NEW TRENDS OF POROUS COATINGS OBTAINED BY PLASMA ELECTROLYTIC OXIDATION

Krzysztof ROKOSZ [1], Tadeusz HRYNIEWICZ [1], Steinar RAAEN [2], Winfried MALORNY [3], Łukasz DUDEK [1], Kornel PIETRZAK [1]

[1] *Division of BioEngineering and Surface Electrochemistry, Department of Engineering and Informatics Systems, Faculty of Mechanical Engineering, Koszalin University of Technology, Poland, EU* *rokosz@tu.koszalin.pl (K.R.); lukasz.dudek@tu.koszalin.pl (Ł.D); kornel.pietrzak@s.tu.koszalin.pl (K.P.)*

[2] *Department of Physics, Norwegian University of Science and Technology (NTNU), Trondheim, Norway* *steinar.raaen@ntnu.no*

[3] *Faculty of Engineering, Hochschule Wismar-University of Applied Sciences Technology, Business and Design, Wismar, Germany, EU, winfried.malorny@hs-wismar.de*

Abstract

Nowadays, the porous coatings enriched in determined chemical elements on CP Titanium Grade 2 may be obtained by Plasma Electrolytic Oxidation (PEO), the process also known as Micro Arc Oxidation (MAO). It should be pointed out that DC, AC, or pulse voltage may be used to create these coatings; however, their structures, chemical composition and mechanical properties are always different than the substructure (matrix). It should be also noted that they may be used in a wide range of applications, such as biomaterials, catalysts, sensors as well as wear resistant coatings. In this paper, the fabrication and characterization of PEO coatings obtained on CP Titanium Grade 2, which are porous and enriched in biologically active chemical elements, are presented.

Keywords: Plasma electrolytic oxidation, porous coatings, DC PEO, CP Titanium Grade 2

1. INTRODUCTION

Plasma electrolytic oxidation process mechanism and coatings properties are well described in literature [1,2], however rather shortly covering light metals including titanium [3], aluminum [4], tantalum [5], zirconium [6], niobium [7] and their alloys [8,9]; they may be processed by PEO technique and because of the beneficial weight-to-strength ratio, corrosion and wear resistance [10,11], are preferably used in a wide range of applications including biomaterials [12], marine engineering [13], and aerospace [14]. Moreover titanium dioxide (TiO_2) is a chemical substance with multiple applications including pigment, cosmetics, sensors, photocatalysis, nanomaterials because of its unique physicochemical properties [15,16]. It is well established in literature, that during PEO process on titanium it is possible to obtain coatings, with well-developed porous structure composed of titanium oxides enriched with particular chemical elements, appropriate to specific application [17]. Rudnev et al. reported catalytic activity of nickel and copper enriched PEO coatings created on titanium with use of alkaline electrolyte based on phosphates, borates, tungstates and silicates (Na_3PO_4, $Na_2B_4O_7$, Na_2WO_4, Na_2SiO_3, NaOH) in reaction of CO oxidation to CO_2 at temperatures exceeding 300-400 °C [18]. A. Kazek-Kęsik et al. reported coatings obtained on β-phase titanium alloy Ti-15Mo enriched in Ca and P, or Ca and Si, or Si as cytocompatible in tests using MG-63 osteoblast-like cells with improved corrosion properties in solution simulating body fluids [19]. M. Shokouhfar and S.R. Allahkaram reported that incorporation of specific nanoparticles may improve the coatings hardness and reduce the surface roughness, friction coefficients and wear resistance [20]. While water based electrolytes during plasma electrolytic oxidation on titanium and it's alloys are dominant in available literature, coatings produced in electrolytes based on concentrated 85% phosphoric acid enriched in biologically active elements - calcium [21,22], magnesium [22], zinc [23,24] , and copper [25] - were described in our previous papers.

The purpose of this study is to investigate morphological properties and chemical composition of titanium coatings enriched during plasma electrolytic oxidation process simultaneously in calcium, magnesium and copper obtained in DC PEO process at the voltages of 500, 575 and 650 V for further applications as biomaterials, sensors or catalysts. Moreover different voltages allow to formulate conclusions of the impact in chemical nature of these three ions (Ca^{2+}, Mg^{2+} and Cu^{2+}) in coating creation and composition.

