Biocoatings synthesized on magnesium alloy in system Ca$_3$(PO$_4$)$_2$–CaSiO$_3$ by micro-arc oxidation method

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Abstract. Biocoatings were formed on the surface of the Mg0.8Ca alloy by the method of micro-arc oxidation, in an electrolyte containing β-Ca$_3$(PO$_4$)$_2$ (β-TCP) and CaSiO$_3$. When the process voltage was varied in the range of 350–500 V, the thickness, roughness, and mass of the coatings increased to the values of 110 µm, 12 µm, and 11 mg, respectively. The presence of the following crystalline phases was determined in the coatings: α-TCP, wollastonite, forsterite and magnesium oxide. Coatings containing these compounds not only reduce the rate of bioresorption of the magnesium alloy, but also promote the process of bone tissue formation.

1. Introduction
Magnesium-based alloys are considered third-generation biomaterials, since they are bioactive, biodegradable, and nontoxic for the human body [1, 2]. Magnesium alloy implants play a role of temporary structure for tissue regeneration and ultimately degrade completely in the biological environment. In addition, magnesium alloys are attracting great attention in the field of fracture treatment and replacement of bone tissue defects due to the value of the elastic modulus (45 GPa), which is close to the elastic modulus of the bone [3, 4].

Nevertheless, the high rate of decomposition of magnesium alloys in the human body and the release of hydrogen limit the clinical use of magnesium implants [5, 6]. Modification of the implant surface using biocoatings is the solution to this problem because the coatings can reduce the rate of the magnesium alloys bioresorption and stimulate the process of bone regeneration [7–10].

The method of micro-arc oxidation (MAO) makes it possible to form coatings of various compositions on the surface of metal implants with complex shapes. Bioactive coatings with a wide range of physicochemical and biological properties can be obtained by varying of the process parameters and electrolytes composition [8]. Calcium orthophosphates such as hydroxyapatite and tricalcium phosphate are widely used to create the bioactive coatings [8–10]. However, calcium and magnesium silicates also have high biological activity and can enhance the osteogenic process [11–13]. In the presence of SiO$_x$$^n$– groups, intense precipitation of Ca$^{2+}$ and PO$_4^{3–}$ occurs, which leads to the formation of hydroxyapatite.
The aim of the presented studies was the formation of biocoatings in the Ca$_3$(PO$_4$)$_2$–CaSiO$_3$ system by the MAO method at the different voltages and the research of their structure, morphology and properties.

2. Materials and methods
Experiments were carried out using the magnesium alloy Mg–0.8 wt% Ca (Mg–0.8Ca) as substrate material. The alloy was produced by permanent mould direct chill casting at Helmholtz Zentrum Geesthacht (Germany) [10]. Metal plates of 10×10×1 mm$^3$ in size from Mg0.8Ca were prepared. The Micro Arc 3.0 System at the Institute of Strength Physics and Materials Science SB RAS (ISPMS SB RAS, Tomsk) was used for the coatings deposition [8, 9].

The process of the coatings formation carried out in the anodic potentiostatic mode with the following parameters: applied voltage of 350–500 V, pulse frequency of 50 Hz, pulse duration of 100 μs and the process duration of 5 min. The electrolyte suspension contained such compounds as: CaSiO$_3$ (wollastonite), β-Ca$_3$(PO$_4$)$_2$, NaOH and Na$_2$SiO$_3$.

The morphology and elemental composition of the coatings were studied with help of the scanning electron microscopy (SEM, Zeiss LEO EVO 50, Germany) in conjunction with energy dispersive analysis (EDX, Pegasus XM2 and INCA, Oxford Instruments) in “Nanotech” center at ISPMS SB RAS. The phase composition of the coatings was determined by the X-ray diffraction (XRD, DRON-07, “Nanotech” center at ISPMS SB RAS) using Co Kα radiation.

3. Results and discussion
The coatings were formed in the system Ca$_3$(PO$_4$)$_2$–CaSiO$_3$ on the bioresorbable Mg0.8Ca alloy by the MAO method, at the process voltages of 350V, 400V, 450V and 500V. The study of the surface morphology of the coatings showed that they have a developed relief due to the accumulation of particles deposited on the surface from the electrolyte during MAO. The SEM image of the coating surface shows the presence of particles of two types (figure 1a).

![Figure 1](image-url)  
**Figure 1.** SEM images of the surface (a) and cross-section (b) of the coating deposited at the applied voltage of 450 V.

These are isometric particles belonging to β-TCP (No. 1, figure 1a) and particles of a characteristic elongated shape, belonging to wollastonite (CaSiO$_3$) (No. 2, figure 1a). In the fields between the particles, the pores are observed in the coating. Analysis of the cross-sectional image (figure 1b) shows that the coating also has an internal porous structure. The pores were formed as a result of the implementation of powerful micro-arc discharges. At the same time, there is a gradient of porosity along the thickness of the coating. In the depth of the coating, near the substrate, a denser layer with smaller pores is observed. The size and number of pores increase closer to the coating surface.
The thickness of the coatings, their mass and Ra roughness increased from 23 to 110 µm, from 4 to 11 mg and from 3 to 12 µm, respectively, with an increase in the voltage of the MAO process in the range of 350–500 V (figure 2).

Figure 2. Graphs of the thickness, mass (a) and roughness (b) of the coatings versus the applied voltage.

XRD results of the research of the coatings phase composition showed that they contain such crystalline phases as wollastonite, α-TCP, forsterite, and magnesium oxide (figure 3). Magnesium oxide MgO appeared in the interface between the magnesium substrate and the coating in the first stage of anodic oxidation. The reflexes from the magnesium substrate are also presented in the X-ray patterns of the coatings. With an increase in the voltage of the MAO process, the reflexes from the magnesium substrate and magnesium oxide become less because the thickness of the coatings rises. The α-TCP phase appeared in the coatings as a result of the β-TCP → α-TCP polymorphic transition at the temperature of 1125 °C. In addition, during the interaction of electrolyte components with a magnesium substrate, plasma-chemical reactions occurred and the phase of Mg$_2$SiO$_4$ was formed.

Figure 3. XRD patterns of the coatings deposited at the applied voltages of 350 V and 500 V.

Elemental EDX analysis showed that with increasing of the process voltage up to the 500 V the calcium content increased dramatically in the coatings (figure 4). In this case, the magnesium content on the contrary significantly decreased, while the silicon content decreased slightly and the phosphorus content remained constant.
4. Conclusions

Thus, the porous biocoatings were formed on the surface of the Mg0.8Ca alloy by the MAO method, in the electrolyte containing β-TCP and CaSiO$_3$. The phase composition of the biocoatings consist of not only initial phases of TCP and wollastonite. Additional crystalline phases, forsterite and magnesium oxide, were formed during the interaction of the electrolyte with the magnesium substrate. When the voltage of the MAO process was varied from 350 V to 500 V, the thickness, roughness, and mass of the coatings increased up to the values of 110 µm, 12 µm and 11 mg, respectively. Coatings containing wollastonite and TCP not only reduce the rate of bioresorption of the magnesium alloy, but also promote the process of bone tissue formation at the bone-implant interface.

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