Influence of ultrasonic field during micro-arc oxidation on the structure and properties of calcium phosphate coatings

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Abstract. The study of the influence of applied external ultrasound (US) field with varied power of 35 or 100 W during the micro-arc oxidation (MAO) processing on the thickness growth, surface roughness, porosity, sizes of structural elements and structural-phase states of the calcium phosphate (CaP) coatings on the titanium surface was performed. It was shown that the US transmittance through the electrolyte for 10 min of MAO processing had led to the increase of the coating thickness from 50 to 60 µm, the surface roughness from 3 to 4.5 µm, and the cross-section porosity from 27 to 40%. However, under the action of external US there was a destruction of structural elements (spheres with pores) on the coating surface and a filling of pores’ spaces by fragments. That led to the decrease of the surface porosity from 30 to 12%. It was revealed by X-ray diffraction (XRD) that all types of the CaP coatings deposited under external US field and without it were in X-ray amorphous state. However, applied US field had led to the increase of the coating crystallinity with incorporation of CaHPO₄ and β-Ca₂P₂O₇ phases.

1. Introduction

One of the most promising approaches in the modern biomedical materials science and bone tissue engineering is the modification and functionalization of the surface of metal implants in order to give them a new set of performance properties. Among other surface treatment methods, the micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO), is a promising method. The MAO method which is characterized by the high productivity, economic efficiency and environmental friendliness allows to form on the metals of the valve group (Al, Ti, Zr, Nb, Mg, etc.) bio-coatings based on calcium phosphate (CaP) with a wide range of physical and chemical properties, such as high corrosion resistance, strong adhesion to the substrate, different degrees of crystallinity, thickness, roughness and porosity [1–3]. MAO is a complex processing that combines diffusion and electrophoresis of elements in the electrolyte, ion transport in discharge channels and electrochemical oxidation of the metal surface. The coating is formed in the regions of micro-discharge breakdown where the anode current is concentrated. Electrolyte is rapidly heated in the channels of micro-discharges to high temperatures (> 2000°C), followed by rapid cooling as the micro-discharges are quenched. This mechanism is accompanied by the formation of pore spaces and cracks in the structure of the growing coatings. This can be a positive factor in the successful osseointegration of the implant with bone tissue. However, local micro-discharges, usually having lifetimes of tens to hundreds µs, lead to the formation of micro-pores with sizes not exceeding tens µm and porosity not exceeding 30%
At the same time, the researchers noted that the bioactive coatings on implants should have an open porosity of 35–50% with the presence of pores of 50–300 µm in size. In this case, the bone can grow through interconnected pore channels. Ordinarily, the problem of increasing the porosity of the MAO-coating and the size of the pores is solved by the development of new electrolyte compositions and supply sources as well as through the optimization of the electrical parameters of the MAO processing.

With the development of scientific direction of sonochemistry or electrochemistry, ultrasound (US) is increasingly used as an effective way of energetic influence on the processes of mass transfer in electrochemical (galvanic) systems. The authors noted that the employing US field during the MAO processing is accompanied by cavitation on the electrodes’ surface, accelerating heat-and-mass transfer in the electrolyte solution, intensification of the electrolyte penetration into the pores and cracks, fragmentation of the agglomerated particles and liquid electrolyte clusters, outgassing, activating crystallization of the molten compounds and electrochemical processes. US vibrations with high frequency and low amplitude created an acoustic field with a high energy level, which allows intensifying the processes of mass transfer in the electrolyte, increasing the coating growth rate as well as controlling the composition, structure and porosity of the formed coatings.

The aim of this work was to study the influence of the applied US field during the MAO processing on the thickness growth, porosity, surface roughness, and structured-phase states of the CaP coatings.

2. Materials and methods

The specimens were cut from the billets of commercially pure titanium (grade 2, Ti) with the plate-like form of 10×10×1 mm³ in size. The specimens were polished with a series of increasingly finer abrasive papers up to 1200 grit. The MAO-coatings were synthesized using the “Micro-arc 3.0” installation with the DC pulsed power source and the titanium electrolytic bath fitted with US power sources modulating sinewave or pulsed wave. The specimen and the electrolytic bath were taken as an anode and cathode, respectively. Electrolyte suspension contained: H₃PO₄ (30% aqueous solution; CaCO₃ (100 g·l⁻¹); nano-sized stoichiometric hydroxyapatite (HA, Ca₅(PO₄)₃(OH)), 60 g·l⁻¹). The MAO processing was carried out in anodic potentiostatic regime at the fixed pulse frequency of 50 Hz, pulse duration of 100 µm and voltage of 200 V for 10 min. These parameters were optimized in the previous works.