2. METHOD

CP Titanium Grade 2 samples with dimensions 10 mm × 10 mm × 2 mm were treated by Plasma Electrolytic Process (PEO) for 3 minutes with use of DC power supply PWR 1600H (KIKUSUI Electronics Corporation International, Yokohama, Kanagawa, Japan) with voltage and current ranges of 0-650 V and 0-8 A, respectively. As electrolyte mixture of three salts calcium nitrate tetrahydrate $Ca(NO_3)_2{\cdot}4H_2O$, magnesium nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$, and copper nitrate hexahydrate $Cu(NO_3)_2{\cdot}3H_2O$ in mass proportion 1:1:1 in summary concentration of 500 g per 1 L of 85% phosphoric acid H_3PO_4 were used. AISI 316L stainless steel was used as cathode and glass vessel as electrolytic bath. For each PEO process 500 mL of electrolyte was used. A scanning electron microscope Quanta 250 FEI with Low Vacuum and ESEM mode and a field emission cathode as well as an energy dispersive EDS system in a Noran System Six with nitrogen-free silicon drift detector were used. X-ray photoelectron spectroscopy (XPS) measurements on studied sample surfaces were performed by means of SCIENCE SES 2002 instrument (SCIENTA AB, ScientaOmicron, Uppsala, Sweden) using a monochromatic (Gammadata-Scienta) Al K(alpha) (hv = 1486.6 eV) X-ray source (18.7 mA, 13.02 kV). Scan analyses were carried out with an analysis area of 1 mm × 3 mm and a pass energy of 500 eV with the energy step 0.2 eV and step time 200 ms. SEM, EDS and XPS methodology was described in details in previous paper [23].

3. RESULTS AND DISCUSSION

SEM images of samples obtained at voltage of 500 V were presented in **Figure 1** with magnifications of 500× (a), 2500× (b). Obtained SEM images prove that well developed, porous surfaces were obtained. Based on EDS results for sample obtained at 500 V, representative values of atomic concentrations for phosphorous (P), calcium (Ca), magnesium (Mg), copper (Cu) and titanium (Ti) equal to 50.15 ± 0.37, 3.09 ± 0.37, 2.87 ± 0.37, 1.86 ± 0.19, 42.03 ± 0.22 in at.% respectively. While peaks of P, Ca, Mg, Cu come from created porous coating, the Ti signal may origin from both coating and titanium matrix, what is because of X-ray nature. Regarding this phenomena, as a reliable parameter of coating properties, the metal-to-phosphorus ratio (M/P), i.e. calcium-to-phosphorus (Ca/P), magnesium-to-phosphorus (Mg/P) and copper-to-phosphorus (Cu/P) were calculated and equal to 0.062, 0.057, 0.037, respectively for currently described sample.

