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

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DOI: 10.17814/mechanik.2015.12.530

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 element 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 H3PO4 with Cu(NO3)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(NO3)2 in H3PO4 electrolyte.

In Figure 2, there is shown the SEM image of surface layer formed on pure niobium after the PEO treatment at voltage of 450 V in 3.20 mol/L of Cu(NO3)2 in H3PO4 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 EDS and which equals to 17.6 ± 0.8 wt%, suggests, similar as in the case of niobium, that the coating is composed of phosphates within oxides/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(NO3)2 in H3PO4 electrolyte can be considered as a biocompatible one.

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(NO3)2 in H3PO4 electrolyte

In Figure 4, there is presented the SEM image of surface layer formed on TNZ alloy after the PEO at voltage of 450 V in 3.20 mol/L of Cu(NO3)2 in H3PO4 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/hydroxides.
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.

Acknowledgments

Prof. Dr.-Ing. Winfried Malorny and Dr Torsten Barfels from Hochschule Wismar, Germany, are highly acknowledged for providing access to the SEM apparatus allowing to perform the studies.

The authors would like to thank Professor Hugo Ricardo Zschommler Sandim, Departamento de Engenharia de Materiais, Escola de Engenharia de Lorena, Universidade de São Paulo, Brazil, for allowing to perform the PEO studies on the obtained niobium samples.

Acknowledgments are sent to Prof. Frédéric Prima, Ecole Nationale Supérieure de Chimie de Paris, France, for the obtained TNZ samples used in this study.

LITERATURE


