Effect of UV irradiation and diffuse plasma on surface properties of micro-arc calcium phosphate coatings

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Abstract. The influence of UV irradiation or plasma of runaway electron preionized diffuse discharge (REP DD) post-modification on the surface properties of the calcium phosphate (CaP) coatings formed by the micro-arc oxidation (MAO) method was investigated. The formed MAO-coatings had porous structure and rough surface morphology with incorporation of spheroidal structural elements with inner pores. It was showed that the UV irradiation or REP DD post-treatment of the MAO-coatings led to the decrease of the coating contact angels with water from 20 to 0 or to 7 degrees, respectively. However, the free surface energy of the coatings did not change after post-treatments and equalled to 74±1 mJ·m⁻². The polar component of the free surface energy of the all types of the coatings exceeded almost 5–6 times the dispersion component that indicated the presence of strong polar bonds on the coating surface, e. g. OH- and PO₄-groups.

1. Introduction

In the last decade, functionalization and modification of materials are widely used in different fields of science (medicine, nanotechnology, microelectronics and metallurgy). It is connected with limitation of initial materials properties. This is especially relevant for biomaterials, which should satisfy many requirements for the adaptation on the living organism. Titanium and its alloys often used for the repair of bone system defects [1]. However, titanium is bioinert material and it cannot provide chemical reaction with the bone and it’s healing. To solve this problem the calcium phosphate (CaP) coatings are used as bioactive layer on the surface of titanium implants [2]. The micro-arc oxidation (MAO) method allows to deposit the porous and rough coatings with a wide range of physical and chemical properties on the bioinert metals and its alloys [3–4]. The following post-treatment of the CaP coatings using ultraviolet (UV) irradiation or plasma of runaway electron preionized diffuse discharge (REP DD) can improves the bioactivity properties and attraction of the protein and biomolecule adsorption, and cell adhesion [5, 6]. Many equipments for irradiation and treatment require special conditions such as vacuum condition, elevated temperature, or any protection devices from the hard-ionizing radiation. UV irradiation is the simple method of modification biomaterials.
because it does not require any intricate equipment [7]. Also, nanosecond diffuse gas discharge at atmospheric pressure in an inhomogeneous electric field with attendant generation of a runaway electron beam and X-rays [8].

The aim of the study is to investigate the influence of UV irradiation and REP DD post-modification on the chemical and physical surface properties of the MAO-coatings.

2. Materials and methods
Titanium (Grade 1) was used as a substrate material. Size of samples was 10×10×10 mm³. The coatings were deposited by the MAO method in anodic mode under following parameters: the pulse duration of 100 µs, the frequency of 50 Hz, the process time of 10 min, and the pulsed voltage of 200 V [1]. The electrolyte contained the phosphoric acid (H₃PO₄), calcium carbonate (CaCO₃) and stoichiometric hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂). To modify the coatings, surface the both post-treatments by UV irradiation and REP DD in the ambient air were carried out. There were three groups of the MAO-coatings: 1 – (CaP), non-treated CaP coating; 2 – (CaP/UV), CaP coating post-treated by UV with KrCl-excilamp (λ = 222 nm, exposure doses of 5.5 mV·cm⁻², irradiation time varied from 1 to 20 min [2]); 3 – (CaP/REP DD), CaP coating post-treated by REP DD (the pulsed voltage of 18 kV with negative polarity, pulse duration of 4 ns, number of pulses varied from 10000 to 80000 [3]).

The morphology of the CaP coatings was examined by scanning electron microscopy (SEM, Zeiss LEO EVO 50) in the “Nanotech” common use center at the Institute of Strength Physics and Materials Science SB RAS, Tomsk, Russia. The surface roughness was estimated with a Hommel–Etamic T1000 profilometer (Jenoptik, Germany) by the average roughness (Ra). The phase composition was determined by X-ray diffraction (XRD, Bruker D8 Advance) in the angular range 2θ = 10–80° with a scan step 0.02° with CuKα radiation. The chemical composition was analyzed with a Fourier Transform Infrared Spectrometer (ALPHA FT-IR Spectrometer, Bruker) in the wave number range of 500–4000 cm⁻¹.

