Formation and properties of micro-arc silicate biocoatings on bioresorbable alloy Mg0.8Ca

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Abstract. The purpose of this study was to form the silicate biocoatings on Mg0.8Ca alloy by the micro-arc oxidation method and to study their structure, elemental and phase composition. With increase in the applied voltage from 350 to 500 V the biocoating thickness grew from 40 to 150 μm. Elongated crystals, which typical for wollastonite, were observed on the coating surface. EDX analysis revealed that the calcium and silicon are localized in the areas with elongated crystals. The wollastonite and akermanite crystalline phases were found in the coatings by XRD studies. Akermanite was formed because of wollastonite interaction with a magnesium substrate during the MAO process. When an applied voltage increased, an amount of akermanite reduced.

1. Introduction

Biocomposites, including a metal and a bioactive coating, are the most used materials in traumathology, orthopedics and dentistry. Due to the good mechanical properties, metals and alloys have great advantages compared with ceramics, polymers and polymer-ceramic composites [1]. Magnesium (Mg) and its alloys are promising materials for implantology because of their biocompatibility, non-toxicity and ability to biodegradation in the human body [2]. The main problem of the Mg and its alloys using is the uncontrolled rate of their bioreorption. Surface modification allows to improve the corrosion resistance of Mg alloys and to reduce the rate of their destruction [3].

The micro-arc oxidation (MAO) method is the most technologically promising for Mg surface modification. Bioactive coatings with a wide range of physicochemical, corrosion protection and biological properties can be formed by this method [4, 5].

As a rule, calcium phosphates such as hydroxyapatite and tricalcium phosphate are used for bioactive coatings production [6, 7]. However, literature reports indicate bioceramics based on silicates can be used as materials for bone tissue regeneration due to their excellent biological properties comparable to that of calcium phosphates [8]. It is shown that bioceramics based on calcium and magnesium silicates stimulate bone tissue regeneration at the interface of the tissue-implant without an intermediate fibrosis layer formation [9]. Silicate coatings, on the one hand can perform a protective function, reducing the corrosion rate of the Mg alloy, and on the other hand, increase the osseointegration [10].

The purpose of the presented studies was to obtain the silicate biocoatings on the surface of bioresorbable Mg alloy by the MAO method and to study the influence of the electrophysical
parameters of the MAO process on the physicochemical properties, surface morphology and structure of the coatings.

2. Materials and methods
Magnesium alloy Mg–0.8 wt% Ca (Mg–0.8Ca) used as substrate material was developed at Helmholtz Zentrum Geesthacht (Germany). The alloy was produced by permanent mould direct chill casting [5]. For the experiments, metal plates of 10×10×1 mm$^3$ in size from Mg0.8Ca were prepared. Coatings were deposited using the Micro Arc 3.0 System at the Institute of Strength Physics and Materials Science SB RAS (ISPMS SB RAS, Tomsk) [5]. The electrolyte suspension contained the following compounds: CaSiO$_3$ (wollastonite), NaOH and NaSiO$_3$.

The coatings deposition carried out in the anodic potentiostatic mode. Applied voltage was varied in the range of 350–500 V. At the same time, the pulse frequency and pulse duration were 50 Hz and 100 μs, respectively. The duration of the MAO process was 5 min.

Surface morphology and elemental composition of the coatings were studied by the scanning electron microscopy (SEM, Zeiss LEO EVO 50, Germany) with an attachment for 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 with a porous structure and a rough relief were obtained by the MAO method. Surface morphology of the coatings is shown in figure 1a,b. Crystals with elongated shape which is typical for wollastonite are observed on the coating surface. Wollastonite powder with crystal sizes from 5 to 25 μm was introduced into the electrolyte. Possibly, elongated wollastonite particles precipitated from the electrolyte onto the coating surface at the last moment of coating formation.

![Figure 1. SEM images of the surface (a), (b) and cross-section (c), (d) of the silicate coatings deposited at the applied voltages of 350 V (a), (c) and 450 V (b), (d).](image-url)
In addition, the coatings contain pores 1.5–5.0 μm in size uniformly distributed over the surface. The pores were formed because of micro-arc discharges migrated over the substrate surface during the MAO process. As the applied voltage increased from 350 V to 500 V, the number of crystals and pores increased noticeably. The coatings thickness grew from 40 to 150 μm, in this case. The coatings deposited at low voltages of 350 V have the roughness (Ra) of 2–3 μm. With increasing voltage to the maximum value (500 V) the coating roughness increases higher than 7 μm. Analysis of the coatings cross-sections (figure 1(c), (d)) shows the porous internal structure in the coatings. The wollastonite crystals are not observed inside the coatings. It can be assumed that in the area of micro-arc discharges the temperature increased greatly, which led to the wollastonite decomposition.