In this work, there were three regimes of the coatings’ synthesis: 1 – MAO (control, without US); 2 – PUS/MAO (pulsed US, P = 35 W, f = 35 kHz); 3 – US/MAO (sinewave US; P = 100 W, f = 35 kHz).

The surface and cross-sectional morphology of the coatings were analyzed 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 sizes of the structural elements in the coatings were measured using SEM-images by the secant method. The coating porosity was calculated as the ratio of the “free” surface area occupied by the pores in the SEM-image to the total area. The phase composition was determined with X-ray diffraction (XRD, Shimadzu XRD 6000) in the angular range of 2θ = 10–90° using Cu Kα radiation with a scan step of 0.02° and exposition time of 3 s. The surface roughness was measured by the contact profilometry (Profilometer-296) via the average roughness parameter (Ra).

3. Results and discussion

Figure 1 a shows the current density of MAO with external US field and without it against the time of synthesis. Presence of fluctuations on all the curves indicates the pulsed nature of micro-arc discharges. Under those influence deposition of the coating occurs. Over time, the current density decreases monotonically to the plateau due to the formation of the CaP coating on the metallic surface. As the thickness of the dielectric CaP coating increases, the resistance increases, and the current density decreases. It should be noted that both 2 and 3 regimes with applied US are characterized by a higher current density than the MAO processing without US. Figure 1b confirms it and shows that the coating thickness growth in the both 2 and 3 regimes with external US occurs more intensively (up to
60 µm) than in the control regime without US (thickness does not exceed 50 µm). For all types of the coatings, the thickness increases by logarithmic law with MAO time.

The coating roughness (Ra) changing in dependence on the MAO time is presented in figure 1c. It can be seen, that the surface roughness increases by logarithmic law from 1.5 to 4.5 µm with the MAO time for the coatings formed in the 2 and 3 regimes with external US. While, the roughness of the coatings synthesized in the control regime practically does not change and equals to 2–3 µm.

Revealed dependences of the coating thickness and roughness with MAO time indicate that the intensity of micro-arc discharges increases under US vibrations passing through the electrolyte, leading to the accelerated rate of the coating deposition. By authors [10] it was shown that under the action of applied US field the MAO voltage and amount and average height of current pulses are increased. This increasing leads to the appearance of additional energy impulse to the micro-plasma-spark effect on the treated sample causing intensification of micro-plasma synthesis of the coatings.

![Graphs of the MAO current density (a), the coating thickness (b) and roughness (c) against the MAO time for different types of the coatings.](image)

**Figure 1.** Graphs of the MAO current density (a), the coating thickness (b) and roughness (c) against the MAO time for different types of the coatings.

SEM studies show that the applied US field during the MAO processing affects the morphology of the coatings. Figure 2 a represents the SEM image of the surface of the MAO-coating deposited in control regime 1. The coating surface morphology includes the structural elements of spheroidal shape (spheres) with inner pores and pores in the interstructural spaces. The formation of spheres and pores in the coating occurs by the model described in [13]. After breakdowns in the discharge channels the electrolyte boils and the vapor-gas bubbles (spheres) are formed. The natural output for the heated plasma is the mouth of the channel (pore) facing the electrolyte. Escaping from the mouth of the channel, the plasma expands and cools rapidly with the formation of solid spheres.
US field passing through the electrolyte during the MAO-processing leads to the partial destruction of the structural elements with the formation of fragmentation elements. On the surface of the coatings deposited in the regime 3 with the highest US power of 100 W the areas with destroyed spheres and their fragments are much larger than on the coatings formed in the regime 2 with a lower US power of 35 W (figures 2c and 2e). Measuring sizes of the structural elements with subsequent statistical analysis shows that for all the types of the coatings, the distributions of spheres and pores by size are single-modal and are in wide intervals of 4–34 µm and 0.5–13 µm, respectively. Average sizes of spheres and pores in the coatings are 18±2 µm and 4.5±0.5 µm, respectively. Destruction of structural elements and a filling of pore spaces with fragments under the action of US vibrations leads to an increase in the heterogeneity of the surface morphology, and, as a consequence, to an increase in roughness (figure 2c), and to reduce the surface porosity from 30 to 15% for PUS/MAO-coating and up to 12% for US/MAO-coting (figure 3a).

