Elaboration and characterization of TiO$_2$ coatings produced by micro-arc oxidation process

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Abstract. In this paper, the coatings were prepared on titanium surfaces by micro-arc oxidation (MAO). Micro-arc oxidation is a relatively new technique to fabricate ceramic coatings on the surface of titanium. The anodic oxidation changes not only the titanium surface topography but also the chemical composition and physical properties of the surface coatings. The electrolyte used in this paper is a mixture consisting: β-glycerophosphate disodium salt pentahydrate (C$_3$H$_7$Na$_2$O$_6$P$^5$H$_2$O) and calcium acetate monohydrate ((CH$_3$-COO)$_2$Ca$\cdot$H$_2$O). The morphology, composition and phase composition of the coatings were investigated with scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and X-Ray Diffraction (XRD). The quality of titania coatings depend of the technique parameters, such as voltage, time, temperature etc.

1. Introduction

Micro-arc oxidation (MAO) is a relatively new technique to fabricate ceramic coatings on the surface of titanium. Gunter Schulz and Betz developed MAO process for the first time and that has been used in the surface treatment of metals in last year’s [1].

In the MAO technique, the high-voltage micro-arc discharges, raise immediately temperature of the sample surface to 2000–3000°C, causing the surface to melt and created as a thin coating of porous bioactive ceramic material [2-3]. The MAO technique is simple, easily controlled and relatively cheap, compared with plasma spraying method.

MAO produced rough, micro-porous, thick, titanium oxide coating containing bioactive compounds [4]. The final surface structure and composition are strongly influenced by the conditions of the deposition process and electrolyte solution [5]. Electrolyte ions are usually incorporated into the coating. The composition of electrolyte has an important effect on the characteristics and structural properties and morphology of the MAO coatings [5-6].

The MAO coatings are utilized in different applications like: anti-friction, anti-corrosion and photoactive layers [7].

The main technological advantage of anodizing titanium is improved adhesion and bonding, which is particularly relevant in the aerospace industry. It can also be used to increase the oxide thickness to increase corrosion protection and decrease ion release, coloration, and porous coatings.
MAO has been employed for modifying the surface of titanium and its alloys intended to use as biomaterials, or for improving the mechanical properties of these materials. By applying a positive voltage to a Ti substrate immersed in an electrolyte, when the applied voltage is increased to a certain point, a micro-arc occurs and a TiO$_2$ layer on the surface is formed.

The microstructure and properties of coatings formed on titanium alloy can be designable and tailored depending on the careful selection and match of electrolyte and electrical parameters, thus wide applications (such as wear resistance and corrosion protection, properties or obtaining various other functional properties including biomedical, catalytic and dielectric), can be found in industrial sectors including automotive, aerospace, marine, textile, electronic [8].

In this paper are presented the experimental results on the elaboration and characterization of TiO$_2$ coatings on commercially titanium by MAO process. The coatings obtained by micro-arc oxidation were characterized by the following techniques: scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and X-Ray Diffraction (XRD).

2. Materials and methods

2.1. Preparation of substrate

Titanium rectangular samples are cut from a sheet of commercially 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 titanium remains. The sample plates were polished using sandpaper gradually (#200–#1000 SiC), degreased and cleaned in an ultrasonic bath, with ethyl alcohol and distilled water.

2.2. MAO setup and parameters

The equipment used for the micro-arc oxidation is similar to that used for conventional anodising, but more complex, primarily due to the need for higher potentials and controlled pulses of current. The MAO equipment was design and manufactured at the University of Pitesti. The experimental set-up consists of an insulated stainless-steel electrolyte cell and a pulsed bipolar DC power supply, figure1. The titanium plate was used as anode and a stainless-steel electrolyte cell was used as cathode.

The electrolyte used was a mixture of 0.4 mol/l – calcium acetate monohydrate (((CH$_3$-COO)$_2$Ca·H$_2$O) and 0.04 mol/l – β-glycerophosphate disodium salt pentahydrate (C$_3$H$_7$Na$_2$O$_6$P * 5H$_2$O), dissolved in distilled water.

The MAO coatings were realized at an applied voltage of 350 V for 5, 10 and 15 min. The MAO treatments were obtained using a pulsed current regime. During the oxidation, the temperature of electrolyte was less than 50°C. After treatment the samples were cleaned with distilled water and dried at room temperature.
2.3. Characterizations
The morphology, composition and phase composition of the coatings were investigated with scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and X-Ray Diffraction (XRD).

