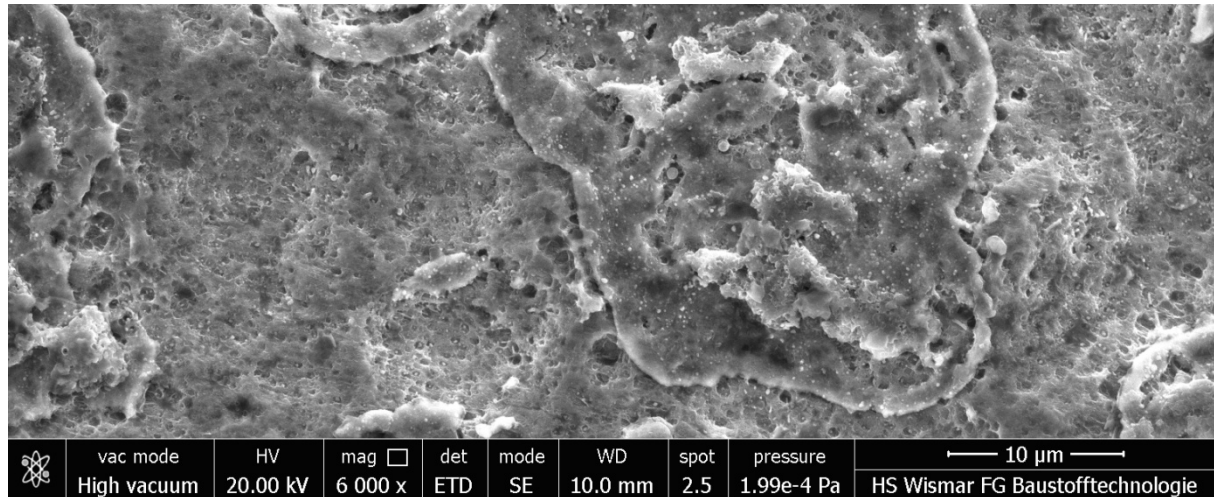


Fig. 1. Scheme of the set-up used for the PEO studies

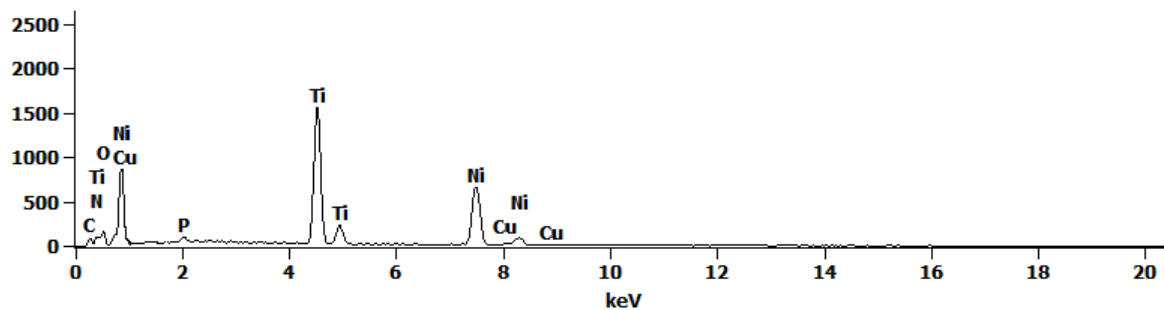
### RESULTS

In Figure 2, there is shown the SEM picture of NiTi alloy sample after the PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 5 g  $\text{Cu}(\text{NO}_3)_2$  in 500 ml  $\text{H}_3\text{PO}_4$ . The obtained surface is not porous and consists mainly of nickel (35.3 wt%) and titanium (28.4 wt%) bonded with oxygen (35.1 wt%) with the small amounts of phosphorus (0.6 wt%) and copper (0.6 wt%) (Fig. 3 and Table 1). This can be explained by the possibility of the surface layer creation in the concentrated phosphoric acid with a dissolved salt therein only, which in this case is the copper nitrate. A better situation is observed after the dissolution of 150 g of copper nitrate in 500 ml of phosphoric acid. After the PEO treatment in that electrolyte there are visible pores (Fig. 4), which surely make the surface more biocompatible. Inside the surface

layer the higher amount of phosphorus (19.7 wt%) and copper (3.7 wt%) were detected, that are depicted in Fig. 5 and Table 2. It should also be admitted that the amount of carcinogenic nickel is much less (12.3 wt%) than that one noted after oxidizing (35.3 wt%) in the electrolyte with a minimum (5g  $\text{Cu}(\text{NO}_3)_2$ ) amount of copper nitrate in the half liter of phosphoric acid.