Wettability test was carried out using an Easy Drop goniometer with the drop shape analysis software DSA1 (Kruss, Germany). Distilled water as a polar liquid and glycerol as a dispersive one was used in the experiment. The sessile drop method was used to measure static contact angles of the liquids on the solid surface. The free surface energy of the coating was calculated according to the Owens-Wendt equation [3, 5]:

\[
\sigma_L (\cos \theta + 1) = 2 \left( \sigma_D^L \right)^{1/2} + 2 \left( \sigma_D^S \sigma_L^S \right)^{1/2}.
\]

Here, \( \sigma_D^L \), \( \sigma_D^S \), \( \sigma_L^L \), \( \sigma_L^S \) are the dispersive and polar components of the free surface energy of the liquid and solid phases, and \( \sigma_L \) is the free surface energy of the test liquid.

3. Results
Figure 1 shows the surface morphology and cross-sectional profile of the non-treated MAO-coating. It can be seen in figure 1a, that the coating surface morphology is represented by the spheroidal structural elements (sphere) with inner pores and pores in the interstructural spaces. The mechanism of the pore’s and sphere’s formation on the coating surface was described in [9]. The average size of spheres and pores equal to 14.3 and 4.7 µm, respectively. The average roughness of the coatings equals to 2.7 µm. Post-treatment by UV irradiation or REP DD does not effect on the morphology of CaP coating surface. The study of the cross-sectional coatings with thickness of 40 µm shows the porous structure including the branched pores different sizes (figure 1b).

The XRD patterns indicate the X-ray amorphous structure of the MAO-coatings (figure 2). This is indicated by the presence of the diffused halo in the angle range of 2θ = 20–40°. Several reflections from titanium substrate were observed in the XRD pattern of coatings. Post-modification with UV irradiation and REP DD does not exhibit changes in the phase composition of the CaP coatings.

Figure 2b shows the IR-spectra of the non-treated MAO-coating, and MAO-coatings modified with
UV irradiation for maximum time of 20 min and with REP DD for maximum pulses number of 80000. The IR spectra of all types of the coatings are presented with intense absorption bands, which belong to asymmetric and symmetric vibrations of the P–O bond of phosphates with maximum absorption in the region of 1000–800 cm\(^{-1}\). The peak in the region of 800–580 cm\(^{-1}\) indicates the presence of oscillations of the P–O–P pyrophosphate. The absorption bands at 690–630 cm\(^{-1}\) belong to the O–H bonds of the acidic phosphates of the HPO\(_4\) groups. The intensity of adsorption bands of the OH\(^-\) and PO\(_4\)\(^-\)-groups insignificantly increased in the coatings after UV post-treatment. After REP DD post-treatment of coatings, the adsorption bands of the OH\(^-\) and PO\(_4\)\(^-\)-groups do not change in compared with non-treated CaP coatings.

![Figure 1. SEM images of the surface (a) and cross-section (b) of the MAO-coatings.](image1)

![Figure 2. XRD pattern (Ti-titanium) (a) and IR spectra (b) of the non-treated (a) and post-treated (a, b) MAO-coatings by the UV irradiation and REP DD.](image2)

It is known that adhesion of bone cell and protein adsorption occur more intensely on the hydrophilic surfaces [5]. Wettability tests show that the MAO-coatings are “super-hydrophilic” because of their contact angles do not exceed 20 degrees with water and 31 degrees with glycerol. UV irradiation post-treatment leads to the decrease of the contact angles to 6 degrees with water and to 15 degrees with glycerol. Also, the REP DD post-treatment leads to the decrease of the contact angles to 0 degrees with water and to 13 degrees with glycerol. The increase of UV irradiation time from 1 to
20 min and number of pulses of REP DD does not contribute to coating contact angles values with water. However, contact angles values with glycerol increase from 15 to 23 degrees with increase of UV irradiation time from 1 min to 20 min. Also, increase in number of pulses of REP DD from 10000 to 80000 leads to decrease of contact angles values with glycerol from 18 to 13 degrees. It can be caused by change in distribution of the electrical charge on the surface depending on the type and condition of the post-treatments.

