Effect of power of ultrasound during micro-arc oxidation on morphology, elemental and phase composition of calcium phosphate coatings

E A Kazantseva\textsuperscript{1,2} and E G Komarova\textsuperscript{1}

\textsuperscript{1}Institute of Strength Physics and Materials Science SB RAS, 2/4 Akademicheskii Pr., Tomsk, 634055, Russia
\textsuperscript{2}National Research Tomsk State University, 36 Lenina Pr., Tomsk, 634050, Russia

E-mail: kati10_95@mail.ru

Abstract. The effect of the magnitude of the US (ultrasound) power applied during the MAO (micro arc oxidation) process on the morphology, elemental and phase composition of the CaP coatings was studied. The US at different power (50-200 W) applying during the MAO process led to the local destruction of the structure elements (spheres and pores) and local filling the pore spaces on the coating surface, and to the formation of local macro-pores inside the coatings near the substrate. Such morphological transformations led to the surface and structure heterogeneity of the coatings, increasing of the surface roughness from 3.0 to 4.5 μm and of the thickness from 50 to 60 μm. The US application at different power did not affect significantly the elemental composition of the coatings. At the same time, under applied US with power more than 100 W, the state of the coatings transformed from X-ray amorphous to the quasiamorphous with the small incorporation of crystalline phases of CaHPO\textsubscript{4} and β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7}.

1. Introduction

Crucial trend in biomedical materials science is the production of calcium phosphate (CaP) materials, in the form of powders, granules, bulk materials, coatings on metals, etc., with an adjustable pore structure as drugs carriers (antibacterial, antitumor, etc.) [1]. The micro-arc oxidation (MAO) is the most promising and technologically advanced method for the formation of the CaP coatings on the metals. MAO CaP coatings are characterized by a wide range of physico-chemical properties and varying in a wide range of crystallinity, thickness, roughness and porosity [2]. It is possible to regulate the porosity, pore size, elemental and phase composition, and the microstructure of MAO coatings by developing the parameters of electrolyte compositions, including containing the dispersed nanoparticles, and by optimizing the electrophysical parameters of MAO, including with the imposition of external influences, for example, ultrasound (US) application [3, 4]. The authors [5-7] reported that the transmission of US waves through the electrolyte during MAO process allow to intensify the diffusion processes and electrochemical reactions in the electrolyte, to increase the thickness of the coating, and can further improve the biological activity of the coatings surface. Currently, researchers are adjusting all the electrical parameters of ultrasound, for example, the wave type, frequency and power, to achieve the desired morphology and structure in the formed MAO coatings [7]. It is assumed that the value of the ultrasonic power will have a significant impact on the
structure and properties of coatings, since it relates the specific heat capacity, mass and temperature change of the liquid medium depending on the processing time [7]. However, the influence of the ultrasonic power on the formation of MAO coatings during their deposition has not yet been studied. In this way, the aim of the work was to study the effect of the magnitude of the US power applied during the MAO process on the morphology, elemental and phase composition of the CaP coatings.

2. Materials and methods

The experimental samples from commercially pure titanium (ASTM Grade 2) with the size of 10×10×1 mm were used. Procedures of sample pre-treatment were described in details in [2, 5]. In order to deposit the CaP coatings on the samples, the MAO method was carried out using the installation Micro-Arc 3.0 in pulsed anodic regime with the following parameters: applied voltage of 200 V, pulse duration of 100 µs, frequency of 50 Hz, and deposition time up to 10 min. The electrolyte with nano-sized hydroxyapatite (HA, Ca_{10}(PO_4)_6(OH)_2) was used as we described earlier [5, 8]. The US field with a sinusoidal waveform, a frequency of 35 kHz and varied power of 50, 100, 150 and 200 W was applied during the MAO process.

The coating surface roughness was measured by the contact profilometry (Profilometer-296) via the standard average roughness parameter (R_a) as the average arithmetic deviation of the profile within several lengths of measurement fragments. The coatings thickness was measured using a digital micrometer Zubr Expert with an accuracy of ±1 µm.

The surface and cross-sectional morphology of the coatings was analyzed by scanning electron microscopy (SEM, Zeiss LEO EVO 50) in the “Nanotech” Common Centre for Collective Use (ISPMS SB RAS, Tomsk, Russia). Elemental composition was examined using electron dispersive X-ray spectroscopy (EDX) on an INCA system coupled to the SEM. The sizes of the coating structural elements were measured by the secant method according to ASTM E1382-9 [9]. 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 = 10-80º, with a scan step of 0.02º, 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.