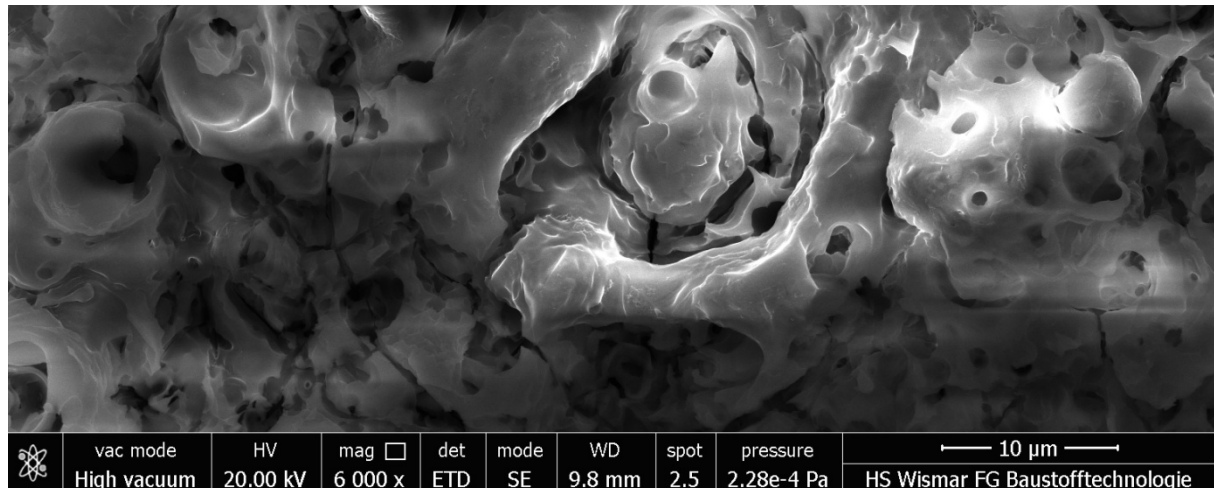
**Fig. 2.** SEM image of NiTi after PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 5 g  $\text{Cu}(\text{NO}_3)_2$  in 500 ml  $\text{H}_3\text{PO}_4$



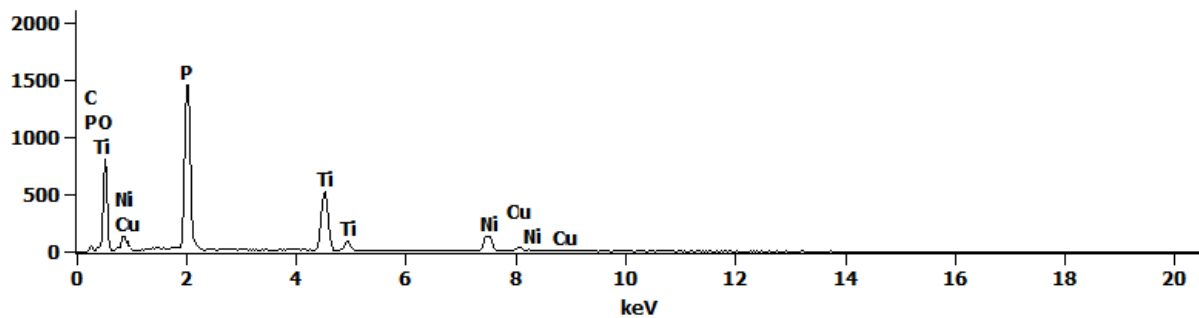
**Fig. 3.** EDS of NiTi after PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 5 g  $\text{Cu}(\text{NO}_3)_2$  in 500 ml  $\text{H}_3\text{PO}_4$