SEM - Scanning electron microscopy - The morphology of treated surfaces was seen on a Scanning Electron Microscope (SEM, Hitachi SU5000). The SEM equipment was operated at 25 kV.

EDX - Energy-dispersive X-ray spectroscopy - The elemental composition was studied with energy dispersive X-ray spectrometer, incorporated into the scanning electron microscope (SEM). EDX was realized at an acceleration voltage of 20 kV.

XRD - X-Ray Diffraction – The crystalline structure of the TiO₂ coatings was analyzed using a Rigaku Ultima IV, with CuKα radiation at 40 kV, with Parallel Beam optics. The measurements were conducted in the 2θ range 10⁰-80⁰, step width 0.050 and 2s as counting time, in Bragg-Brentano configuration.

3. Results and discussion
3.1. SEM results
Figure 2 (a-c) reveals SEM morphologies of the titanium substrate treated by MAO technique. These micrographs show the uniform porous morphology of the coating’s surface. The pores were homogeneously distributed over the surface, with no noticeable cracks. The porous structure is due by the melt flowing out of the discharge channel that rapidly solidified [9].

![SEM micrographs at different magnifications of the coatings surface prepared for 15 min: a. X500, b. X600, c. X900](image)

After MAO treatment, a porous titania coating was formed on the titanium surface whit numerous opened micropores. The pores diameters varied from 1.4 μm and 9 μm (figure 3). The holes in the surface were channels of micro-arc discharge in electrolyte.
3.2. EDX measurements

The elemental composition for titanium substrate MAO modified was identified with the EDX characterization technique (figure 4).

The coatings obtained contain calcium and phosphorus as well as titanium and oxygen. Sodium was not observed in the prepared coatings. It is important to note that the electrolyte components can get incorporated into the formed coatings, with their contents changing depending on oxidation time, electrolyte concentration, and other parameters [10].

Figure 4 indicate incorporation of calcium and phosphorus, in the entire oxide coating created in the process of spark anodisation. Equivalent phenomena were described in following references [11-14].

The contents of the elements are shown in Table 1.

| Table 1. Composition and content of MAO coating |
|--------------------------------------------|
| **Element** | **Wt%** | **Wt% Sigma** |
| C         | 4.24   | 0.05        |
| O         | 43.05  | 0.08        |
| P         | 4.78   | 0.01        |
| Ca        | 9.33   | 0.02        |
| Ti        | 38.60  | 0.06        |
| Total     | 100    |             |
From the table above, it can be noted that the predominant chemical elements of the oxide coating are oxygen and titanium.

3.3. XRD measurements

The figures 5 and 6 shows the spectra of θ/2θ X-ray diffraction for the MAO coatings obtained at 350 V and the oxidation time variable: 5 and 10 minutes. The intensity is represented in arbitrary units. Following the analysis of the qualitative phase, we can see in the figure 5, the coatings are highly crystalline and mainly composed of anatase, rutile and a mixture of calcium phosphate phases.

Figure 5.XRD diffraction spectrum treated at 350 V and 5 minutes

For TiO$_2$ obtained at 350 V and 10 minutes (figure 6), we can observe that the predominant TiO$_2$ phases in the surface are anatase and rutile. From the qualitative observations, regarding the intensities of the diffraction lines, corresponding to the phases rich in calcium and phosphorus, we found a decrease / disappearance of the calcium phosphorus compounds.

Figure 6.XRD diffraction spectrum treated at 350 V and 10 minutes

We can observe qualitatively, that the ratio of the peak intensities corresponding to the TiO$_2$ anatase and TiO$_2$ rutile phases changes with the working conditions. The authors in [15-17] showed that as the MAO anodizing voltage or discharge duration time increases, the intensity of the TiO$_2$ rutile phases increases, while that of the TiO$_2$ anatase phases decreases.
4. Conclusions
The TiO$_2$ coatings were grown on commercially titanium (grade 2) by micro-arc oxidation technique, in electrolyte solution consisting of calcium acetate monohydrate and β-glycerophosphate disodium salt pentahydrate. The following conclusions were drawn:

- The porous titania coatings present numerous opened micropores. The pores were homogeneously distributed over the surface, with no noticeable cracks.
- The diameters of pores were different and the sizes were from approximately 1.4 μm and 9 μm, with pores of lower diameter found often in larger pores.
- The coatings obtained contain calcium and phosphorus as well as titanium and oxygen. Sodium was not observed in the prepared coatings.
- Following the analysis of the qualitative phase, the coatings are highly crystalline and mainly composed of anatase, rutile and a mixture of calcium phosphate phases.

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