3. Results and discussion

Figure 1 shows the SEM images of the surface of the control MAO coating and US-assisted at the different US power MAO coatings. The surface morphology of the control MAO coating includes the structural spheroidal elements (spheres and hemispheres) with the inner pores and outer pores between the spheres. The applied US at different powers did not influence on the size of the structural elements. For all the coatings, average sizes of spheres and pores in the coatings were 17 and 4 µm, respectively (figure 1 (a)). On the surface of all the US-assisted MAO coatings, the areas with structural elements as well as local fracture areas containing destroyed spheres and fragments were observed (figure 1 (b–e)). We calculated the percentage of the fracture area as the ratio of that area to the total area of the SEM-image. The percentage of the fracture area on the surface of the US-assisted (at power of 50 W) MAO coating was insignificant and amounted to 6%. Subsequent increasing the US power from 100 to 200 W led to the significant increase of the fracture area up to 25%. Destruction of structural elements and a filling of pore spaces with fragments under the action of US vibrations led to an increasing the heterogeneity of the surface morphology, and, as a consequence, to an increase in the surface roughness (R_a) from 3.0 to 4.5 µm. Structural elements on the surface of coatings can be destroyed as a result of the impact of shock waves appearing during the collapse of cavitation bubbles in the electrolyte irradiating with ultrasound. These data are in a good agreement with our previous results where the US-assisted with different waveforms (sinusoidal, pulsed) MAO coatings had also heterogenic surface with incorporation of destroyed regions [3, 8]. However, researches [10] reported a beneficial effect of ultrasound in refining the grain size of the composite coatings achieving a smoother finish partly due to a significantly more uniform distribution of well-
dispersed particles. In [6], it is shown that the introduction of US waves improves the uniformity of the thickness distribution of the micro-arc oxidation coating, the bonding strength and the amount of cation deposition.

Figure 1. SEM-images of the surface of the MAO coating (a) and US-assisted MAO coatings under different US power (W): 50 (b), 100 (c), 150 (d), 200 (e). The destruction regions are marked by dotted line.

The SEM-images of the cross-sectional MAO coatings show the complex porous hierarchical structure with numerous adjacent pores and pore channels (figure 2). The US application during the MAO led to formation of local macro-pores with the sizes of 15-30 μm in the coatings near the interface with the substrate (figure 2 (b-e)). As a result, with an increasing the US power from 50 to 100 W the average size of the pores inside the coatings increased from 2.5 to 4.7 μm. However, with the subsequent increasing the US power up to 200 W the average size of pores did not change and was 4.5 μm. The formation of pore spaces inside the coating under the US action led to an increasing the coating thickness up to 60 μm, while the thickness of the control coatings was 50 μm.
The formation of macro-pores in the coating structure can be associated with an increase in the intensity of micro-arc discharges under the influence of US vibrations, which create acoustic cavitation with a high level of energy. As a result, the intensive cascades of micro-arc discharges in the localized area are created, leading to an increasing in the size of the “free” porous spaces.

![SEM-images of the cross-sectional MAO coating](image)

Figure 2. SEM-images of the cross-sectional MAO coating (a) and US-assisted MAO coatings under different US power (W): 50 (b), 100 (c), 150 (d), 200 (e). The macro-pores are marked by dotted line.

The results of the quantitative EDX microanalysis of the control MAO and US-assisted MAO coatings are represented in table 1. As can be seen in table 1, the US application with different powers did not lead to the change of elemental composition on the coating surfaces. At the same time, a slight decrease in the concentration of titanium and phosphorus, and an increase in oxygen in the coating cross sections were observed.

Figure 3 represents the XRD patterns of the control MAO coating and US-assisted (US power was 100 and 200 W) MAO coatings. As can be seen in the XRD patterns, all the MAO coatings were 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°, corresponding to the amorphous CaPs [5]. All the XRD patterns included the reflection peaks of the hexagonal α-phase Ti (ICDD #00-044-1294), corresponding to the substrate material. The XRD patterns of the US-assisted (US power higher than 100 W) MAO coatings included both the diffuse scattering region and weak reflection peaks of the CaHPO₄ (monetite, ICDD #00-009-0080) and β-Ca₃P₂O₇ (ICDD #00-009-0346). In this case, the intensity of the Ti reflection peaks decreased in the XRD patterns of the US-assisted MAO coatings compared to the control MAO coating. This may be result of the increasing the MAO/US thickness. Previously [5] we reported that the formation of CaHPO₄ and β-Ca₃P₂O₇ phases in the coatings could
be associated with recrystallization of the amorphous CaP substance as a result of increasing the electrolyte temperature under US activation of the MAO processing.