Figure 2(b)–(e) shows the elements distribution maps obtained from the selected area (figure 2(a)) of the silicate coating surface (marked with a yellow line). It is obvious, calcium and silicon are mainly concentrated in the areas with the needle-like crystals. It can confirms the presence of wollastonite in the coatings. Magnesium is mainly located in the valleys of the coating (figure 2(e)).

Figure 2. SEM image of silicate biocoating (a) and elements maps distribution (b)–(e).

Dependences of the calcium, magnesium and silicon concentrations in the coating surface on the applied voltage are represented in the figure 3. With an increase in the voltage of the MAO process in the range of 350–500 V the calcium content in the coatings increased from 7 to 14 at. % and the magnesium content reduced from 6.5 to 3.0 at. %. At the same time, the concentration of silicon remained unchanged, equaled to 17 at. %.

Figure 3. Content of calcium, magnesium and silicon in the coatings depending on the applied voltage.
XRD analysis showed that the coatings have a crystalline structure. The crystalline phases of wollastonite and akermanite (CaSiO$_3$ and Ca$_2$MgSi$_2$O$_5$) were found in the coatings. In addition, strong reflexes from magnesium are observed in XRD patterns. It can be assumed that akermanite was formed because of plasma chemical interaction between electrolyte component such as wollastonite and Mg substrate during the MAO process.

When an applied voltage increased, the coating thickness grew, and the reflections from magnesium substrate became weaker. In this case, the main diffraction maximum of wollastonite ($d = 0.297$ nm) became dominant. At the same time, the intensity of the reflexes related to akermanite decreased with increasing in applied voltage. Perhaps, the akermanite formation in the coatings occurred more intensively in the inner layers of the coating close to the Mg substrate.

![XRD patterns](image)

**Figure 4.** XRD patterns of the silicate coatings deposited at the different applied voltages.

The XRD results are consistent with the results of elemental analysis (figure 3) showing a decrease of the Mg content in the coatings with increasing of the coating thickness due to applied voltage increase.

As reported previously wollastonite-containing coatings were deposited on titanium in an acidic electrolyte in the voltage range of 130–150 V [11]. However, increasing the voltage in the range of 200–300 V led to the destruction of wollastonite both inside the coating and on it’s surface. Thus, wollastonite is more stable in alkaline electrolyte and remains on the coating surface even in the voltage range of 350–500 V.

It is known that bioceramics in the system CaO–MgO–SiO$_2$ such as wollastonite, bredigite (Ca$_7$Mg$_{3-4}$(OH)$_6$), akermanite (Ca$_2$MgSi$_2$O$_7$) and diopside (CaMgSi$_2$O$_6$) demonstrate excellent ability to apatite mineralization and stimulate bone cell proliferation [9]. In addition, the study [11] earlier performed that the coatings containing wollastonite show active osteoconductive properties against fibroblast-like cells which adhere, expand their cell mass and actively migrate forming a monolayer during the period of cultivation. The high cell culture viability including their mobility at the “coating-cell” interface and ability to promote in vitro osteogenic potential of fibroblast-like adherent cells with wollastonite coatings contact were revealed.

Thus, it is interesting and promising approach to produce a biphasic coating containing wollastonite and akermanite on the Mg0.8Ca alloy by the MAO method. However, further studies of the osteoconductive properties of silicate biocoatings are required.
4. Conclusions

Micro-arc silicate coatings were formed on the Mg0.8Ca alloy and their structure, elemental and phase composition were studied. The coating thickness grew from 40 to 150 μm when the applied voltage increased in range of 350–500 V. The coating roughness (Ra) increased from 2 to 7 μm or higher, in this case. Crystals with elongated shape, which are typical for wollastonite, formed the coating relief. Besides, the pores (1.5–5.0 μm) were observed in the coatings. It can be noted that calcium and silicon were localized in the areas with needle-like crystals that confirm the presence of wollastonite in the coatings. When the applied voltage varied in the range of 350-500 V the calcium content in the coatings increased up to 14 at. %, while the magnesium content decreased up to 3.0 at. %. At the same time, the concentration of silicon remained unchanged and equaled to 17 at. %. The crystalline phases of wollastonite and akermanite (CaSiO₃ and Ca₃MgSi₂O₈) were found in the coatings. Akermanite was formed because of wollastonite interaction with a magnesium substrate during the MAO process. When an applied voltage increased, an amount of akermanite reduced.

The biphasic coatings on the Mg0.8Ca alloy containing wollastonite and akermanite produced by the MAO method are capable to reduce the rate of magnesium bioresorption and to intensify the osteointegration processes, therefore they are promising for creating of bioresorbable implants.

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