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Micro-arc oxidation as a method of reducing biodegradation of Mg–Ca–Zn alloy

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In this work, the influence of the exposure time in the electrolyte during microarc oxidation of the Mg–Ca–Zn alloy on the structural-phase composition and biodegradation is studied. The test results showed that the exposure time is 5 min. not enough to form a uniform coating. The coating is amorphous and consists of elements O, P, Mg with F-based inclusions. It has been established that the formed coatings successfully reduce the biodegradation of the Mg–Ca–Zn alloy, as evidenced by a significant reduction in weight loss under *in vitro* conditions

Keywords: magnesium alloys, coating, microarc oxidation, structure, XRD, biodegradation.

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Owing to its ability to biodegrade and capacity for stimulation of osteogenesis, magnesium is a promising material for medicine [1]. However, pure magnesium has a low corrosion resistance and degrades rapidly, and the time interval within which magnesium items lose mechanical integrity is too short for new bone tissue to form [2,3]. Adding calcium and zinc to magnesium alloys, one may raise their strength, hardness, and corrosion resistance [3,4]. The examination of a Mg–Ca–Zn alloy revealed that alloying does not lead to any significant reduction of the biodegradation rate [5,6]. Therefore, the issue of combining the methods for suppressing biodegradation and enhancing the mechanical parameters of magnesium alloys remains topical. The microarc oxidation method (MAO) is promising for the production of coatings for magnesium-based bioresorbable materials. Since the coating deposition is performed in a bath with salt solutions, no local overheating of a magnesium alloy is expected, and a stable coating should be formed. In addition, MAO coatings reduce the Mg alloy corrosion rate, provide a better basis for cell adhesion, and exhibit fine biocompatibility [7,8].

The aim of the present study is to examine the influence of time of exposure in an electrolyte during microarc oxidation of a Mg–Ca–Zn alloy on the structure and phase composition and biodegradation parameters.

The examined Mg–Ca–Zn ternary alloy chosen as a substrate had the following percentage ratio of masses: Mg — 98%, Ca — 0.5%, Zn — 1.5%. A MAO coating was deposited onto the obtained Mg–Ca–Zn alloy samples with a size of $2 \times 10 \times 10$ mm in a stainless-steel bath 10 l in volume with bubbling performed to stir the electrolyte, which was cooled with the use of cooling coils. The electrolyte temperature was maintained within the 20–25°C interval. A Manel-W (pH = 8–9) weakly alkaline phosphate-borate electrolyte, which was developed

and patented by AO MANEL, was used for coating. The following coating regime was set: a voltage of 450 V, a pulse duration of 150 μ s, and a pulse repetition rate of 50 Hz. Samples were held for 5, 10, and 20 min (samples Nos. 1, 2, and 3, respectively) in the electrolyte in order to determine the optimum phase composition and surface properties.

The phase composition and structural parameters of samples were examined with an XRD-6000 (Shimadzu, Japan) diffractometer and $\text{CuK}\alpha$ -radiation. The POWDER CELL 2.4 software and the PDF4+ crystal structure database were used for qualitative analysis. The microstructure, surface morphology, and integrity of coatings were characterized with an Axia ChemiSEM (Thermo Fisher Scientific, USA) scanning electron microscope with an elemental composition microanalyzer.

In order to estimate the parameters of biodegradation, samples were introduced aseptically into a DMPI-1840 synthetic culture medium with a low amount of micronutrients: 5.9 g/l NaCl, 0.4 g/l KCl, 0.8 g/l $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, 0.1 g/l $\text{Ca}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.049 g/l MgSO_4 , amino acids, and vitamins (Sigma-Aldrich, USA) at 37°C (1 ml of this medium were used for each sample in accordance with ISO 10993-6). Samples were retrieved from the medium 21 days later and dried in air at a temperature of 22°C for 14 days. The change in their mass was then determined using a VM-II analytical balance.