**Table 1.** Chemical composition of PEO layer formed on NiTi treated at 450 V for 3 minutes in the electrolyte consisting of 5 g  $\text{Cu}(\text{NO}_3)_2$  in 500 ml  $\text{H}_3\text{PO}_4$

Elements	wt%	wt% ERROR	at%	at% ERROR
O K	35.1	---	64.2	± 7.28
P K	0.6	± 0.04	0.6	± 0.07
Ti K	28.4	± 0.21	17.3	± 0.25
Ni K	35.3	± 0.61	17.6	± 0.59
Cu K	0.6	± 0.21	0.3	± 0.18



**Fig. 4.** SEM image of NiTi surface after PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 150 g Cu(NO<sub>3</sub>)<sub>2</sub> in 500 ml H<sub>3</sub>PO<sub>4</sub>



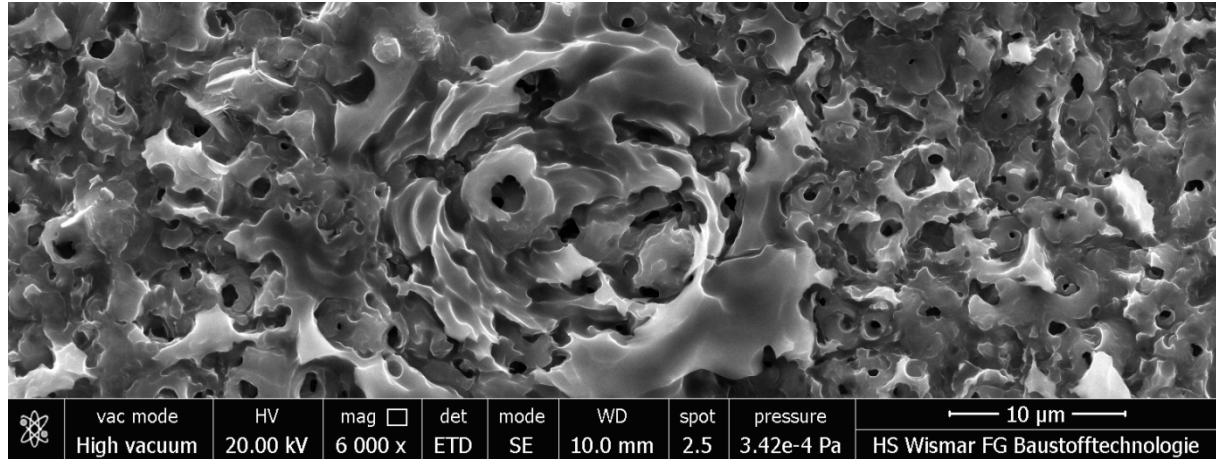
**Fig. 5.** EDS of NiTi surface after PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 150 g Cu(NO<sub>3</sub>)<sub>2</sub> in 500 ml H<sub>3</sub>PO<sub>4</sub>

**Table 2.** Chemical composition of PEO layer formed on NiTi treated at 450 V for 3 minutes in the electrolyte consisting of 150 g Cu(NO<sub>3</sub>)<sub>2</sub> in 500 ml H<sub>3</sub>PO<sub>4</sub>

