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Effect of the microarc oxidation time on the corrosion resistance and biodegradation of Mg–Ca–Zn alloys

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The effect of the microarc oxidation (MAO) time on the structure, corrosion resistance and biocompatibility of Mg–Ca–Zn alloy coatings in a weakly alkaline phosphate-borate electrolyte is considered. The MAO time was varied from 15 to 35 min. The created coatings exhibit different structures, porosities, and electrochemical behaviors depending on MAO. All the coatings had a multilayer structure with an outer layer based on O, Mg and P and inner layer based on F. It was found that the coating of the sample formed after MAO treatment for 15 min has the highest corrosion resistance and low porosity.

Keywords: magnesium, microarc oxidation, structure, implant, corrosion.

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Magnesium alloys are regarded as promising materials for creating implants due to their ability to biodegrade in the body's physiological environment, which makes unnecessary re-surgery for removing the implant [1]. However, too intense corrosion in biological environments may lead to premature loss of mechanical properties and to side effects caused by active emission of hydrogen [2]. To stabilize the dissolution process, a promising way is formation of oxide

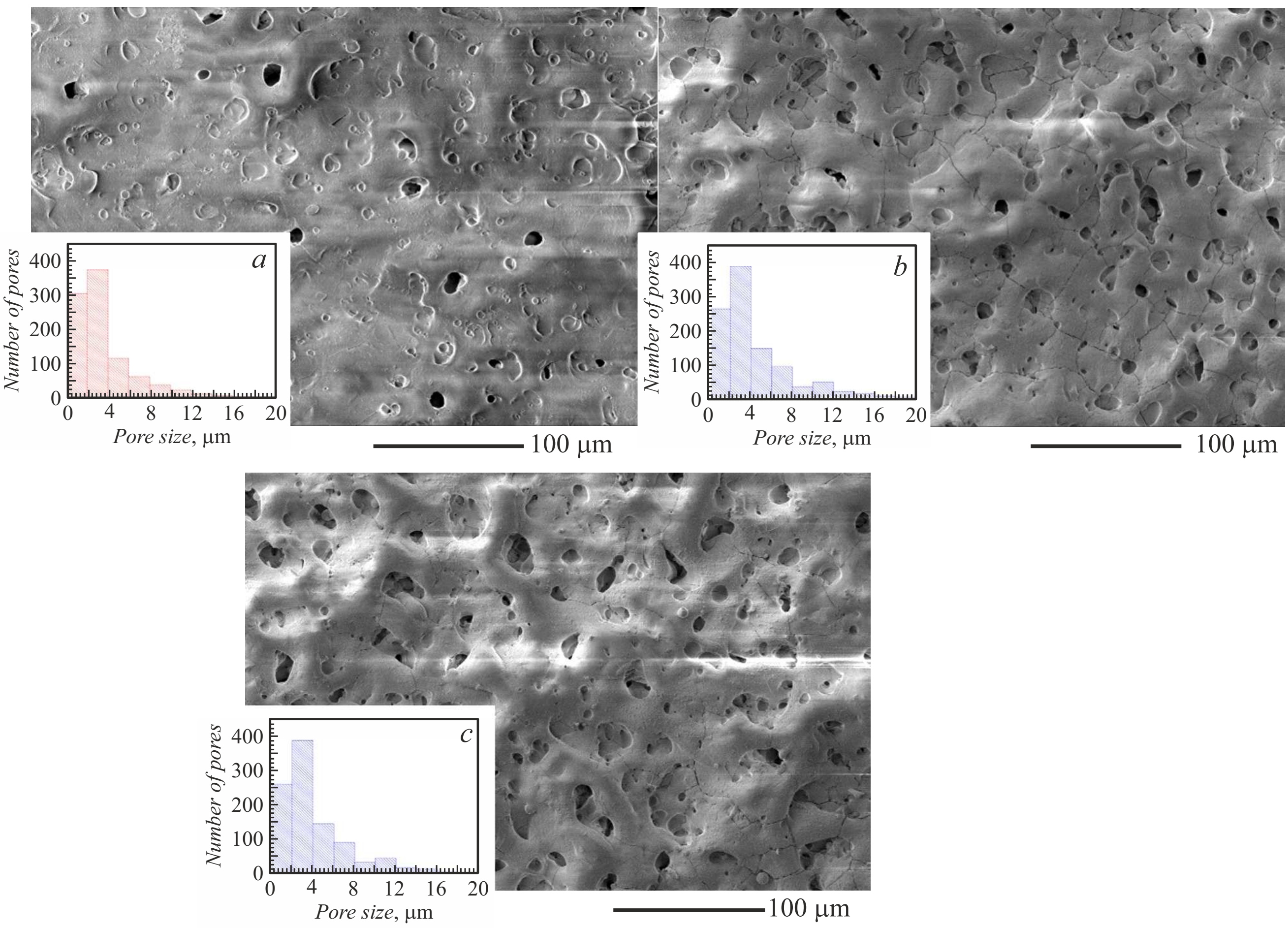

Figure 1. SEM images with histograms of pore size distribution for the samples MAO-treated for 15 (a), 25 (b) and 35 min (s).

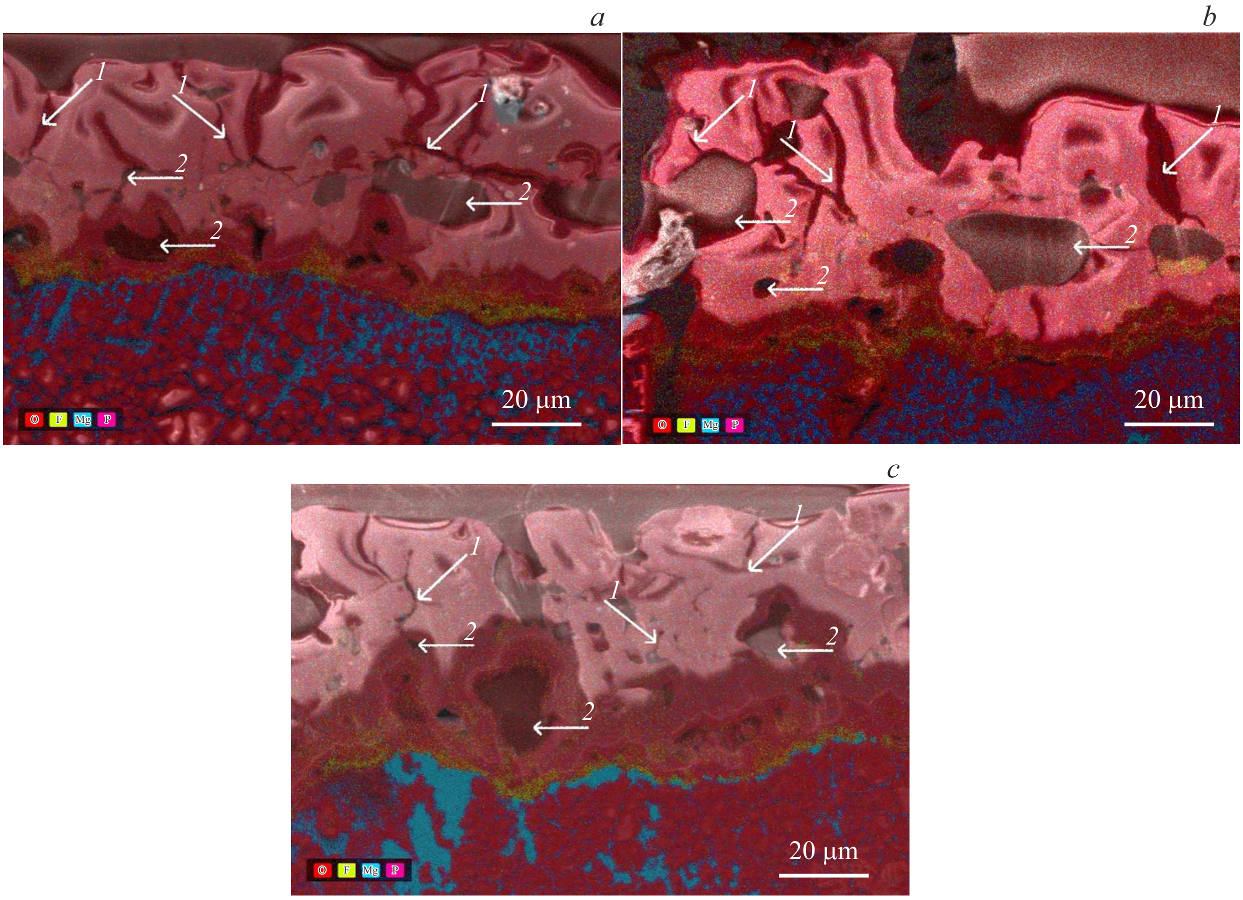

Figure 2. Cross-sectional phase-contrast SEM images of the samples after MAO treatment for 15 (*a*), 25 (*b*) and 35 min (*s*). The arrows indicate discharge channels (*1*) and pores (*2*).

