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Researches concerning the titania coatings formed on titanium by plasma electrolytic oxidation

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This paper relieves the elaboration and characterization of titania coatings formed on titanium by a relative new plasma electrolytic oxidation method (PEO). During the oxidation treatment, the titanium sample was immersed in electrolytic solution containing calcium acetate monohydrate ($(CH_3\text{-}COO)_2Ca•H_2O$) and β-glycerophosphate disodium salt pentahydrate ($C_3H_7Na_2O_6P$ * $5H_2O$) in distilled water. The obtained coatings were characterized using electronic scanning microscopy (SEM) and X-rays analysis (XRD). During the anodic oxidation changes not only the titanium surface topography but also the chemical composition and physical properties of the surface layers. The quality of titania coatings depend of the technique parameters, such as voltage, time, temperature etc. It can be observed that high quality coatings can be formed using properly selected deposition parameters.

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1. Introduction

Plasma electrolytic oxidation (PEO) is an effective new technique used to deposit ceramic coatings on the surfaces of titanium. This technique presents the various advantages: improved adhesion of oxides, protection against corrosion, and mechanical/chemical properties of oxides and the absence of size/shape restrictions of samples [1-6].

PEO yields rough and porous ceramic layers, whose composition depends on the chemical composition of the electrolyte solution employed and on the substrate material.

From the adequate materials for dental and orthopedic implants or prostheses are titanium and titanium alloys due to their corrosion resistance, biocompatibility, durability and strength. The species incorporated into the coating from the electrolyte greatly affect the structures of PEO coatings on titanium, which crystallinity are being suppressed in silicon-containing coatings, phosphorus and calcium species [7-12].

The plasma electrolytic oxidation uses the dielectric breakdown of the oxide film of the metal anode in the aqueous electrolyte. This transformation of the film is accompanied by sparks visible on the treated surface. The porous oxide coatings are formed on the surface as a result of the thermal action of the sparks [13].

Some of the physic-chemical properties of the obtained oxide layer on titanium, such as thickness, morphology, chemical composition and degree of crystallinity can be relatively easy to be established by applying an electrochemical oxidizing in appropriate conditions: electrolyte, current density and voltage. Several studies have shown, that the use of a voltage higher than the breakdown voltage can cause the formation of micropores with a several micrometer diameter on the surface of materials and ions contained in the electrolyte can be adsorbed into the inside of the porous oxide layer [14-16]. The temperature of the areas of glow discharge may reach as much as 2000 ^{0}C [14], which leads to local evaporation of the solution and crystallization of its constituents, and next, to their incorporation in the oxide layer. It is possible to incorporate calcium, phosphorus and silicon into the oxide layer on titanium during plasma electrolytic oxidation using an appropriate electrolyte [17–20]. The PEO-synthesized coatings are utilized in various applications such as anti-corrosion, anti-friction, and photoactive layers [21–25].

In this paper, experimental results on the elaboration of TiO_2 coatings on commercially titanium by plasma electrolytic oxidation are categorized and explained. The surface and cross-section morphology and phase component of the oxide layers were characterized by SEM and XRD.

2. Material and methods

2.1. Sample preparation

Titanium samples were cut from a sheet of titanium (commercially pure titanium - grade 2) and used as substrate. The chemical composition of titanium samples is: Fe 0.105 %; C 0.011 %; O 0.175 %; N 0.006 %; H 0.0005 % and Ti remains.

Prior to PEO treatment, the titanium plates were polished using #200 – #1000 SiC sandpaper gradually, degreased and cleaned in an ultrasonic bath with ethyl alcohol and distilled water, successively.

2.2. PEO process

The PEO equipment, shown in Fig. 1, was design and manufactured at the University of Pitesti.

Fig. 1. PEO experimental equipment.

The experimental set-up consists of: an insulated stainless steel electrolyte cell with a stirrer and a pulsed bipolar DC power supply. The titanium plate was used as anode, while a stainless steel cell was used as cathode.

