Effect of ultraviolet irradiation or diffuse discharge plasma on structure and surface electrical charge of micro-arc calcium phosphate coatings

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Abstract. The studies of the effect of ultraviolet (UV) irradiation and plasma of a runaway electron preionized diffuse discharge (REP DD) post-treatments on the surface structure and electrical charge of the micro-arc oxidation (MAO) coatings were performed. The UV irradiation and plasma treatment did not effect on the morphology, roughness and thickness of the MAO coatings. However, these post-treatments led to formation of the small fraction of the crystalline CaHPO₄ phase in the X-ray amorphous structure of the coatings. Moreover, the UV and REP DD plasma treatments increased the electrostatic potential (EP) negative values from −85 mV to −126 mV of the coatings in the following order: MAO < MAO/UV (for 5 min) < MAO/Plasma (with 10,000 pulses) < MAO/UV (for 20 min) < MAO/Plasma (with 80,000 pulses).

1. Introduction

Ultraviolet (UV) photofunctionalization has been used since 1977 for the surface treatment of metal implants [1, 2], and with the development of bioactive materials, it has been successfully used for electrization of calcium phosphate (CaP) ceramics, for example, hydroxyapatite HA [3] and oxide coatings on metals [4, 5]. The authors of [1-5] noted the positive effect of UV radiation on the physicochemical and biological properties of materials, which are removal of hydrocarbons from the surface of metals, photocatalytic activation of metals and CaP ceramics, for example, hydroxyapatite (HA), with the formation of reactive oxygen species (ROS), which are responsible for the decomposition of the outer membrane of microorganisms and provide an antibacterial effect, increasing the hydrophilicity of the surface, stimulating osteogenic cellular activity and adsorption of human blood plasma proteins.

The use of plasma processing in the field of biomaterials includes a wide range of applications in cardiovascular and reconstructive surgery, orthopedics and dentistry [6, 7]. Low-temperature plasma exposure, in particular the effect of a plasma of a runaway electron preionized diffuse discharge...
(REP DD) in atmospheric pressure, has a great potential for improving the bioactivity of polymers, metals, CaP ceramics and composite materials of the polymer/CaP ceramics system. The authors of [8-10] note that the use of low-temperature plasma leads to the change in surface properties, such as electrochemical charge, oxidation state, addition or modification of chemical groups connected with the surface. In addition, plasma exposure leads to the increased corrosion resistance, hardness, wettability, water absorption capacity, improved adsorption of specific proteins and biomolecules. In [11], it is shown that surfaces modified by low-temperature plasma have improved bioactive properties in vitro and in vivo, and are also sterile, which eliminates the need for additional procedures for preparing the implant before packaging.

Microarc oxidation (MAO) is a promising method for the production of biologically active CaP coatings with a wide range of physicochemical properties on the surface of titanium (Ti) and its alloys. The high-voltage mode of MAO provides the presence of local micro-discharges moving along the metal surface during polarization, under the influence of which the coating grows [12]. With such a complex electrophysical and plasma-chemical effect on the metal, various types of polarization can appear in the layers of the growing dielectric coating.

The effect of UV photofunctionalization or REP DD plasma on the physicochemical and electrical properties of MAO CaP coatings with a bulk pore structure and micro-rough relief has not been previously studied. Therefore, the purpose of this work was to study the effect of UV irradiation and REP DD plasma post-treatments on the surface structure and electrical charge of the MAO coatings.

