

SEM, EDS AND XPS ANALYSIS OF NANOSTRUCTURED COATING FORMED ON NiTi BIOMATERIAL ALLOY BY PLASMA ELECTROLYTIC OXIDATION (PEO)

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Original scientific paper

Plasma Electrolytic Oxidation (PEO) of NiTi alloy was studied in the electrolyte consisting generally of concentrated orthophosphoric acid with an addition of copper II nitrate. The PEO process was used to obtain a nanostructured coating on the Nitinol surface. The surface layer analyses methods, such as scanning electron microscopy (SEM) with the energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS), allowed determining the structure and composition of the most expected coatings and revealing the conditions for obtaining them. It was found that the porous PEO coating obtained in the electrolyte containing copper nitrate in an amount higher than 1,6 mol/L consists mainly of copper-titanium-nickel phosphates. Moreover, in comparison with matrix, the emergence of carcinogenic nickel appearing in the coating fortunately appears in very small quantities, *i.e.* below 1 at%.

Keywords: biomaterials; coatings; electrochemical techniques; energy dispersive X-ray spectroscopy (EDS); NiTi alloy; X-ray photoelectron spectroscopy (XPS)

SEM, EDS i XPS analiza nanostrukturirane prevlake koja se stvara na leguri od NiTi biomaterijala plasma elektrolitičkom oksidacijom (PEO)

Izvorni znanstveni članak

Plasma elektrolitička oksidacija (PEO) NiTi legure proučavana je u elektrolitu koji se uobičajeno sastojao od koncentrirane ortofosforične kiseline s dodatkom nitrata bakra II. Taj se PEO postupak primijenio za dobivanje nanostrukturirane prevlake na Nitinol površini. Metode analize površinskog sloja kao što su skeniranje elektronskim mikroskopom (SEM) s energetski disperzivnom rendgenskom spektroskopijom (EDS) i rendgenskom fotoelektronskom spektroskopijom (XPS), omogućile su određivanje strukture i sastava najočekivanijih prevlaka i otkrivanje uvjeta za njihovo dobivanje. Ustanovilo se da se porozna PEO prevlaka dobivena u elektrolitu koji je sadržavao bakreni nitrat u količini većoj od 1,6 mol/L sastoji uglavnom od fosfata bakra-titanija-nikla. Uz to, u usporedbi s matricom, karcinogeni nikel u prevlaci srećom se javlja u vrlo malim količinama, tj. ispod 1 at%.

Ključne riječi: biomaterijali; prevlake; elektrokemijske metode; energetski disperzivna rendgenska spektroskopija (EDS); legura NiTi; rendgenska fotoelektronska spektroskopija (XPS)

1 Introduction

Nitinol (nickel-titanium alloy), similar as other metals (titanium, tantalum, niobium, zirconium) and their alloys, can be treated *inter alia* by Electropolishing (EP) and Magneto-electropolishing (MEP) [1÷7], as well as by Plasma Electrolytic Oxidation - PEO (Micro Arc Oxidation - MOA) [8÷23]. Concerning the nickel-titanium alloy surface treatment, our electrochemical experiments show that generally the electropolishing process is mostly run when using the voltage under 80 V. With increasing the voltage of the electrochemical treatment, the plasma in electrolyte is created and then the conditions for the plasma electrolytic oxidation (PEO) treatment are achieved. Another important feature of the PEO process is the electrolyte composition. In fact it is composed of a concentrated acid, usually orthophosphoric, and a salt of the bactericidal metals, e.g. silver [24÷26] or copper [27÷29]. These metals are important to cooperate and be compatible with the human being tissue.

In present work, the study of nanostructured coating obtained on one of the intermetallic compounds used for biomaterials, known as Nitinol, is presented. The PEO process was studied to obtain the porous coating on NiTi surface. The analyses methods used in this work, such as SEM, EDS, and XPS, allowed determining the structure and composition of the most expected coatings and revealing the conditions for obtaining them.