X-ray diffraction patterns were obtained in the symmetric Bragg–Brentano geometry for three Mg–Ca–Zn samples with different times of exposure in the electrolyte (Fig. 1). X-ray spectra were interpreted and revealed the presence of the Mg substrate phase. The nonlinear behavior of the diffraction pattern in the $2\theta = 20\text{--}40^\circ$ angle interval is indicative of an amorphous state of the coating. The amorphous component becomes more prominent at longer exposure times, indicating that the coating thickness increases.

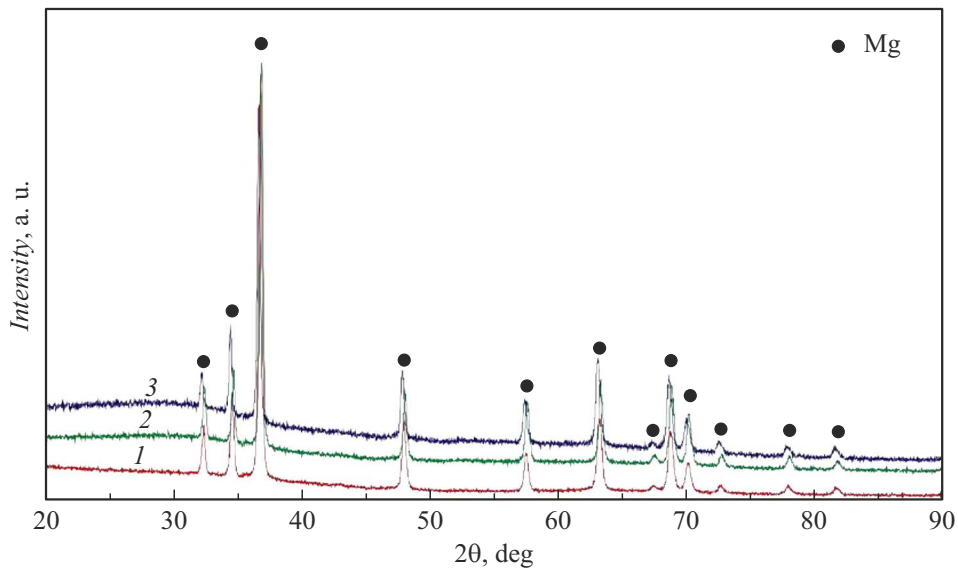


Figure 1. Diffraction patterns of Mg–Ca–Zn alloy samples with coatings obtained with different times of exposure in an electrolyte. The numbers next to curves correspond to the numbers of samples.

