Characterisation of porous coatings formed on titanium under AC plasma electrolytic oxidation

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Abstract. The Plasma Electrolytic Oxidation (PEO) process may be used to fabricate porous coatings on titanium. The ranges of voltages used in case of these plasma treatments are different. It has been found that for DC PEO processing the voltage must be higher than that in the case of AC PEO treatment. In addition, the shape and frequency of the voltage signal have also an influence. In the paper scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy and glow discharge optical emission spectroscopy (GDEOS) were used to characterise obtained coatings. It was found that it is possible to obtain the porous coatings enriched with phosphorus and copper by use of AC-PEO at only 200 Vpp, while increasing the PEO voltage results in non-porous and cracked coatings. Based on GDEOS for 200 Vpp three sublayers were used, with ranges of 0-400, and 400-2400, and 2400-3600 seconds of sputtering time for first, and second, and transition sublayers respectively. XPS spectra for sample processed at 200 Vpp indicate in top 10 nm layer presence of titanium as Ti^{4+} and phosphorous as phosphates (most likely PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$, $P_2O_7^{3-}$).

1 Introduction

Light metals such as titanium, niobium, tantalum, zirconium, and their alloys may be treated by Plasma Electrolytic Oxidation also known as Micro Arc Oxidation (MAO). Nowadays, for biomedical and industrial applications the titanium [9-11] and its alloys [12-24] are mostly used. The main advantage of use of that electrolytical method is possibility of forming the porous micro-coatings, which may be enriched with selected materials. It

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should be also pointed out that in literature there are informations about nano-layers, that may be obtained by the electropolishing techniques [1-8]. The PEO coatings used as biomaterials should have hydroxyapatite-like structure enriched with bactericidal copper [10, 25-29], what is very important in the case of surgery of human and animal bodies. The coatings are fabricated at DC or AC voltages of several hundred volts. It addition, it should be noted that errors related to the voltage instability as well as with the distortion associated with the shape of the wave are also affected [30-31]. Porous coatings obtained by DC PEO processes with the use of concentrated phosphoric acid based electrolyte were described in previous papers [32-37].

2 Methods

The titanium samples (10×10×2 mm) were treated by PEO treatment in electrolyte consisting of 1 L of 85% phosphoric acid H_3PO_4 with 500 g copper nitrate trihydrate $Cu(NO_3)_2{\cdot}3H_2O$ for 3 min at voltages of 200 Vpp, 250 Vpp and 300 Vpp (volts peak-to-peak) by using 50 Hz alternating current transformer. The set ups of SEM, EDS, GDOES, XPS measuring systems were described earlier in [18, 20, 31].

3 Results and discussion

In Figure 1, SEM micrographs of coatings formed on titanium after AC PEO treatment at voltages 200, 250, and 300 V_{pp}, are presented. The coating obtained at the voltage of 200 V_{pp} may be characterized as porous with well-developed surface. The developed morphology type can be used for different applications (biomaterials, catalysts, as well as for air and space industry).

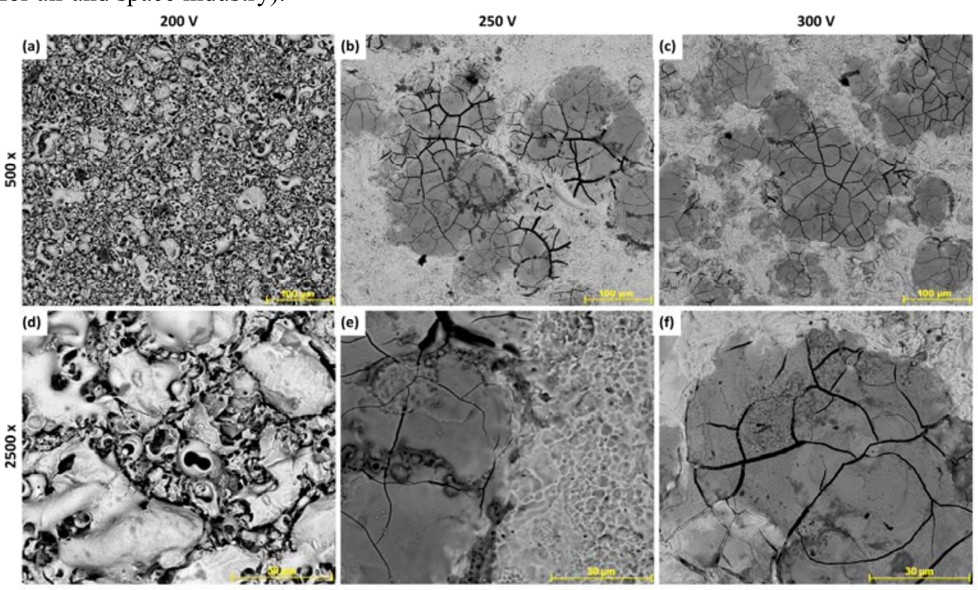

Fig. 1. SEM pictures of coatings formed on Titanium Grade 2 after AC PEO treatment at voltages of 200 V_{pp}, 250 V_{pp}, 300 V_{pp}. Magnifications 500 and 2500 times.

The surfaces obtained at voltages of 250 and 300 V_{pp} look not so well developed as that one obtained at 200 V_{pp}. Higher voltage correlates with more energy delivered to create plasma on the material surface during the process. Under these conditions, the increasing voltage seems to have a negative influence on building porous, well developed surfaces.