coatings by the MAO method. In the process of MAO, a multilayer ceramic coating gets formed on the metal surface [3]. One of the important parameters of the process is its duration which affects the coating morphology and corrosion properties. Thus, the goal of this work was to study the influence of the MAO duration on the structure and corrosion characteristics of the Mg–Ca–Zn alloy.

Figs. 1 and 2 present SEM images (jointly with histograms of the size distribution) of the structure of MAO coatings formed on the Mg–Ca–Zn alloy surface and of cross-section of the coating on a thin foil; the images were obtained with electron microscope Axia ChemiSEM (Thermo Fisher Scientific, USA). A substrate based on magnesium with addition of 0.5 mass% of Ca and 1.5 mass% of Zn was fabricated by chill casting with simultaneous vibration treatment during crystallization which, as shown in previous studies [4], allows reducing the cast alloy porosity. The coatings were formed in a 10 l stainless-steel MAO bath with bubbling ensuring the electrolyte homogeneity and with a cooling system maintaining the temperature of 20–25 °C. Power was supplied by a 6 kW unipolar pulse source ARCCOR developed at JSC EleSi. The coatings were created by using phosphate-borate electrolyte Manel-W (pH = 8–9) developed and patented by JSC MANEL [5] at the voltage of 450 V, pulse duration of 150 μs, and frequency of 50 Hz. The MAO time was varied from 15 to 35 min. The solution contained up to 50 mass% of Na_2HPO_4, 40 mass% of $Na_2B_4O_7$, and 13 mass% of NaF.

All the oxide layers had a pronounced layered structure, dense barrier sublayer near the metal, and more porous outer layer. When the MAO time increased from 15 to 35 min, there was observed an increase in the coating thickness and porosity from 50 to 70 μm and from 4 to 9 %, respectively. At the substrate/coating interface there was a thin dense layer above which formation of small sparks resulted in point formation of internal pores (3–5 μm). Intensification of the process led to formation of large pores (15–20 μm). When the process slowed down, an outer crater structure got formed (Fig. 1), from which discharge channels extended into the depth (Fig. 2, *a*–*c*).

Phase analysis carried out using diffractometer Haoyuan DX-2700BH has shown that, regardless of the treatment time, the coatings are predominantly amorphous; this is confirmed by the presence of diffuse halos in the X-ray diffraction patterns presented in Fig. 3. The amorphous phase content was assessed from the X-ray diffraction