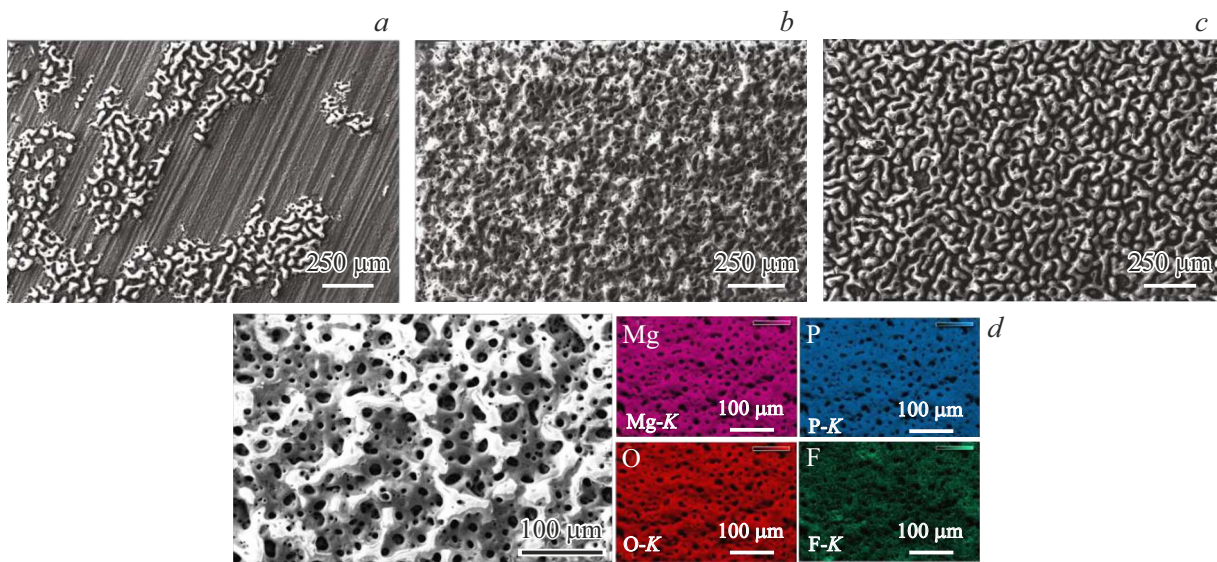


Figure 2. Morphology of the surface of coatings on samples Nos. 1 (*a*), 2 (*b*, *d*), and 3 (*c*). The results of energy-dispersive analysis of the surface of sample No. 2 is presented in the right part of panel *d*.

The surfaces of Mg–Ca–Zn alloy samples with an exposure time of 5, 10, and 20 min (Figs. 2, *a–c*) were examined with a scanning electron microscope. The coatings on all samples have a porous structure typical of microarc oxidation. It turned out that a 5-min-long exposure of samples in the electrolyte is too short for a uniform coating to form (Fig. 2, *a*).

It follows from the results of energy-dispersive analysis that O, P, and Mg are dominant elements in the coating composition (Fig. 2, *d*). Regions enriched with F were also found. The concentration of P and O increases with time of exposure in the electrolyte, indicating that the coating thickness increases (Table 1). At the same time,

the concentration of F-based inclusions decreases at longer exposures.

Table 1. Quantitative energy-dispersive analysis of Mg–Ca–Zn samples with a MAO coating

Sample number	Element concentration, at.%					
	Mg	P	O	F	Ca	Zn
1	25.9	6.9	62.5	3.9	0.2	0.6
2	22.2	8.9	65.7	2.6	0.2	0.4
3	22.5	9.1	67.1	0.9	0.2	0.2

Table 2. Results of estimation of biodegradation of Mg–Ca–Zn samples with coatings and a reference uncoated sample

Sample	Initial sample mass, g	Mass after 21 days, g	Mass loss, g
№ 1	0.496	0.456	0.04
№ 2	0.551	0.520	0.03
№ 3	0.559	0.519	0.04
Uncoated	0.459	0.298	0.16

Quantitative measurements of the mass loss were performed by immersing alloys into an aggressive solution for estimation of their corrosion behavior and biodegradation. The values of initial mass and end mass, which was determined after 21 days of immersion in a DMPI-1840 culture medium, are listed in Table 2. The degradation rate of all coated Mg–Ca–Zn samples was lower than the one of the reference sample. Therefore, the formed coating provides efficient protection of Mg–Ca–Zn alloys against biodegradation.

Thus, coatings for an Mg–Ca–Zn alloy were formed by microarc oxidation with 5, 10, and 20 min of exposure in an electrolyte. These coatings were amorphous and contained O, P, Mg, and F-based inclusions. The concentration of P and O increased with time of exposure in the electrolyte, indicating that the coating thickness increased. Coatings formed by exposing Mg–Ca–Zn to the electrolyte for 10 and 20 min were the most uniform. It was found that 5 min of exposure in the electrolyte are not enough to form a uniform and solid coating. A significant reduction in the mass loss *in vitro* suggests that the coatings efficiently suppressed biodegradation of the Mg–Ca–Zn alloy.

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Conflict of interest

The authors declare that they have no conflict of interest.

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