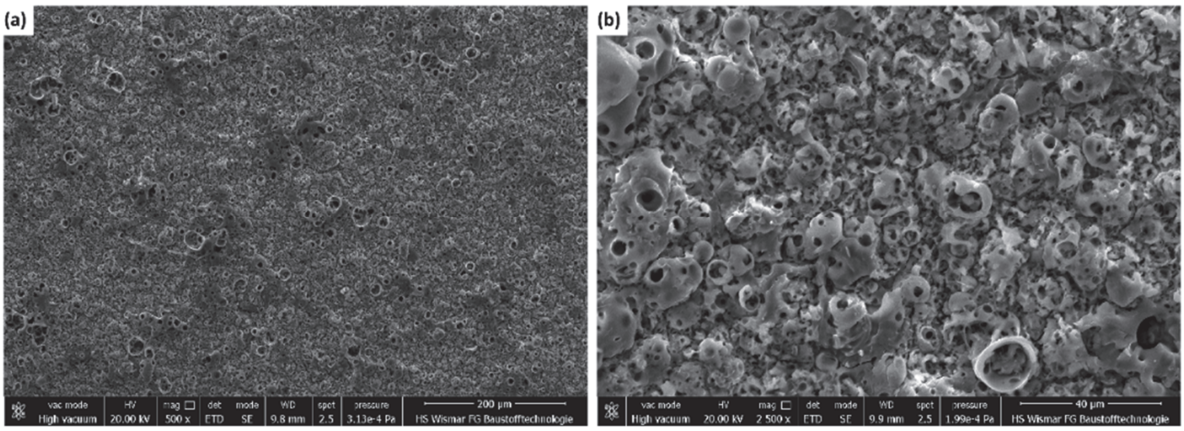

Figure 1 SEM images in magnifications of 500× (a), 2500× (b) of samples obtained on titanium at 500 V

SEM images of samples obtained at voltage of 575 V in **Figure 2** with magnifications of 500× (a), and 2500× (b) are presented. Obtained SEM micrographs prove the presence of well developed porous surfaces. Based on EDS results for the sample obtained at 575 V, representative values of atomic concentrations for oxygen (O), phosphorous (P), calcium (Ca), magnesium (Mg), copper (Cu) and titanium (Ti) equals to 51.39 ± 0.38, 3.41 ± 0.08, 3.11 ± 0.11, 2.33 ± 0.23, 39.76 ± 0.26 in at.% respectively. Peaks of P, Ca, Mg, Cu come from created porous coating, whereas titanium signal may come from both coating and titanium matrix. Because of this phenomena, as a reliable parameter of coating properties, the metal-to-phosphorus ratio (M/P), i.e. calcium-to-phosphorus (Ca/P), magnesium-to-phosphorus (Mg/P) and copper-to-phosphorus (Cu/P) were calculated and equal to 0.066, 0.061, 0.045 respectively for currently described sample. All the M/P ratios are higher than those calculated for the sample obtained at 500 V.

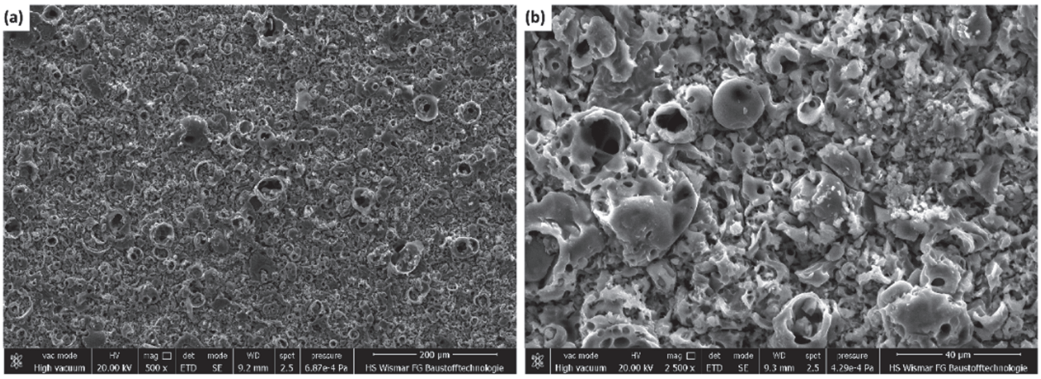

Figure 2 SEM images in magnifications of 500× (a), 2500× (b) of samples obtained on titanium at 575 V

SEM micrographs of samples obtained at voltage of 650 V were presented in **Figure 3** with magnifications of 500× (a), 2500× (b). Obtained SEM images prove that well developed, porous surfaces were obtained. EDS results for sample obtained at 650 V, as representative values of atomic concentrations for phosphorous (P), calcium (Ca), magnesium (Mg), copper (Cu) and titanium (Ti) equals to 50.23 ± 0.39, 3.64 ± 0.08, 3.21 ± 0.12, 2.87 ± 0.27, 40.05 ± 0.27 in at.% respectively. Peaks of P, O, Ca, Mg, Cu come from created porous coating, while titanium signal most probably comes from both coating and titanium matrix. Because of this phenomena, as reliable parameter of coating properties the metal-to- phosphorus ratio (M/P), i.e. calcium-to-phosphorus (Ca/P), magnesium-to-phosphorus (Mg/P) and copper-to- phosphorus (Cu/P) were calculated and equal to 0.072, 0.064, and 0.057, respectively for currently described sample. The M/P ratios are higher than those calculated for sample obtained at 500 and 575 V.

