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Charakterystyka porowatych powłok otrzymanych na niobie i stopie Ti-Nb-Zr (TNZ) w procesie elektrolitycznego utleniania plazmowego (PEO)

Characteristics of porous biocompatible coatings obtained on Niobium and Titanium-Niobium-Zirconium (TNZ) alloy by Plasma Electrolytic Oxidation

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Elektrolityczne utlenianie plazmowe (POE) zastosowano do biomateriałów metalowych, takich jak niob i stop Ti-Nb-Zr (TNZ). Obróbkę prowadzono w elektrolicie kwasu H_3PO_4 z dodatkiem azotanu miedzi. Otrzymane porowate powłoki badano z użyciem SEM/EDX. Badania uzyskanych powłok wykazały, że są one wzbogacone w jony miedzi (ponad 3,5 %mas.), podczas gdy Cu/P oraz Cu/(P+osnowa) wynosiły odpowiednio 0,2 i 0,07. Taka charakterystyka sprzyja poprawie biokompatybilności badanego biomateriału.

SŁOWA KLUCZOWE: niob; stop Ti-Nb-Zr (TNZ); elektrolityczne utlenianie plazmowe (PEO); SEM/EDX; powłoka porowata

The Niobium and Titanium-Niobium-Zirconium (TNZ) alloy biomaterials were treated by Plasma Electrolytic Oxidation (PEO) in view of getting porous surface layers. For the PEO process, a special set up was built to perform the experiments in the electrolyte composed of concentrated H_3PO_4, with an addition of copper II nitrate. The surface layers were studied by means of SEM and EDS methods to reveal the effects of porosity and compositions. It was found one may create porous coatings on niobium and on TNZ alloy, enriched with copper ions. Over 3.5 wt% content of copper, with Cu/P and Cu/(P+Matrix) ratios equaling to 0.2 and 0.07, respectively, may assure a better biocompatibility of the biomaterials.

KEYWORDS: Niobium; Titanium-Niobium-Zirconium (TNZ) Alloy; Plasma Electrolytic Oxidation (PEO); SEM/EDX; Porous coatings

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Introduction

Titanium, Niobium, Zirconium as well as their alloys are increasingly used as biomaterials, because of their good biocompatibility and high corrosion resistance in human solutions, such as *e.g.* blood, Ringer's and/or Hank's solutions. A lot of present studies have been focused on metallic biomaterials to apply a proper surface treatment method to achieve the goal [1-5]. It is obvious that to implant any biomaterial into the human body, it is necessary to prepare its surface. The characteristic feature expected to reach on the biomaterial surface is very often its porous structure. Moreover, the coating with porous structure should contain some specific elements inserted within to ensure the chemical compositions similar, *e.g.* to human bone, *i.e.* containing calcium and phosphorus.

These specific surface properties can be achieved by Plasma Electrolytic Oxidation (PEO) also known as Micro Arc Oxidation (MAO) [1-6] with eventual electrochemical pre-treatments, realized by Electropolishing (EP) [7-17], Magnetoelectropolishing (MEP) [13-33] and/or High-Current Density Electropolishing (HDEP) processes [34-37]. Another important feature of the PEO (MAO) is that it allows to introduce the additional bactericidal ions of silver [38-41] and/or copper [42-46]. Such processes make it possible to control a doping of coating composition by chemical elements, with the result of better characteristics expected concerning the biocompatibility of metallic biomaterials.

Method

■ Material

The Niobium and Titanium-Niobium-Zirconium alloy (Ti 74 wt%, Nb 20 wt%, Zr 6 wt%) samples, as received, served for the study. The samples were prepared in the form of rectangular specimens of dimensions 5 × 30 mm cut off from the metal sheet 1 mm thick.

■ Set up and parameters

The plasma electrolytic oxidation (PEO) was performed at the voltage of 450±10 V. The main elements of the set-up were: a processing cell, a dc power supply, the electrodes and connecting wiring, with the schematic given in **Figure 1**. The experiments were carried out in the electrolyte of initial temperature of 20±2 °C. For the studies, the electrolyte composed of concentrated orthophosphoric acid, with an addition of copper II nitrate, was used. For each run, the electrolytic cell made of glass was employed, containing up to 500 ml of the electrolyte.