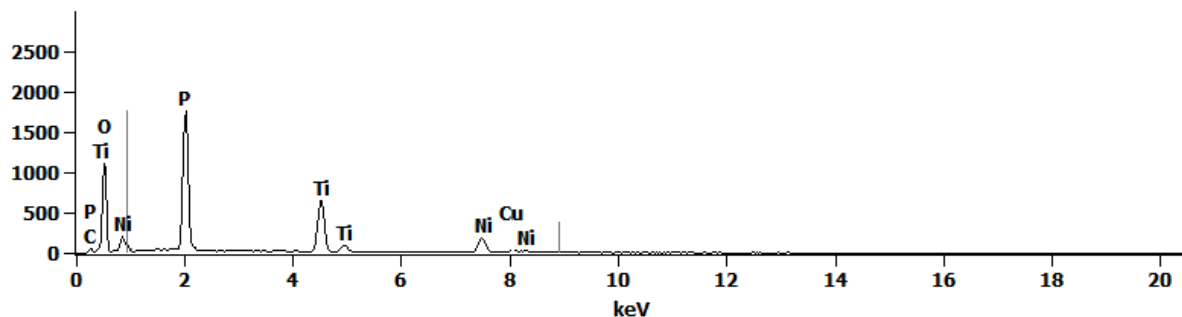
Elements	wt%	wt% ERROR	at%	at% ERROR
O K	46.9	---	69.8	± 2.02
P K	19.7	± 0.22	15.1	± 0.33
Ti K	17.4	± 0.21	8.7	± 0.21
Ni K	12.3	± 0.58	5	± 0.47
Cu K	3.7	± 0.34	1.4	± 0.25

In Figure 6, there is shown the SEM picture of NiTi alloy sample after the PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 300 g Cu(NO<sub>3</sub>)<sub>2</sub> in 500 ml H<sub>3</sub>PO<sub>4</sub>. The high porosity with minimum of two pore levels are visualized. The chemical composition of the obtained layer is very similar to the second one, which was oxidized in the electrolyte with 150 g of copper nitrate. The EDS results shown in Fig. 5 and Table 2, indicate that copper (3.7 ± 0.34 wt%) and phosphorus (19.7 ± 0.22 wt%) amounts are very close to those ones presented in Figure 7 and Table 3 (3.3 ± 0.3 wt% of copper; 19.01 ± 0.21 wt% of phosphorus).

In this paper there are shown the preliminary studies of single measurements which do not allow to reveal the significant differences between the obtained results. For this reason the additional studies with a minimum of five repetitions are planned in the future, in order to carry out the tests of significance.



**Fig. 6.** SEM image of NiTi surface after PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 300 g Cu(NO<sub>3</sub>)<sub>2</sub> in 500 ml H<sub>3</sub>PO<sub>4</sub>



**Fig. 7.** EDS of NiTi surface after PEO treatment at 450 V for 3 minutes in the electrolyte consisting of 300 g Cu(NO<sub>3</sub>)<sub>2</sub> in 500 ml H<sub>3</sub>PO<sub>4</sub>

**Table 3.** Chemical composition of PEO layer formed on NiTi treated at 450 V for 3 minutes in the electrolyte consisting of 300 g Cu(NO<sub>3</sub>)<sub>2</sub> in 500 ml H<sub>3</sub>PO<sub>4</sub>

Elements	wt%	wt% ERROR	at%	at% ERROR
O K	46.2	---	69.5	± 1.99
P K	19.1	± 0.21	14.8	± 0.32
Ti K	17.6	± 0.27	8.8	± 0.26
Ni K	13.8	± 0.55	5.7	± 0.44
Cu K	3.3	± 0.30	1.2	± 0.22

## CONCLUSIONS

In that paper, the results of the surface layers formed on the nickel-titanium alloy after the Plasma Electrolytic Oxidation (PEO), known also as a Micro Arc Oxidation (MAO), in the electrolyte consisting of phosphoric acid and copper nitrate, are presented. The main problem to solve was to put/insert copper ions inside the POE layer, and this task has been successfully done. The biggest amount of copper in the surface layer was recorded after the PEO treatment in the electrolytes consisting of 150 g and 300 g of copper nitrate in 500 ml of phosphoric acid and it was equal over 3 weight percent. Trace amounts of copper ( $0.6 \pm 0.21$  wt%) and phosphorus ( $0.6 \pm 0.04$  wt%) after the treatment in the electrolyte with 5g  $\text{Cu}(\text{NO}_3)_2$ , were found. Following these results it can be concluded that in the absence of copper nitrate the surface layer consists mainly of nickel-titanium with some inclusions of copper phosphates and alloying elements. It should be also noted that the layers with the least amount of carcinogenic nickel (below 13 wt%) are formed with a large amount of copper nitrate in the electrolyte.

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