The electrolyte in the electrolyte cell was an aqueous solution containing 0.3 mol/l calcium acetate monohydrate ($(CH_3\text{-}COO)_2Ca\cdot H_2O$) and 0.04 mol/l β-glycerophosphate disodium salt pentahydrate ($C_3H_7Na_2O_6P$ * $5H_2O$) in distilled water.

PEO was carried out at an applied voltage of 370 V for 2, 6 and 10 min. The PEO treatments were obtained using a pulsed current regime. During the oxidation, the temperature of electrolyte was less than 50°C. After the PEO treatment the samples were washed with distilled water and dried at room temperature.

2.3. Characterization of oxide layer

The surface and cross-section morphologies of coatings were observed using electronic scanning microscopy (SEM, Low-vaccum Inspect S – FEI Company).

The X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV system (CuK_α radiation) with Parallel Beam optics. The divergence angle of emitted beam from the multilayer mirror is approximately 0.05^0. This kind of optics is suitable for analysis because of increased beam intensity and significant reduction of instrumental aberrations. For the qualitative phase analysis the X-ray diffraction patterns were acquired in Bragg-Brentano geometry, in the 2θ range 20^0-73^0, step width 0.05^0 and 5s as counting time.

3. Results and discussion

Plasma electrolytic oxidation has been employed in order to modify the surface of titanium intended for use as biomaterials, or for improving the mechanical properties of these materials.

Fig. 2 (a-b) shows the SEM micrographs at different magnifications of the surface of oxidized samples at 370 V for 2 min. It is obvious that there exist many micropores in the outer surface of coatings, which is the typical feature of plasma electrolytic oxidation coatings. Also, the size of pores remained after sparks decayed ranges. Therefore, the increasing pore size inevitably leads to the increasing rough surface morphology. The pore diameter varies from 2 to 9 µm.

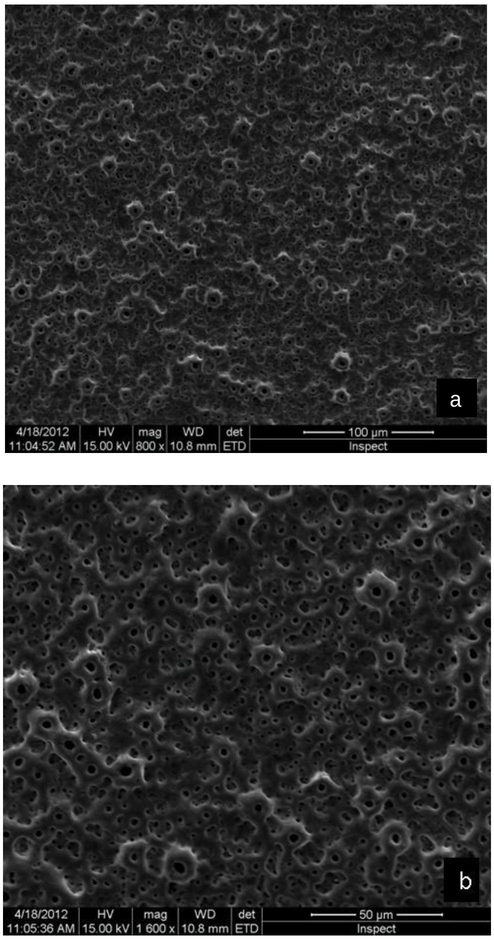

Fig. 2. SEM micrographs at different magnifications of the coatings surface processed for 2 min.

On the surface which is a porous coat are distinguished the micropores which are evenly distributed over the surface. The surface appears due to high temperatures in the exhaust channels for the PEO transformation. We can observe by analyzing the micrographs that the surface is almost unchanged after increasing oxidation time.

The fluctuations of surface temperature due to periodical plasma discharges cause repeated melting and solidification in the outer layer, leading to a porous structure.

The pores on the surface are probably caused by the oxygen bubbles produced in the anodic reaction during the PEO process.

