Protective PEO-coatings on titanium shape memory alloy for medical implants

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Abstract. The use of titanium shape memory alloy Ti-18Zr-15Nb with promising coatings for the manufacture of medical implants is considered. In this paper, we examined plasma electrolytic oxidation (PEO) in a pulsed bipolar mode with different frequencies to protect the surface from the aggressive environment of the human body. Two frequencies of 300 and 1000 Hz were used. The results of SEM, EDS, XRD analysis, and electrochemical tests of the coatings were discussed. As a result of comparison, it was shown that carrying out the PEO process at 1000 Hz provides the formation of a more uniform coating with higher quality than the coating obtained at 300 Hz.

1. Introduction

The development of the processes of transplantation of biomaterials into the human body has revealed the problem of the lack of technologies for the creation of bone implants that are biologically compatible with bone tissue. The practice of using titanium implants in surgical traumatology for bone reconstruction in bone tumors, revision arthroplasty does not always guarantee the absence of inflammation or necrosis of the tissues surrounding the material and poses the problem of developing a technology for creating bone implants with a high level of biocompatibility [1].

An example of a new structural biomaterial for permanent bone implants is a nickel-free shape memory alloy (SMA) based on the Ti-Zr-Nb system, containing only biocompatible (non-toxic) components and having a low Young's modulus close to that of bone tissue (up to 30 GPa). Due to the unique combination of biochemical and biomechanical compatibility, this alloy is the most promising among metallic biomaterials for permanent bone implants [2]. To have a smooth transition of the physicochemical properties of the implant material to the human bone, the surface of the device must be modified with a protective functional coating. Currently, one of the promising technologies to improve the corrosion, wear resistance and biocompatibility of permanent bone implants made of titanium and titanium alloys is plasma electrolytic oxidation (PEO) [3, 4].

The PEO of β-titanium alloys Ti-Zr-Nb and Ti-Zr-Nb-Ta was studied using direct current (DC) and pulsed DC regimes, and the improvement in the biocompatibility was shown [5-7]. However, compared to these regimes, pulsed bipolar PEO appears to be an advanced modification of the plasma electrolytic oxidation which previously showed promising results in the development of biocompatible coatings on Ti [8-10]. Therefore, the aim of this study is an investigation of the PEO coatings produced at different frequencies in pulsed bipolar regime on a novel Ti-18Zr-15Nb shape memory alloy.
2. Experimental

The studies were carried out on samples in the shape of disks with a diameter of 9 mm cut from the β-titanium alloy Ti-18Zr-15Nb developed at the National Research Technological University MISiS. Plasma electrolytic oxidation was carried out in a pulsed bipolar mode at frequencies of 300 and 1000 Hz. An aqueous solution of 20 g / L Na$_3$PO$_4$·12H$_2$O was used as the electrolyte; its temperature was kept constant at 20 ± 1 °C; the electrolyte volume was 5 L. Other parameters of the PEO process are shown in Table 1.

| Sample code | Frequency (Hz) | Voltage pulse amplitude (V) | Positive pulse duty cycle (%) | Negative pulse duty cycle (%) | Time (min) |
|-------------|----------------|-----------------------------|-----------------------------|-------------------------------|-------------|
| TZN_300     | 300            | 470                         | 51                          | 26                            | 5           |
| TZN_1000    | 1000           | 430                         | 26                          | 26                            | 2.5         |

The top view of PEO coating was studied using the JEOL JSM-6490LV scanning electron microscope with INCAx attachment for the EDS analysis. The distribution of the points for measuring the elemental composition was chosen in such a way as to estimate the characteristic areas on the surface of the sample and to be able to construct a map of the distribution of various elements in the studied PEO coatings. The phase composition of the coating was investigated using X-ray diffractometer (XRD) Ultima IV (Rigaku, Japan) equipped with a Cu-Kα X-ray source. The scanning was performed from 2θ = 20° to 2θ = 80° with the step of 0.02° and the measurement time at each step amounted 1 s. The phase composition of the surface was studied for both the uncoated alloy and all coatings obtained. Phase identification and semiquantitative analysis were performed using Philips X’Pert HighScore Plus software with the PDF2 databank. The coating porosity was calculated from the SEM images using ImageJ software. The surface roughness Ra was measured with a TR 220 profilometer. Coating thickness h was measured with a Defelsko Positector 6000 eddy current probe with an accuracy of +/- 0.1 μm. Electrochemical studies were carried out using an Elins P-5X potentiostat-galvanostat-impedance meter (Russia) in Ringer's solution in a three-electrode cell with a volume of 100 ml with a silver chloride reference electrode and a graphite electrode. The corrosion potential and current density as well as the polarization resistance were evaluated.

3. Results and discussion

The resulting PEO coatings for two processing modes at 300 and 1000 Hz appear as dense gray films. At the same time, the coatings obtained in the 300 Hz mode have a lighter white-gray tint, while when formed at a frequency of 1000 Hz, a uniform gray coating is observed.

SEM images presented in figure 1 show the top views of the PEO coatings on Ti-Zr-Nb alloy for the two processing modes at 300 and 1000 Hz. An analysis of the images obtained at the magnification of 500 shows that the protective layers formed at 1000 Hz (figure 1, b) have a more uniform distribution of pores compared to that at 300 Hz (figure 1, a). The surface layer at 300 Hz has predominantly round pores, while at 1000 Hz elongated pores and grooves appear. The pore sizes vary from 0.5 to 10 μm, while the grooves have the widths of 3-5 μm and lengths up to 30 μm. The oxide films obtained have the thickness of 21.2 ± 1.2 μm for the frequency of 300 Hz and 17.3 ± 5.3 μm for 1000 Hz.