2. Materials and methods

Commercial pure titanium (ASTM Grade 2) plates (thickness, 1 mm; width, 10 mm, length, 10 mm) (VSMPO-AVISMA Corp., Verkhnaya Salda, Russia) were used in this study. The sample pretreatment procedures were described in details in [12, 13]. The Microarc – 3.0 installation with pulsed DC power supply developed at the Institute of Strength Physics and Materials Science SB RAS (ISPMS SB RAS, Tomsk, Russia) was used to carry out the MAO process. In order to synthesize the CaP coatings, the electrolyte contained 5 wt.% nanosized HA (Ca_{10}(PO_4)_{6}(OH)_2), 7 wt.% CaCO_3, 27 wt.% H_3PO_4, and distilled water as a balance [12, 13]. The MAO process was carried out in anodic potentiostatic regime at the fixed pulse frequency of 50 Hz, pulse duration of 100 µs and applied voltage of 200 V for 10 min. Electrolyte composition and MAO electrical parameters were optimized in the previous works [12-14]. Some CaP coatings after MAO were UV irradiated at 222 nm wavelength (exposure dose of 5.5 mW/cm²) for 5, 10, 15 and 20 min using a KrCl excilamp developed at the Institute of High Current Electronics SB RAS (IHCE SB RAS, Tomsk, Russia) [15]. Some coatings were REP DD plasma irradiated using short-pulse high-voltage generators NPG18-3500N (Megaimpulse Ltd., St. Petersburg, Russia). The titanium cathode in the form of a tube with a diameter of 12 mm was used for plasma irradiation. The conditions of the REP DD plasma irradiation were following: plasma stream diameter of 10 mm, cathodic pulsed voltage of 12 kV, pulse duration of 4 ns, and varied pulses number from 10,000 to 80,000 with the step of 20,000 [16].

The surface and cross-sectional morphology of the coatings were analyzed by scanning electron microscopy (SEM, Zeiss LEO EVO 50) in the “Nanotech” Common Center for Collective Use (ISPMS SB RAS, Tomsk, Russia). The surface roughness was measured by the contact profilometry (Profilometer-296) via the standard average roughness parameter (R_a). The phase composition was determined with X-ray diffraction (XRD, Shimadzu XRD 6000, Tomsk Materials Science Center for Collective Use) in the Bragg-Brentano geometry in Cu-Kα radiation in the angular range of 2θ = 10-80° with a scanning step of 0.02° and acquisition time of 3 s. For the phase identification and interpretation of XRD patterns, the International Centre for Diffraction Data (ICDD) database as references was used.

The electrostatic potential (EP) of the coatings surface was measured by the compensation method, which is a modification of the Kelvin scanning probe method, on a specialized scanning installation developed at the Belarusian National Technical University (Minsk, Belarus) [17]. The unique measuring complex allows visualizing the spatial distribution of the electrostatic potential, determined
by the contact potential difference (CPD) relative to the probe sample, on the surface of materials with a micrometer spatial resolution.

3. Results and discussion

SEM images represent the typical surface and cross-sectional morphology of the MAO CaP coatings before and after post-treatment with UV irradiation or REP DD plasma (figure 1). As can be seen, the coatings are characterized by a complex hierarchical structure: numerous adjacent pores and pore channels represent the internal morphology, and on the surface there are sphere-shaped structural elements (spheres) with internal pores and pores located in the spaces between the spheres. The thickness and the surface roughness ($R_a$) of all the coatings were 50±4 µm and 2.8±0.4 µm, respectively. Thus, the post-treatment with UV irradiation or REP DD plasma did not affect the morphology, roughness and thickness of the MAO coatings.

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

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

Figure 2 represents the XRD patterns of the control MAO coating, UV irradiated (for maximum 20 min) MAO coating, and plasma-treated (with maximum 80,000 pulses). XRD studies revealed that all the MAO coatings are found to be mainly in the X-ray amorphous state. It is evident due to the appearance of diffuse scattering region in the range of 2θ angles from 15° to 37° in the XRD patterns. XRD patterns include the reflection peaks of the hexagonal $\alpha$-phase Ti (ICDD #44-1294), corresponding to the substrate material. The appearance of weak reflection peaks (020), (220), (1T2) of the monetite phase (CaHPO$_4$, ICDD #09-0080) and decreasing the intensity of diffuse scattering region and of reflection peaks of the Ti are observed on the XRD patterns of both the UV and plasma-treated MAO coatings. Such structured changes occur more efficiently in the plasma-treated MAO coatings compared to UV-irradiated MAO coatings. We assume that an energy of low-temperature plasma and a slightly weaker energy of UV light induce the ordering of atoms in the CaP amorphous substance, and the simultaneous the growth of monetite crystallites. At the same time, the ordered structure of the coatings reduces its transmission capacity for X-ray radiation, as a result of which there is a decrease in the intensity of the reflection peaks of Ti substrate.