2 Method

The chemical composition of NiTi rectangular samples with dimensions 5 × 30 × 1 mm, which were used in experiments, is presented in Fig. 1. The PEO process was done at average voltage 450 V with pulsation of 300 Hz with amplitude of 92 V. The detailed description of the set up dedicated to PEO (MOA) process as well as to SEM, EDS and XPS equipment, is presented in references [18÷21].

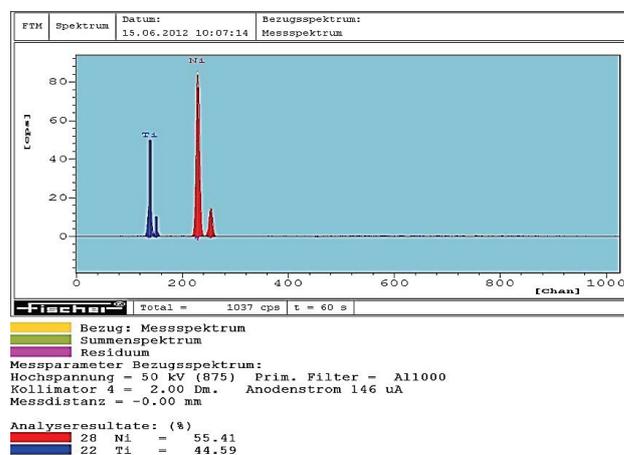


Figure 1 EDS results of NiTi alloy before treatment (as received)

3 Results and discussion

In Fig. 2, the SEM images of surface layer formed on NiTi alloy after the PEO treatment at voltage of 450 V in

0,05 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte, are shown. One may notice that obtained surface is not porous within small amount of copper ($0,4 \pm 0,2$ wt%), the results are displayed in Fig. 3 and Tab. 1.

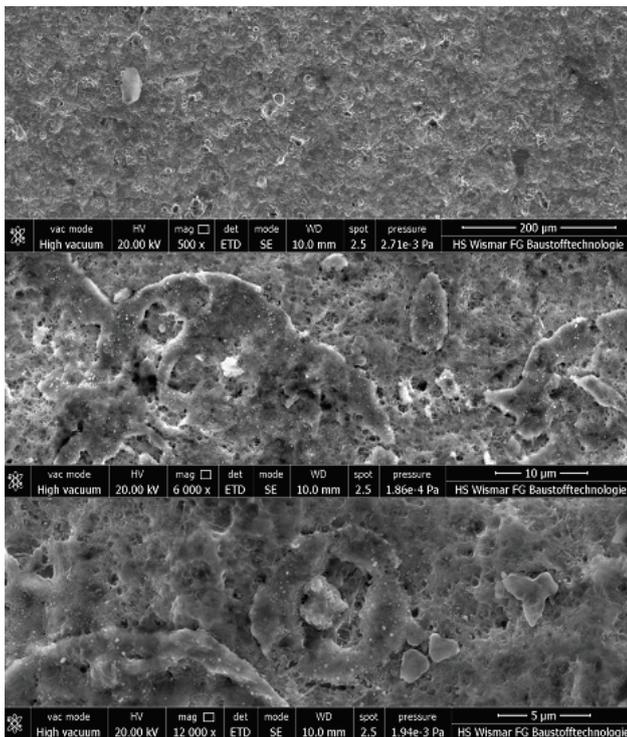


Figure 2 SEM picture of surface layer formed on NiTi alloy after PEO at voltage of 450 V in 0,05 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte

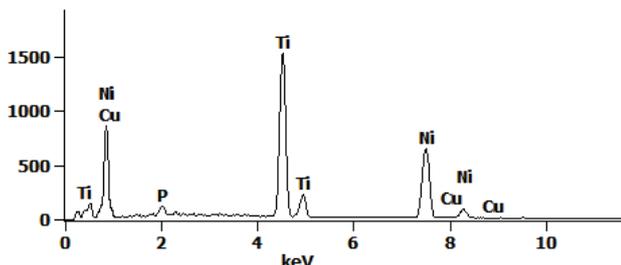


Figure 3 EDS result of surface layer formed on NiTi alloy after PEO at voltage of 450 V in 0,05 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte