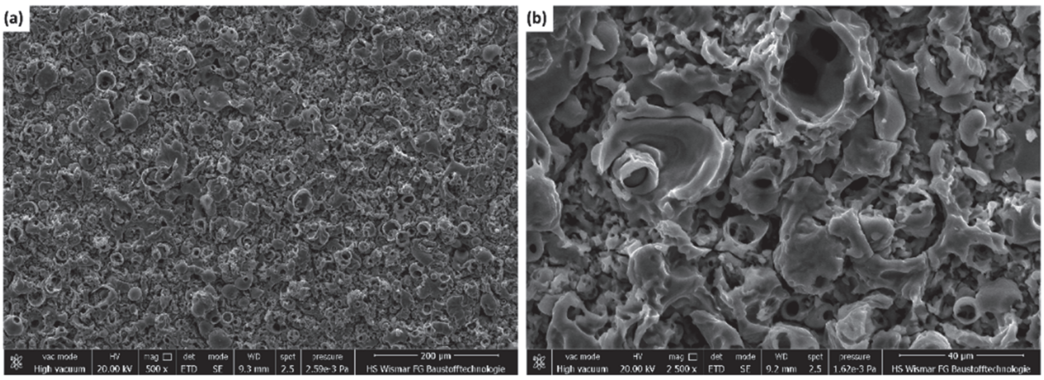

Figure 3 SEM images in magnifications of 500× (a), 2500× (b) of samples obtained on titanium at 650 V

Results of EDS investigations for samples obtained at the voltages of 500, 575 and 650 V, as Ca/P, Mg/P and Cu/P are summarized in **Figure 4**. It can be clearly observed that with increasing voltage, the M/P ratios rise.

Considering the extreme investigating voltages, i.e. 500 V and 650 V, the slopes calculated as M/P ratio change per 100 V for Ca/P, Mg/P and Cu/P are as follows: 0.0072/100V; 0.0045/100V and 0.0133/100V. Based on the calculation it can be concluded that Cu/P ratio is one the most sensitive parameter of described for voltage change, and the Mg/P ratio - the least sensitive one. Higher energy delivered to the plasma oxidation process, understood here as higher voltage, results in higher metal-to-phosphorus ratios, that agrees with the previous papers describing PEO coatings obtained in similar conditions with the use of electrolytes enriched in one kind of salt [22,23]. However, the differences in calcium-, magnesium- and zinc- to-phosphorus ratios characteristics probably originate from both, differences in chemical nature of these elements and mechanisms of plasma electrolytic oxidation process during formation of these coatings.

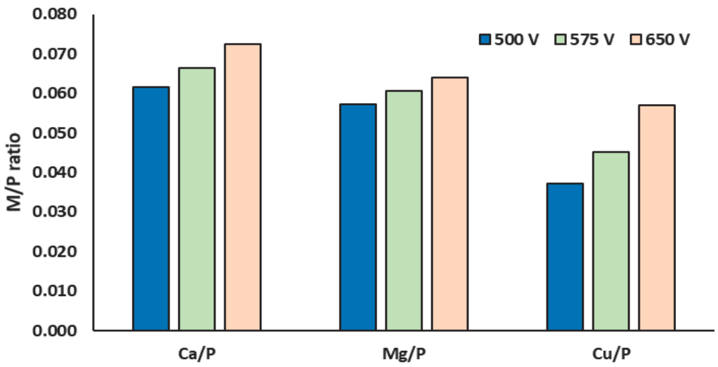

Figure 4 EDS results presented as Ca/P, Mg/P and Cu/P ratios of samples obtained on titanium at three voltages of 500, 575 and 650 V

In **Figure 5** XPS spectra of sample obtained at voltage of 575 V was presented. Based on the obtained specta in top ca. 10 nm of coating, it is composed of titanium as Ti^{4+} (Ti 2p, 460.0 eV), calcium as Ca^{2+} (Ca 2p 347.1 eV), magnesium as Mg^{2+} (Mg 2s, 89.0 eV, Mg KLL 306.1 eV), copper as Cu^{+} or Cu^{2+} (Cu $2p_{3/3}$ 932.8eV), phosphates as PO_4^{3-}, or HPO_4^{2-}, or $H_2PO_4^{-}$, or $P_2O_7^{4-}$ (P 2p 133.7 eV).