Fig. 3 (a-c) shows the spectra of θ/2θ X-ray diffraction for the PEO coatings obtained at 370 V and the oxidation time variable. The intensity is represented in arbitrary units.

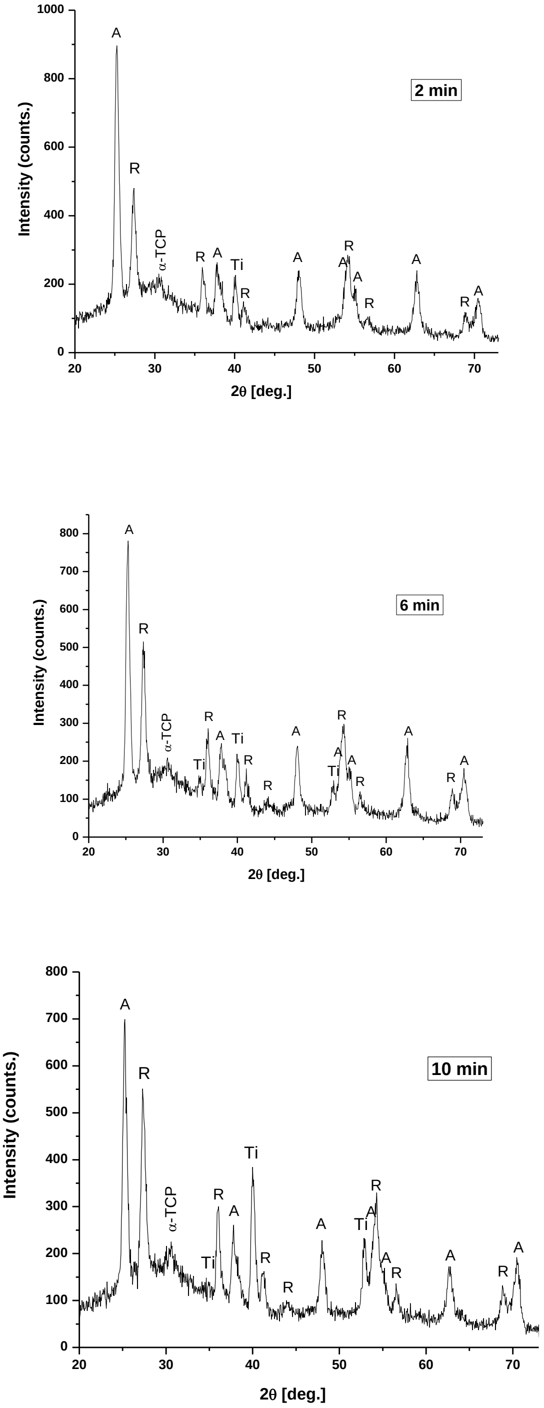

Fig. 3. XRD pattern of the PEO sample obtained at 370 V for: a) 2 min b) 6 min c) 10 min.

The coatings obtained by the PEO technique at 370 V are forming a mixture of phases: anatase, rutile, and the form of the alpha phase of tricalcium phosphate (α - TCP). Unlike other series of experiments, these treatments are less crystalline, probably due to the electrolyte solution used for treatment.

Fig. 4 (a-c) shows the images obtained by electronic scanning microscopy on cross - sections morphologies of the treatment obtained at 370 V for 2, 6 and 10 minutes. We can observe that the coating is continuous and uniform.