The compensation method as modification of the Kelvin scanning probe method showed that all the control and post-treated MAO coatings had negative surface electrostatic potential which varied in the range from $-85$ mV to $-126$ mV. As can be seen in figure 3, the UV and plasma treatments increased the EP negative values for the coatings in the following order: MAO < AO/UV (5 min) < MAO/plasma (10,000 pulses) < MAO/UV (20 min) < MAO/plasma (80,000 pulses).
Figure 2. XRD patterns of the control, UV-irradiated and plasma-treated MAO coatings.

Figure 3. Electrostatic potential of the control, UV-irradiated and plasma-treated MAO coatings.

Figure 4 illustrates the 2D- and 3D-distributions of the EP on the surface of the control MAO coating, UV-irradiated (for 20 min) MAO coating and plasma-treated (with 80,000 pulses) MAO coating. The electrostatic charge was distributed fairly uniformly over the surface of the control MAO coating (figure 4 (a, b)). There was a slight drop in EP value along the surface of the control sample when moving from one face to the opposite. We attribute this to the possible drainage of the charge in the coating directly during its deposition during MAO, since the samples are mounted vertically in the electrochemical cell. A similar surface EP distribution was obtained for UV-irradiated MAO coating (figure 4 (c, b)). At the same time, a slight increase in the negative charge was observed in the central region (area $4 \times 4 \text{ mm}^2$) of MAO/UV coating. However, currently we cannot explain the reason for this phenomenon, since the size of the excilamp is much larger than the size of the irradiated sample and the UV light source acts on the entire surface of the sample with the same energy. At the same time, the effect of low-temperature plasma on MAO coating had the greatest influence on the size and distribution of its surface EP. Figure 4 (e, f) represents a clear increase in the negative charge on the coating surface along the circle line corresponding to the size of plasma flow, which is explained by the use of a tubular electrode.

Obtained data of the coating surface EP are in a good agreement with our previous results of the coating wettability studies and Fourier transform infrared spectroscopy (FT IRS) [14]. Previously, it was shown [14] that the UV irradiation and REP DD plasma treatment led to the increase of the coating wettability and of polar covalent bonds (e.g. OH$^-$ groups, phosphates, and oxides) in the coatings. Moreover, these data are in an agreement with the previous measurements of the surface zeta potential by the steam potential method and of the electrical potential by the Eguchi method [13]. The
MAO coatings deposited at applied voltage were characterized by zeta-potential of $-53 \text{ mV}$ and electrical potential of $-456 \text{ mV}$.

**Figure 4.** 2D (a, c, e) and 3D (b, d, e) distributions of the electrostatic potential on the surface of the MAO coating (a, b), MAO/UV coating (c, d) and MAO/Plasma coating (e, f).
4. Conclusion
The studies of the effect of UV irradiation and REP DD plasma post-treatments on the surface structure and electrical charge of the MAO coatings were performed. The UV irradiation and plasma treatment did not effect on the morphology, roughness and thickness of the MAO coatings. However, these post-treatments led to the formation of the small fraction of the crystalline CaHPO₄ phase in the X-ray amorphous structure of the coatings. Moreover, the UV and plasma treatments increased the EP negative values from –85 mV to –126 mV of the coatings in the following order: MAO < MAO/UV (5 min) < MAO/plasma (10,000 pulses) < MAO/UV (20 min) < MAO/plasma (80,000 pulses).

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