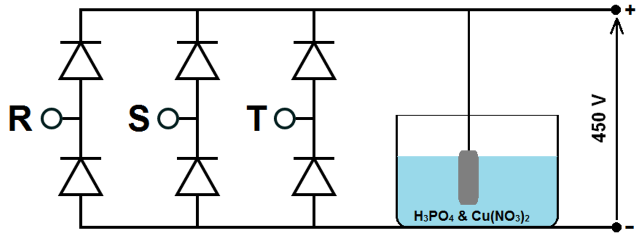


Fig. 1. Set up for the PEO treatment at voltage of 450 V in electrolyte containing H_3PO_4 within $Cu(NO_3)_2$

■ SEM and EDS studies

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 used. The magnifications of 500 and 6000 times for SEM images were used. The EDS analyses were performed from the whole frame for magnification of 6000×.

Results and discussion

Numerous PEO experiments were performed by the authors on Nb and TNZ biomaterials to obtain expected features of the treated surfaces. Apart from the electric conditions [34-37] of the study, the composition of the electrolyte used to the experiments was very important variable. The studies were carried out with 3.20 mol/L concentration of $Cu(NO_3)_2$ in H_3PO_4 electrolyte.

In **Figure 2**, there is shown the SEM image of surface layer formed on pure niobium after the PEO at voltage of 450 V in 3.20 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte. One may notice the obtained surface is porous and contains copper (3.7 ± 0.4 wt%), that is shown in **Figure 3**. The amount of phosphorus, which was detected by the EDS and which equals to 18.5 ± 0.3 wt%, suggests that the coating is composed of phosphates within oxides/hydroxides. The Cu/P ratio for that coating is equal to 0.2, whereas the Cu/(P+Nb) = 0.07. In the summary it should be emphasized that the coating obtained on niobium after the PEO at voltage of 450 V in 3.2 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte can be considered as a biocompatible one.

In **Figure 4**, there is presented the SEM image of surface layer formed on TZN alloy after the PEO at voltage of 450 V in 3.20 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte. One may easily notice that obtained surface is porous and contains copper in the coating volume (3.5 ± 0.3 wt%), with the plot given in **Figure 5.** The amount of phosphorus, which was detected by EDS and which equals to 17.6 ± 0.8 wt%, suggests, similar as in the case of niobium, that the coating is generally composed of phosphates within oxides/

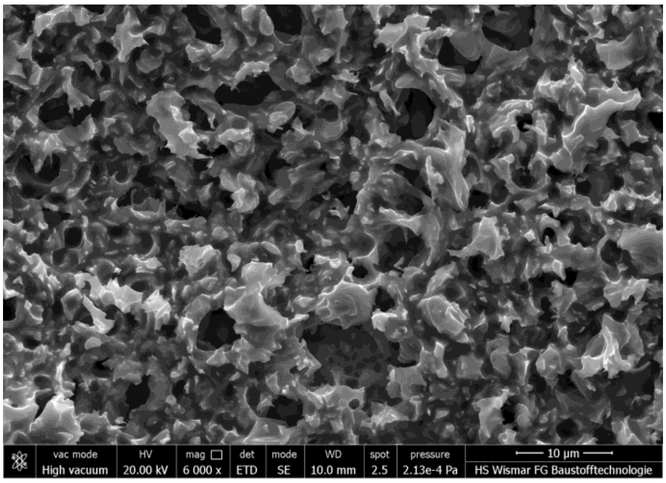
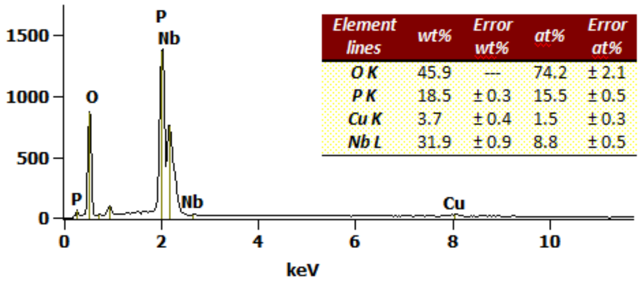


Fig. 2. SEM picture of surface layer formed on Niobium after the PEO treatment at voltage of 450 V in 3.20 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte