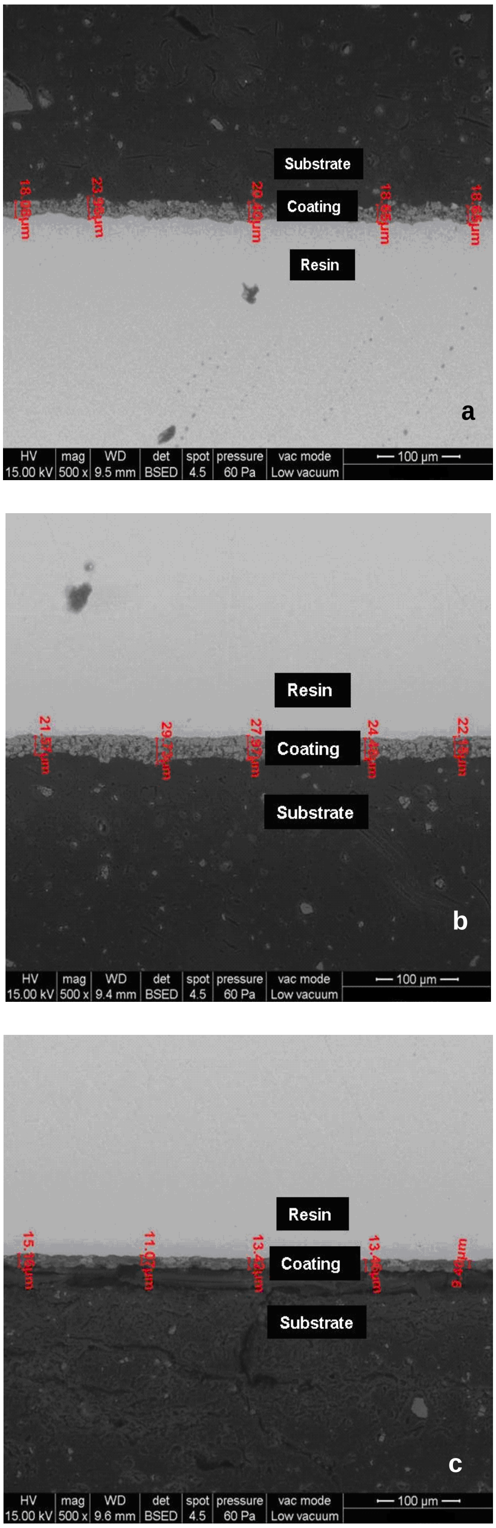

Fig. 4. Cross-sections of the oxide layers produced at 370 V for: a. 2 min, b. 6 min. c. 10 min on titanium by PEO.

The thickness of the layers produced by plasma electrolytic oxidation during of 2 min, 6 min and 10 minutes were approximately 20, 25 and 13 µm. The thickness of the oxide layers deposited was measured in several places, and the final thickness value was obtained by averaging these values.

There was no obvious discontinuity between the film and the underlying substrate, which indicated that the layer could be tightly adhered to the substrate.

In this study, it is observed that with increasing oxidation time, the thickness of the deposited layers increases. When the oxidation time reaches a certain value, the layer easily avalanched from the substrate. This situation occurs during oxidation for 10 minutes. In this case, the layer appeared to avalanche and the thickness of layer decreased.

4. Conclusions

This work explains how a simple method, plasma electrolytic oxidation, can be used to form titanium coatings.

The TiO_2 coatings were grown on commercially titanium (grade 2) by plasma electrolytic oxidation method in electrolyte containing calcium acetate monohydrate and β-glycerophosphate disodium salt pentahydrate.

XRD results indicate that the oxide layers obtained by PEO in the solution containing Ca and P, are composed of three phases. The coatings are mainly consisted of anatase and rutile TiO_2 phase. The ratio between these forms is variable. The alpha phase of tricalcium phosphate (α - TCP) is new phase that appeared with the increase of oxidation time.

The porous titania coating present numerous opened micropores. The pores on the surface are probably caused by the oxygen bubbles produced in the anodic reaction during the PEO process. These pores were well distributed homogeneously over the samples.

The thickness of the layer prepared by plasma electrolytic oxidation could reached about 25 µm and the diameter of the pores varied from 2 to 9 µm.

The important application consist in enrich the TiO_2 layer with calcium and phosphorus in the studied baths. That can significantly contribute to an increase in bioactivity of implants. Moreover, for the futures studies it is important to evaluate the safety of the functionalized surfaces before clinical uses.

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