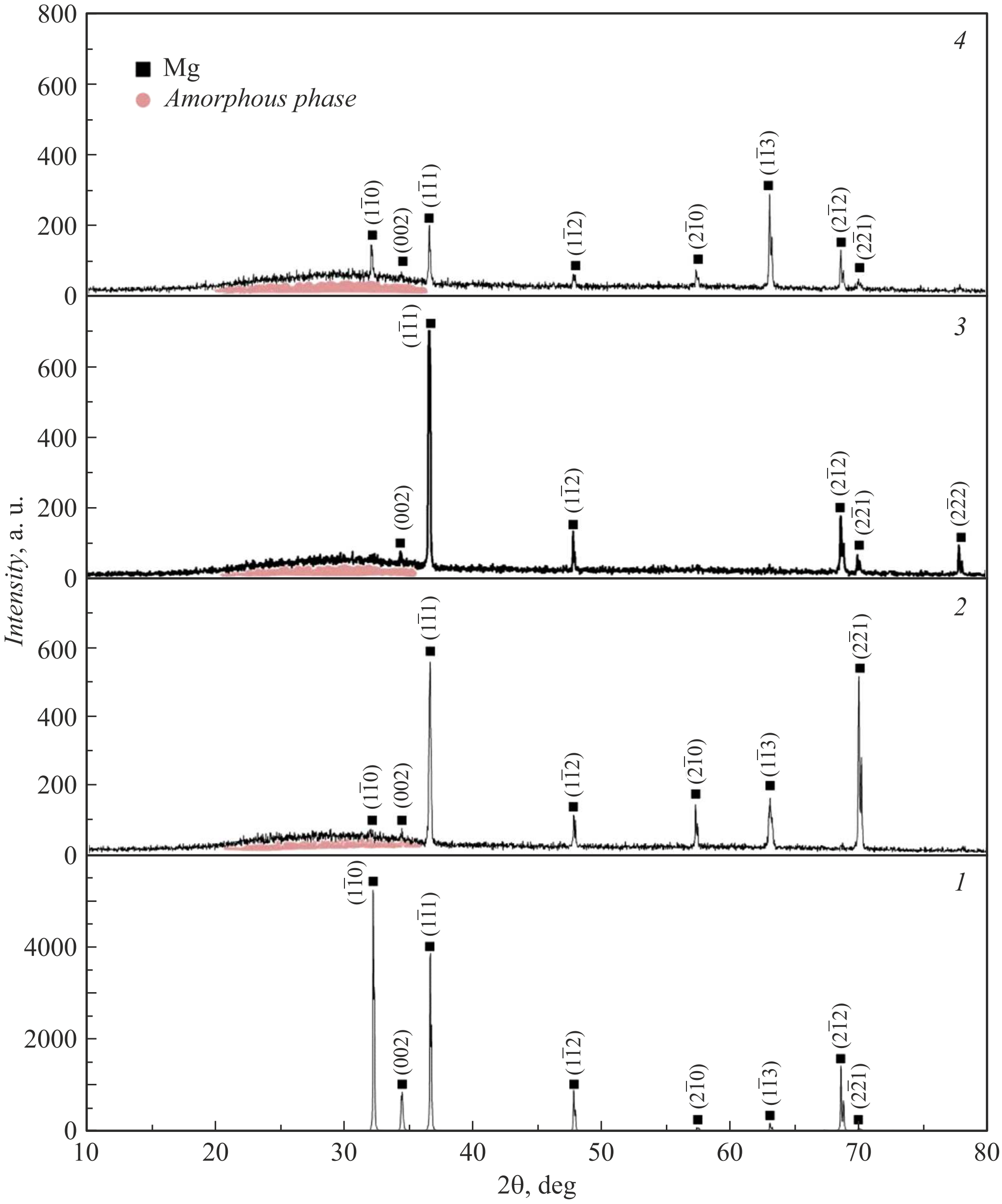

Figure 3. X-ray diffraction patterns of the coating-free magnesium sample (*1*) and samples MAO-treated for 15 (*2*), 25 (*3*) and 35 min (*4*).

patterns by using the Profex program code. To eliminate the influence of substrate, a similar method [6] was used. The sample MAO-treated for 15 min contained the largest portion of the amorphous phase (18.7 %); when the treatment time was increased, this portion decreased to 15.4 % (25 min) and 15.8 % (35 min). The presence of an amorphous structure reduces the number of interphase boundaries and defects and thereby promotes an increase in the resistance to electrochemical dissolution [7].

Studies of the materials' corrosion properties by the methods of electrochemical impedance spectroscopy and potentiodynamic polarization [8] showed that the sample of the Mg−Ca−Zn alloy with the MAO coating of minimal thickness exhibits the lowest corrosion-current density (0.60 μA/cm^2), the highest polarization resistance ($R_p = 723.26\,\text{k}\Omega \cdot \text{cm}^2$) and protective oxide layer resistance (47.52 k$\Omega \cdot$ cm^2), and low-frequency scalar impedance of 0.1 Hz (36.11 k$\Omega \cdot$ cm^2) (see the Table).

Thus, the data obtained show that the optimal MAO time for the Mg−Ca−Zn alloy in the electrolyte with the above-given composition is 15 min. This sample has the lowest porosity (4.28 %) at the coating thickness of 50 μm. The coating has a multilayer structure and maximum amorphous phase content (18.7 %). As per the electrochemical test, the sample treated by MAO for 15 min has the best corrosion resistance.

Corrosion characteristics of samples treated by MAO for 15, 25 and 35 min

MAO duration, min	Corrosion current density, $\mu A/cm^2$	Polarization resistance, $k\Omega \cdot cm^2$	Oxide layer resistance, $k\Omega \cdot cm^2$	Scalar impedance, $k\Omega \cdot cm^2$
15	0.60	723.26	47.52	36.11
25	1.55	283.39	25.17	20.49
35	1.65	255.42	0.59	7.82

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Conflict of interests

The authors declare that they have no conflict of interests.

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