Table 1 Quantitative results of weight and atomic concentration of selected elements on the basis of EDS presented in Fig. 3

Element lines	wt%	Error wt%	at%	Error at%
O K	34,4	---	63,5	$\pm 19,1$
P K	0,7	$\pm 0,1$	0,7	$\pm 0,1$
Ti K	28,2	$\pm 0,3$	17,4	$\pm 0,3$
Ni K	36,3	$\pm 0,6$	18,2	$\pm 0,6$
Cu K	0,4	$\pm 0,2$	0,2	$\pm 0,2$

It should be also noted that the obtained coating contains a small amount of phosphorus ($0,7 \pm 0,1$ wt%) with very large amount of oxygen what may indicate that the coating consists mainly of oxides and hydroxides with a small amount of phosphates. It was recorded that there is relatively a high amount of titanium ($28,2 \pm 0,3$ wt%) and nickel ($36,3 \pm 0,6$ wt%). Due to the carcinogenic action of nickel, the obtained coating cannot be used for medical applications as a biomaterial. On the other hand, however, it should be noted that a part of titanium and nickel signal may come from the substrate (matrix), what

would mean that the obtained PEO oxide layer is very thin. In the summary it should be emphasized that the coating obtained on NiTi alloy after the PEO at voltage of 450 V in 0,05 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte cannot be used as a biocompatible metallic material.

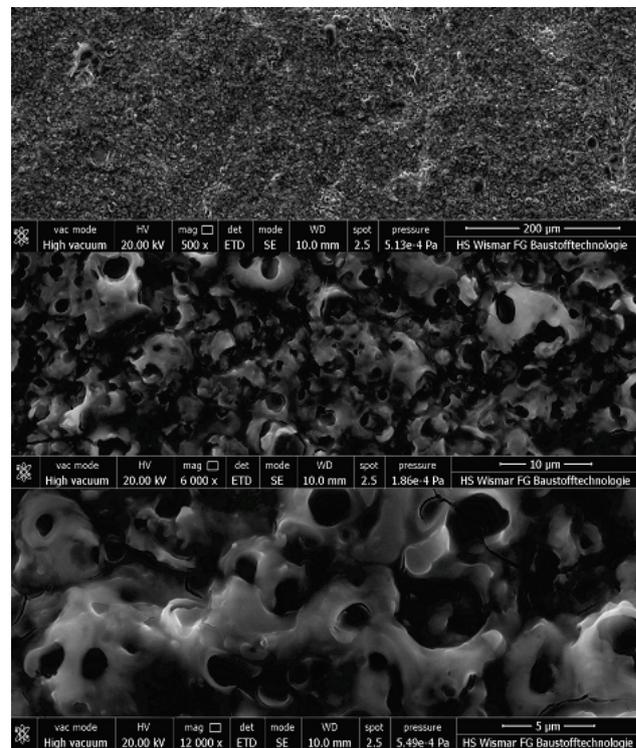


Figure 4 SEM picture of surface layer formed on NiTi alloy after PEO at voltage of 450 V in 1,60 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte

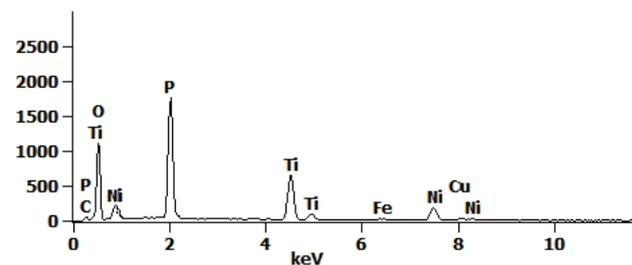
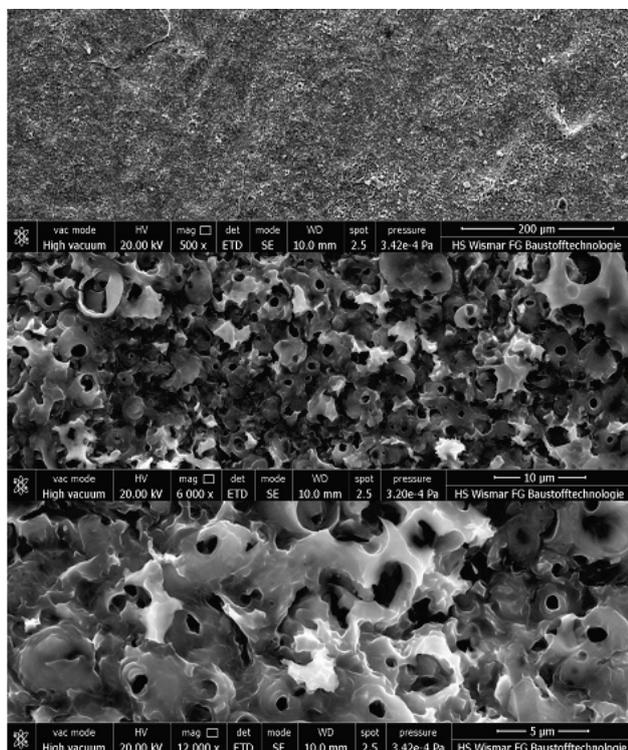


Figure 5 EDS result of surface layer formed on NiTi alloy after PEO at voltage of 450 V in 1,60 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte

In Fig. 4, the SEM images of surface layer created on NiTi alloy after the PEO at voltage of 450 V in 1,60 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte, are presented. The displayed pictures clearly prove that obtained surface is porous and the EDS measurements results show (Fig. 5 and Tab. 2) it contains copper in the amount of $3,3 \pm 0,3$ wt%. The nickel ($13,9 \pm 0,6$ wt%) and titanium ($17,6 \pm 0,3$ wt%) amounts indicate that the obtained coating is thicker than the one formed in the electrolyte within 0,05 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 . Additionally, the amount of phosphorus, as detected by EDS and equaling $19,1 \pm 0,2$ wt%, suggests that the coating is composed of oxides/hydroxides and phosphates. In this case one should emphasize that the coating obtained on NiTi alloy after the PEO at voltage of 450 V in 1,6 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte can be considered as a biocompatible one.

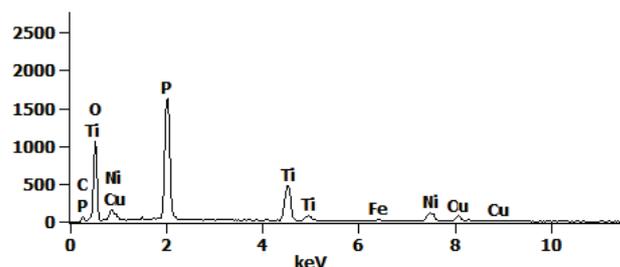
Table 2 Quantitative results of weight and atomic concentration of selected elements on the basis of EDS presented in Fig. 5

Element lines	wt%	Error wt%	at%	Error at%
O K	46,1	---	69,4	± 1,9
P K	19,1	± 0,2	14,8	± 0,3
Ti K	17,6	± 0,3	8,9	± 0,3
Ni K	13,9	± 0,6	5,6	± 0,4
Cu K	3,3	± 0,3	1,3	± 0,2

**Figure 6** SEM picture of surface layer formed on NiTi alloy after PEO at voltage of 450 V in 3,20 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte

In Fig. 6, the SEM pictures of the surface layer formed on NiTi alloy after the PEO at voltage of 450 V in 3,2 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte are given. The results show that the obtained surface is porous and the surface layer contains the highest amount of copper ($5,2 \pm 0,6$ wt%), as presented in Fig. 7 and Tab. 3. It should be noted that the pore structure is different than that one created in electrolyte containing 1,60 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte. The amount of

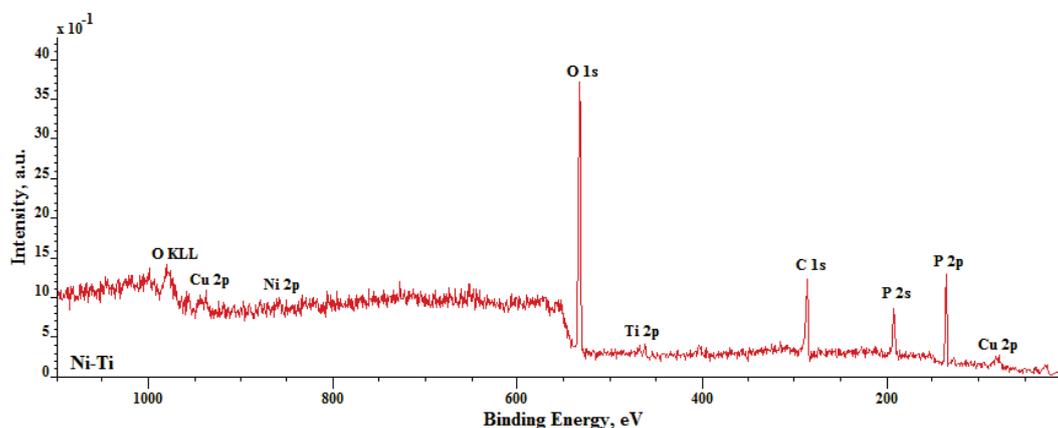
phosphorus, which is equal to $21,2 \pm 0,2$ wt%, suggests that the coating is enriched with a high amount of phosphates combined with oxides/hydroxides. These conditions of the PEO experiment, performed at the voltage of 450 V in 3,2 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte, allow to conclude that the coating obtained on NiTi alloy can be considered as a biocompatible one. The nickel ($10,8 \pm 0,5$ wt%) and titanium ($14,8 \pm 0,3$ wt%) contents clearly indicate that the obtained coating is most likely the thickest one, with the thickness bigger than that of two others discussed above.

**Figure 7** EDS result of surface layer formed on NiTi alloy after PEO at voltage of 450 in 3,20 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte

Because by the EDS measurements the signals of matrix cannot be separated from the signals of coatings, to get more results the additional measurements, i.e. coming from the X-ray Photoelectron Spectroscopy (XPS), were planned. The XPS measurements of the surface layer formed on NiTi alloy after the PEO at voltage of 450 V in 3,20 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte, were performed. The most important task of the XPS study was to demonstrate the contents of chemical elements coming from coatings as well as to find their chemical states.

Table 3 Quantitative results of weight and atomic concentration of selected elements on the basis of EDS presented in Fig. 7

Element lines	wt%	Error wt%	at%	Error at%
O K	48	---	70,5	± 1,7
P K	21,2	± 0,2	16	± 0,3
Ti K	14,8	± 0,3	7,3	± 0,3
Ni K	10,8	± 0,5	4,3	± 0,4
Cu K	5,2	± 0,6	1,9	± 0,4

**Figure 8** Survey of XPS spectra of surface layer formed on NiTi alloy after PEO at voltage of 450 in 3,20 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte

In Fig. 8, the survey of XPS spectra of the surface layer formed on NiTi alloy after the PEO treatment at the voltage of 450 V in 3,20 mol/L of $\text{Cu}(\text{NO}_3)_2$ in H_3PO_4 electrolyte, is presented. In the survey spectrum there are visible the big signals coming from titanium (Ti 2p), nickel (Ni 2p), copper (Cu 2p), phosphorus (P 2p) as well as these referred to oxygen (O 1s) and carbon (C 1s).