Figure 2. SEM-images of the surface (a, c, e) and cross-section (b, d, f) of the MAO-coating (a, b), PUS/MAO-coating (c, d) and PUS/MAO-coating (e, f).
The SEM-images of the cross-sectional coatings show the complex porous structure with a large number of branched pores of 0.5–15 µm in sizes for all the types of the coatings (figures 2b, 2d, 2f). However, the action of the external US field during the coating synthesis leads not only to a more intensive thickness growth of the coatings (figure 1a), but also to increasing of pores’ sizes and formation of local inner macropores of 15–40 µm in the coating structure (figures 2d and 2f). The formation of such macropores in the structure of coatings 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 increase in size of the “free” porous spaces. It was found that the application of US vibrations through the electrolyte leads to an increase of the cross-section porosity up to 40±3%, whereas the coatings formed without an external US field have a cross-section porosity of 27±3% (figure 3b).

![Graph](image1)

**Figure 3.** Surface porosity (a) and cross-section porosity (b) of all the types of coatings.

XRD shows that all the types of coatings are in the X-ray amorphous state, as evidenced by the presence of a diffuse halo at small angles 2θ = 20–35° in XRD patterns (figure 4). In addition, all XRD patterns includes the reflections from the crystalline phase α-Ti (PDF4+ No. 44-1294), corresponding to the substrate material. It can be seen in the XRD patterns of the coatings deposited in 2 and 3 regimes with applied US (PUS/MAO and US/MAO), there are weak reflections from crystalline phases of dicalcium phosphate anhydrous (CaHPO₄, DCPA, crystal monetite, PDF4+ No. 09-0080) and β-calcium pyrophosphate (β-Ca₂P₂O₇, β-CPP, PDF4+ No. 09-0346). The intensity of the reflections from α-Ti reduces with application of the external US that can be due to an increase in the thickness of the coatings (figure 1b).

![Graph](image2)

**Figure 4.** XRD-patterns of all the types of coatings.
The formation of $\beta$-Ca$_2$P$_2$O$_7$ and CaHPO$_4$ phases in the coatings can be associated with recrystallization of the amorphous CaP substance as a result of increase of the electrolyte temperature under US activation of the MAO processing. The mechanism of the phase formation is following [14]:

$$
\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{135^\circ\text{C}} \text{CaHPO}_4 \xrightarrow{360-450^\circ\text{C}} \text{amorphous-Ca}_2\text{P}_2\text{O}_7 \xrightarrow{530^\circ\text{C}} \gamma-\text{Ca}_2\text{P}_2\text{O}_7 \xrightarrow{750^\circ\text{C}} \beta-\text{Ca}_2\text{P}_2\text{O}_7 \xrightarrow{1171-1191^\circ\text{C}} \alpha-\text{Ca}_2\text{P}_2\text{O}_7
$$

(1)

An increase of the electrolyte temperature in the micro-arc discharge channel above 135°C contributes to the dehydration of dicalcium phosphate dihydrate (DCPD) contained in the electrolyte with transformation to DCPA [4, 11]. With a further increase in temperature over 400°C, DCPA transforms into CPP, first in the amorphous phase, and then in the metastable $\beta$, $\gamma$ and $\alpha$ phases. Polymorphic transformation of CPP from an amorphous phase into metastable phase occurs due to the combustion of anodic micro-arc discharge and heating of the electrolyte in the micro-arc discharge channel from 500 to 2000°C [4, 5].

The DCPA content in the coating is of particular interest due to its chemical similarity with the bone matrix and a large specific surface area. DCPA refers to acidic calcium phosphates, easily soluble in body fluids. It also promotes the bone apatite formation and growth with subsequent mineralization. This is due to the fact that the acidic pH values created by such phosphates at the interface with the bone tissue etch bone apatite and cause desorption of specific osteoinductive proteins such as BMP-type [4]. Authors [9] reported that $\beta$-CPP incorporated in the coatings can stimulate osteogenesis is very similar to the HA.

4. Conclusion
The investigations of the influence of applied external US field with varied power (35 and 100 W) during the MAO-processing on the thickness growth, surface roughness, porosity, sizes of structural elements and structural-phase states of the CaP coatings on the titanium surface have been performed. It was shown that the US transmittance through the electrolyte for 10 min of MAO processing had led to the increase of the coating thickness from 50 to 60 µm, the surface roughness from 3 to 4.5 µm, and the cross-section porosity from 27 to 40%. Moreover, under the action of external US there was a destruction of structural elements (spheres with pores) on the coating surface and a filling of pore spaces by fragments, which had led to the decrease of the surface porosity from 30 to 12%. It was revealed that all the types of coatings deposited under external US field and without it were in X-ray amorphous state. However, applied US field led to the increase of the coating crystallinity with incorporation of CaHPO$_4$ and $\beta$-Ca$_2$P$_2$O$_7$ phases.

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