**Table 1.** Quantitative elemental composition of the MAO coating and US-assisted MAO coatings.

| Element (at.%) | MAO  | MAO/US 50 W | MAO/US 100 W | MAO/US 150 W | MAO/US 200 W |
|----------------|------|-------------|--------------|--------------|--------------|
| Coating surface |      |             |              |              |              |
| Ca Kα          | 4.5 ± 0.2 | 4.8 ± 0.3 | 4.8 ± 0.4 | 4.8 ± 0.3 | 4.9 ± 0.5 |
| P Kα           | 14.9 ± 0.5 | 15.7 ± 0.2 | 15.4 ± 0.1 | 15.2 ± 0.2 | 15.2 ± 0.1 |
| O Kα           | 69.7 ± 3.2 | 69.6 ± 2.2 | 68.7 ± 2.6 | 69.3 ± 3.4 | 69.2 ± 2.3 |
| Ti Kα          | 10.9 ± 0.3 | 9.9 ± 0.2 | 11.0 ± 0.5 | 10.7 ± 0.3 | 10.7 ± 0.2 |
| Ca/P           | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Coating cross-section | | | | | |
| Ca Kα          | 4.2 ± 0.2 | 3.7 ± 0.2 | 3.9 ± 0.5 | 3.6 ± 0.4 | 4.0 ± 0.6 |
| P Kα           | 16.2 ± 0.4 | 15.4 ± 0.4 | 15.9 ± 0.3 | 15.4 ± 0.2 | 15.2 ± 0.1 |
| O Kα           | 66.1 ± 2.9 | 72.0 ± 3.8 | 68.8 ± 2.9 | 72.2 ± 3.6 | 70.1 ± 2.5 |
| Ti Kα          | 13.5 ± 1.1 | 9.1 ± 0.9 | 11.4 ± 0.7 | 9.1 ± 0.2 | 10.7 ± 0.4 |
| Ca/P           | 0.3 | 0.2 | 0.2 | 0.2 | 0.3 |

**Figure 3.** XRD patterns of the MAO coating and US-assisted MAO coatings.

4. **Conclusion**

The effect of the magnitude of the US power applied during the MAO process on the morphology, elemental and phase composition of the CaP coatings was studied. The US at different power (50-200 W) applying during the MAO process led to the local destruction of the structure elements (spheres and pores) and local filling the pore spaces on the coating surface, and the formation of local macro-pores inside the coatings near the substrate. Such morphological transformations led to the surface and structure heterogeneity of the coatings, to the increasing of the surface roughness from 3.0 to 4.5 μm and of the thickness from 50 to 60 μm. The US application at different power did not significantly affect the elemental composition of the coatings. At the same time, under the applied US with the power more than 100 W, the state of the coatings transformed from X-ray amorphous to the quasiamorphous with the small incorporation of crystalline phases of CaHPO$_4$ and $\beta$-Ca$_2$P$_2$O$_7$. 
Acknowledgments
The work has been financially supported by the Russian Science Foundation (Project No. 21-73-10265). Authors wish to acknowledge assistance or encouragement from Dr. V.V. Chebodaeva and Dr. M.A. Khimich (ISPMS SB RAS, Tomsk, Russia).

References
[1] Evdokimov P V, Putlyaev V I, Ievlev V M, Klimashina E S and Safronova T V 2015 Dokl. Chem. 460 61–5
[2] Sedelnikova M B, Komarova E G, Sharkeev Yu P, Ugodchikova A V, Mushtovatova L S, Karpova M R, Sheikin V V, Litvinova L S and Khlusov I A 2019 Surf. Coat. Tech. 369 52–68
[3] Legostaeva E V, Sharkeev Yu P, Epple M and Primak O 2014 Russ. Phys. J. 56 1130–6
[4] Narayanan T S N S, Park I S and Lee M H 2014 Prog. Mater. Sci. 60 1–71
[5] Komarova E G, Kazantseva E A, Sedelnikova M B and Sharkeev Yu P 2019 J. Phys. Conf. Ser. 1393 012098
[6] Hu J, Li H, Wang X, Yang L, Chen M, Wang R, Qin G, Chend D and Zhang E 2020 Mater. Sci. Eng. C 115 110921
[7] Costa J M and Almeida Neto A F 2020 Ultrason. Sonochem. 68 105193
[8] Kazantseva E A, Komarova E G and Sharkeev Yu P 2019 AIP Conf. Proc. 2167 020155
[9] ASTM E1382–97 2015 Standard Test Methods for Determining Average Grain Size Using Semiautomatic and Automatic Image Analysis (West Conshohocken, PA, USA: ASTM International)
[10] Tudela I, Zhang Y, Pal M, Kerr I and Cobley A J 2014 Surf. Coat. Tech. 259 363–73