From these data it follows that the PEO coating is composed mainly of phosphorus and oxygen with a small amount of copper, titanium and nickel. In order to better determine the chemical composition of the PEO coating, the high resolution XPS measurements were performed, which are given in Fig. 9.

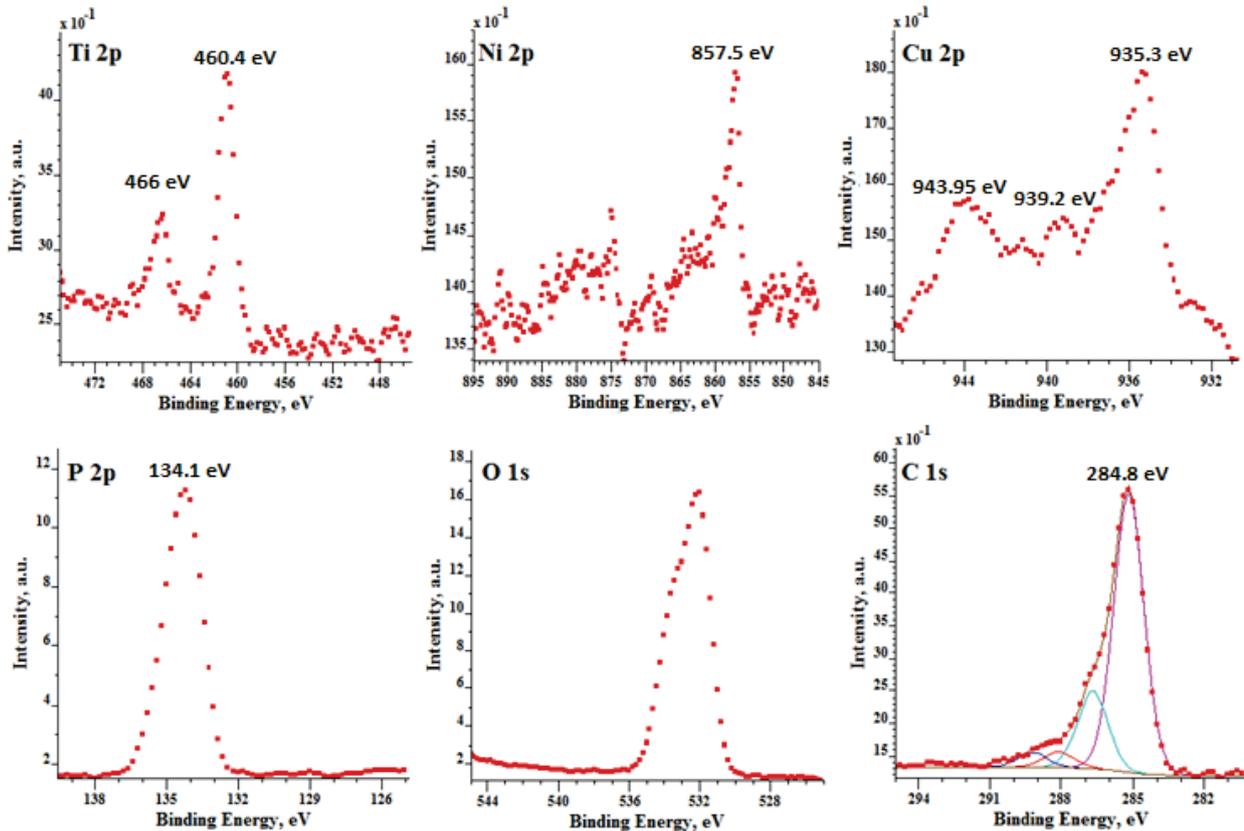


Figure 9 XPS high resolution spectra of surface layer formed on NiTi alloy after PEO

Table 4 Total chemical composition of carbon contaminations and PEO coating formed on NiTi, at%