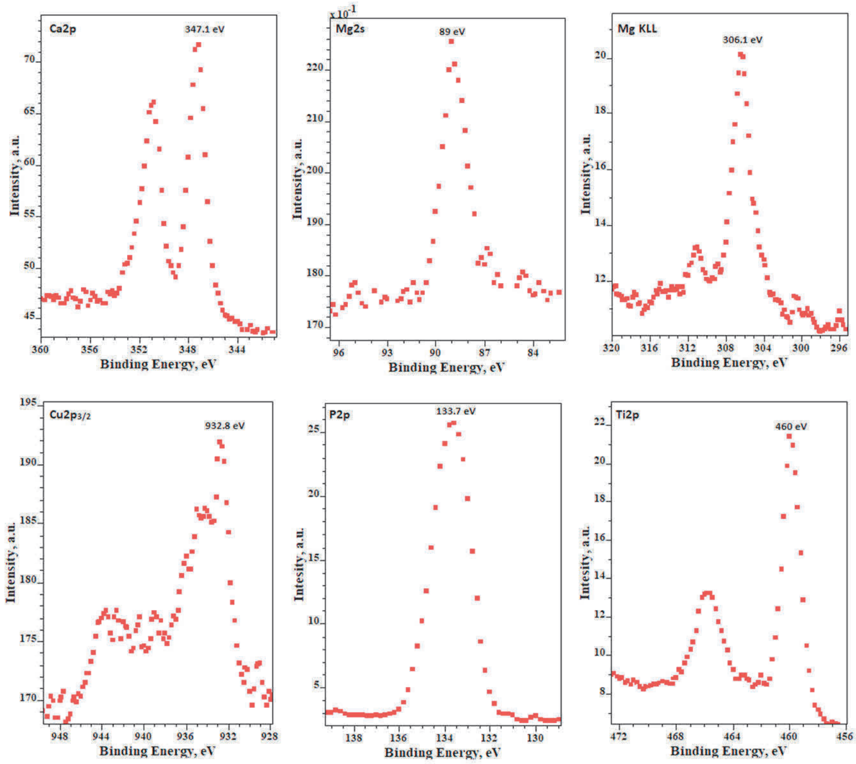

Figure 5 XPS spectra of sample obtained on titanium at voltage of 575 V

In summary, the composition of top 10 nm layer include anions of phosphates and kations of titanium, calcium, magnesium, copper in possible forms of salts and oxides, most likely including titanium oxides.

4. CONCLUSIONS:

- During DC PEO process performed for 3 minutes at voltages of 500, 575 and 650 V with the use of DC power supply PWR 1600H in the electrolyte mixture of three salts $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ in mass proportion 1:1:1 in summary concentration of 500 g per 1 L of 85% H_3PO_4 porous coatings on CP Titanium Grade 2 for possible applications as biomaterials, catalysts, sensors were created.
- Based on EDS studies, the coatings - beside oxygen and phosphorus - were enriched with calcium, magnesium and copper.
- Positive correlation between the applied voltage ranging in 500-650 V, and Ca/P, Mg/P, Cu/P ratios was observed.
- Differences in calcium-, magnesium-, and zinc-to-phosphorus ratios to voltage characteristics probably originate from both, differences in chemical nature of these elements and mechanisms of plasma electrolytic oxidation process during formation of these coatings.
- Based on XPS studies, 10 nm top composition of the coating may be described as phosphate-based with the additions of ions of titanium, calcium, magnesium and copper.

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