Also, as a result of the PEO process mechanism, rough surfaces with a significant number of open pores were formed, both in the case of TZN_300 and TZN_1000. Application of the frequency of 1000 Hz allows obtaining a more uniform coating without surface defects, which appear at 300 Hz in the form of areas with very small and very large pores. The porosity of the coatings obtained is 8.0 - 10.7% at 300 Hz and 12.5 - 15.5% at 1000 Hz. The results of the study of the surface roughness showed that the coating obtained at 1000 Hz had a lower roughness in comparison with the PEO coating processed at a frequency of 300 Hz (figure 1).
Figure 1. SEM images of the PEO coatings at different frequencies: 300 Hz (a) and 1000 Hz (b).

A detailed analysis of micrographs of the surface of PEO coatings shows that there is a change in the surface morphology. Also, a partial sealing of the pores is observed at 300 Hz. The presence of pores on the surface of samples with PEO-coatings promotes better adhesion of osteogenic cells and adsorption of proteins. Moreover, this also increases the contact area during the bone integration and decreases the level of mechanical stress [11-12].

As follows from the EDS analysis (table 2), the PEO coating includes not only the constituent elements of the substrate but also electrolyte component elements, in this case, phosphates which participate in the formation of the coating and promote the coating growth.

The qualitative composition of the investigated coatings containing Ti, Zr, Nb, O, P is very similar. Analysis of the EDS mapping shows that the coating contains oxides of Ti, Zr, and Nb. Titanium is evenly distributed over the surface, while Zr, Nb, and O appear less in the pores of the coating. For the TZN_300 sample, the surface defects contain a significant amount of P, while for the TZN_1000, phosphorus was not detected in the phase composition. This may indicate that longer PEO pulses favor the deposition of the electrolyte component into the coating.

Figure 2 shows X-ray diffraction patterns of samples made of Ti-Zr-Nb alloy in the initial state and with the PEO coatings obtained at different frequencies. A comparison of the samples with the coatings and in the initial state shows that the three peaks coincide and correspond to the β-phase of the titanium alloy. Analyzing the PEO coatings obtained at different frequencies, one can assume the presence of TiO$_2$ (anatase and rutile) in the surface layer. Also, other oxides based on Nb (Nb$_2$O$_5$, NbO$_2$) and Zr (ZrO$_2$) appear in the surface layer of the TZN_300 sample, while TZN_1000 contains only traces of NbO$_2$. This can be caused by the effect of the higher power of the microdischarges appearing due to the longer voltage pulses. Titanium has the lowest melting temperature ($T_m$ = 1670°C) among the substrate elements and to oxidize zirconium ($T_m$ = 1852°C) and niobium ($T_m$ = 2468°C), higher microdischarge energy is required.

Analysis of the corrosion properties of PEO coatings obtained at different frequencies for uncoated and PEO coated samples is shown in figure 3. The study of the corrosion potential ($E_{corr}$) shows (figure 3a) that TZN_300 treatment provides surface passivation in comparison with the substrate material TZN, while the TZN_1000 has increased surface activity. Probably, higher porosity for this sample facilitates the penetration of corrosive media, which reduces the surface passivation. Corrosion current, $i_{corr}$, correlates with the porosity of the coating and its thickness (figure 3b). Uncoated material has the highest value of $i_{corr}$, while TZN_1000 shows the lowest corrosion current. The polarization resistance $R_p$ (figure 3c) for TZN_1000, accordingly, increases. Therefore, TZN_1000 shows better corrosion performance.
Table 2. Elemental composition of the surface of the Ti-18Zr-15Nb alloy with the PEO coating.

| Sample code | Point | O   | Ti  | Nb  | Zr  | P   | Others |
|-------------|-------|-----|-----|-----|-----|-----|--------|
| TZN_300     | 1     | 48.38 | 19.89 | 8.17 | 20.10 | 3.45 | -      |
|             | 2     | 32.11 | 27.08 | 9.65 | 25.17 | 5.99 | -      |
|             | 3     | 20.80 | 33.90 | 12.62 | 27.65 | 5.03 | -      |
|             | 4 (pore) | 0.00 | 78.90 | 3.90 | 13.03 | 4.17 | -      |
| TZN_1000    | 1     | 30.93 | 23.28 | 1.80 | 42.10 | -    | 1.89   |
|             | 2     | 35.14 | 23.07 | 3.19 | 37.26 | -    | 1.34   |
|             | 3 (pore) | 11.51 | 49.50 | 4.39 | 33.41 | -    | 1.19   |

Figure 2. X-ray diffractograms of the Ti-18Zr-15Nb samples with the PEO coating obtained at the frequencies 300 and 1000 Hz.

Figure 3. Results of electrochemical tests of Ti-Zr-Nb alloy samples without and with PEO coating in different modes: corrosion potential $-E_{corr}$ (a); corrosion current density $i_{corr}$ (b); polarization resistance $R_p$ (c).
4. Conclusion
The study of samples with PEO coatings on the Ti-18Zr-15Nb shape memory alloy showed the possibility of obtaining continuous coatings on this alloy. Plasma electrolytic oxidation of Ti-Zr-Nb alloy at a frequency of 1000 Hz provides a more uniform surface layer with a better quality than when processing at 300 Hz. It is expected that the observed porous morphology of the coating will facilitate integration with the bone tissue, and the presence of an inert oxide will reduce the release of metal ions into body fluids.

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