10 nm of PEO layer on NiTi, at%					
Titanium	Nickel	Copper	Phosphorus	Oxygen	Carbon
0,8	0,6	1,3	18,0	51,6	27,7

Table 5 Carbon contamination of PEO coating formed on NiTi, at%

NiTi, carbon contamination nano-layer, at%				
	C-C C-H	C-OH C-O-C	C=O	O-C=O
C 1s, eV	284,8	+1,5 eV	+2,9 eV	+4 eV
Carbon	72,2	19,9	4,0	3,9
Oxide	–	<2,8; 5,5>	1,1	2,2

On the basis of high resolution XPS spectra of oxygen (O 1s) and carbon (C 1s) it is possible to separate the contamination layer and the PEO coating. The total chemical composition of PEO coating, which was measured by the XPS technique, is shown in Tab. 4. Oxygen bonded with carbon (contamination layer), presented in Tab. 5, was separated from that one bonded with the chemical elements of passive layers (Tab. 6). The carbon-oxygen ratio in the contamination layer was solved based on the stoichiometric rules. Carbon contamination layer formed on the NiTi surface consists of about 80 at% of carbon and 20 at% of oxygen. Additionally, the Cu/P, Cu/Ti, Ti/P and Cu/(Ti+Ni+P)

coefficients were found to allow comparing the obtained coating with other ones proposed by the other researchers [19, 20]:

$$\frac{\text{Cu}}{\text{P}} = 0,07; \frac{\text{Cu}}{\text{Ti}} = 1,67; \frac{\text{Ti}}{\text{P}} = 0,04; \frac{\text{Cu}}{\text{Ti} + \text{Ni} + \text{P}} = 0,05.$$

Table 6 PEO coating formed on NiTi, at% (after removal of carbon contaminations)

10 nm of PEO layer on NiTi, at%				
Titanium	Nickel	Copper	Phosphorus	Oxygen
1,2	0,9	2,0	27,5	68,4

Based on the spectra shown in Fig. 9, it is possible to note that the binding energies of Ti 2p_{3/2} and Ti 2p_{1/2}, are equaling to 460,4 eV and 466 eV, respectively. Those binding energies suggest in fact the presence of titanium on the fourth stage of oxidation (Ti⁴⁺) in the surface layer [18, 19]. On the basis of P 2p spectrum, where the maximum is observed at 134,1 eV, one can assume the presence of titanium and/or copper and/or nickel phosphates in the PEO coating. The Cu 2p spectrum has three local maxima for the following binding energies: 935,3 eV, 939,2 eV and 943,95 eV. All the presented maxima of Cu 2p spectrum can be interpreted as the copper on the second stage of oxidation, i.e. Cu²⁺. The

maximum of Ni 2p spectrum at the binding energy equaling 857,5 eV can be interpreted as nickel phosphate. Summing up, it should be noticed that the surface layer consists mainly of Ti^{4+} , Cu^{2+} , Ni^{2+} and PO_4^{3-} , which may form the compounds such as $Ti_3(PO_4)_4 \cdot Cu_3(PO_4)_2 \cdot Ni_3(PO_4)_2$.

3 Conclusions

Based on the experimental results, the following conclusions can be formulated:

- it is possible to create a porous coating on NiTi alloy, enriched with copper ions; for this purpose the Plasma Electrolytic Oxidation (PEO) at voltage of 450 V was used and the process was carried out in the electrolyte containing concentrated H_3PO_4 within $Cu(NO_3)_2$ in the amount higher than 1,6 mol/L
- the porous PEO coating obtained in the electrolyte containing copper nitrate in an amount higher than 1,6 mol/L consists mainly of copper-titanium-nickel phosphates
- a negative aspect of the coating is the emergence of carcinogenic nickel appearing inside, fortunately in very small quantities, *i.e.* below 1 at%, in comparison with matrix
- the obtained PEO coating consists mainly of Ti^{4+} , Cu^{2+} , Ni^{2+} and PO_4^{3-} .

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