Element lines	wt%	Error wt%	at%	Error at%
O K	45.9	---	74.2	± 2.1
P K	18.5	± 0.3	15.5	± 0.5
Cu K	3.7	± 0.4	1.5	± 0.3
Nb L	31.9	± 0.9	8.8	± 0.5

Fig. 3. EDS result of surface layer formed on Niobium after the PEO treatment at voltage of 450 V in 3.20 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte

hydroxides. The Cu/P ratio for that coating is equal to 0.2, and the Cu/(P+Ti+Nb+Zr) = 0.07, with Ti+Nb+Zr = Matrix. In the summary it should be emphasized that the coating obtained on niobium after the PEO at voltage of 450 V in 3.2 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte can be considered as a biocompatible one.

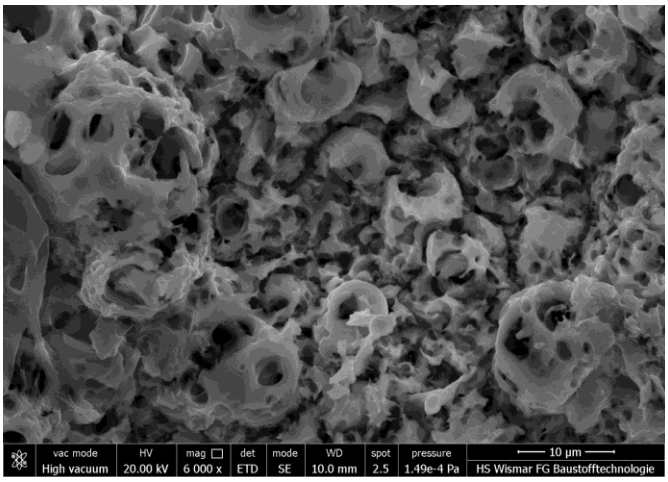
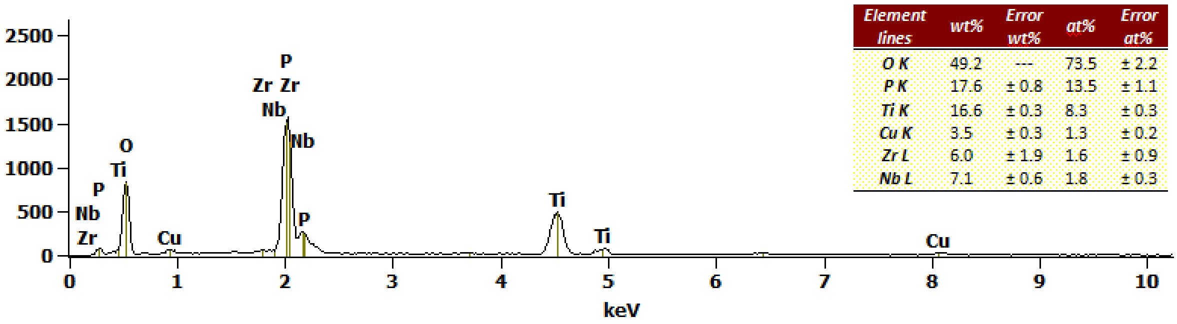


Fig. 4. SEM picture of surface layer formed on TNZ alloy after the PEO treatment at voltage of 450 V in 3.20 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte



Element lines	wt%	Error wt%	at%	Error at%
O K	49.2	---	73.5	± 2.2
P K	17.6	± 0.8	13.5	± 1.1
Ti K	16.6	± 0.3	8.3	± 0.3
Cu K	3.5	± 0.3	1.3	± 0.2
Zr L	6.0	± 1.9	1.6	± 0.9
Nb L	7.1	± 0.6	1.8	± 0.3

Fig. 5. EDS result of surface layer formed on TNZ alloy after the PEO treatment at voltage of 450 V in 3.20 mol/L of $Cu(NO_3)_2$ in H_3PO_4 electrolyte

Conclusion

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

- it is possible to create a porous coating on pure niobium as well as on the TNZ alloy, enriched in copper ions
- the coatings formed on niobium and TNZ alloy contain over 3.5 wt% of copper
- the Cu/P and Cu/(P + Matrix) ratios are equal to 0.2 and 0.07, respectively.

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