Calculation of the free surface energy shows that the non-treated MAO-coating and the coatings after post-treatments with UV irradiation and REP DD have similar surface energy equaled to 74±1 mJ·m⁻² (table 1). There is no change in the free surface energy values can be results of the very high surface energy for the all types of the coatings. Such high free surface energy values exceed surface tension of the most of liquids (glycerol, benzol, formamide, hexane) and equaled to the water surface tension (73 mJ·m⁻²). The polar component of the free surface energy of the all types of the coatings exceeds almost 5–6 times the dispersion component (table 1). It indicates the presence of strong polar bonds on the coating surface, e. g. OH–groups and phosphates [5]. These results confirm the IR spectroscopy data (figure 2b). Both post-treatments lead to the increase of the dispersive component of the free surface energy to 14 mJ·m⁻². While, the dispersive component for the non-treated coatings does not exceed 8 mJ·m⁻². It should be noted, that the UV post-treatments duration leads to decrease of surface energy dispersive component of CaP coatings from 13 to 10 mJ·m⁻² and increase from 12 to 14 mJ·m⁻² with increase of number of pulses of REP DD. Dispersive component is responsible for nonpolar Van-der Waals forces. The increase of dispersive components caused by enhancement of intermolecular interactions on the coating surface. In this case, polar component does not change significantly and varies in the range of 60–65 mJ·m⁻² for the all types of the coatings.

| Table 1. Contact angle and free surface energy of the non-treated and post-treated MAO-coatings by the UV irradiation and REP DD. |
|---|
| Types of the coatings | Water contact angle (degrees) | Glycerol contact angle (degrees) | Dispersive component (mJ·m⁻²) | Polar component (mJ·m⁻²) | Surface energy (mJ·m⁻²) |
|---|---|---|---|---|---|
| CaP | 20.5±1.7 | 31.0±2.2 | 7.9±0.5 | 64.7±1.2 | 72.6±1.7 |
| CaP/UV Irradiation time (min) | 1 | 6.9±0.7 | 15.9±2.2 | 13.5±0.7 | 60.1±0.9 | 73.6±0.8 |
| | 5 | 6.5±0.7 | 15.4±2.4 | 12.8±0.7 | 61.2±1.0 | 73.9±0.8 |
| | 10 | 6.4±0.4 | 19.5±2.4 | 11.8±0.6 | 62.6±0.8 | 74.4±1.6 |
| | 15 | 6.1±0.4 | 19.6±2.3 | 11.6±0.3 | 62.8±0.5 | 74.4±1.7 |
| | 20 | 7.1±0.8 | 23.3±1.2 | 10.1±0.2 | 65.3±0.5 | 75.4±1.6 |
| CaP/REP DD Number of pulses | 10000 | 0.0 | 18.2±1.0 | 11.9±2.3 | 62.9±2.2 | 74.9±2.3 |
| | 20000 | 0.0 | 17.0±1.4 | 12.5±1.7 | 62.1±2.0 | 74.6±1.7 |
| | 40000 | 0.0 | 16.6±1.9 | 12.6±1.8 | 61.9±1.9 | 74.6±1.8 |
| | 60000 | 0.0 | 17.3±1.3 | 12.4±1.7 | 62.3±1.4 | 74.7±1.7 |
| | 80000 | 0.0 | 13.2±2.4 | 14.0±1.6 | 60.0±1.7 | 74.0±1.7 |
4. Conclusions
Thus, the investigations of the morphology, structure, and some physical and chemical properties of coatings formed by MAO method and post-modified using UV irradiation and REP DD were performed. All types of the coatings were in X-ray amorphous state. The UV-irradiated and REP DD treated MAO-coatings did not exhibit any obvious change in surface morphology, pores and structural elements sizes, and surface roughness in compared with the non-treated coating. Both post-treated coatings had lower contact angles with water and glycerol than the non-treated coatings. However, non-treated MAO-coating and both post-treated coatings had similar surface energy equalled to 74±1 mJ·m⁻². The polar component of the free surface energy of the all types of the coatings exceeded almost 5–6 times the dispersion component that indicated the presence of strong polar bonds on the coating surface, e. g. OH- and PO₄-groups.

Further investigations of the electrical charge on the surface of the post-treated coating will be carried out and the mechanisms by which UV and REP DD treatments alters the coating surface properties will be analyzed.

Acknowledgments
The work has been financially supported by the Fundamental Research Program of the State Academies of Sciences for 2013-2020, direction of research III.23.2. The authors are grateful to M.A. Kimich and A.I. Tolmachev, Kazakbaeva A. (ISPMS SB RAS, Tomsk, Russia) and our colleagues Prof. M. Eppe and Dr. O. Prymak (The University of Duisburg-Essen, Essen, Germany) for their assistance in carrying out work.

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