In vitro corrosion performance of bioresorbable Mg-Ca alloy with hydroxyapatite-containing protective coating

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Abstract. The paper presents the results of the study of protective properties of hydroxyapatite-containing coatings obtained on the surface of bioresorbable magnesium alloy Mg-0.8Ca using plasma electrolytic oxidation (PEO) method. Using traditional electrochemical methods (EIS, PDP) it was established that the PEO treatment of Mg-0.8Ca surface leads to a significant increase in corrosion resistance of the material in minimum essential medium (MEM). The forming of an oxide layer on a magnesium alloy surface contributes to a decrease in corrosion current density (I_C) values for more than three times. The increase in the impedance modulus measured on low frequency values ($|Z|_{f=0.1\ Hz}$) for a coated material was two times compared to an uncoated one.

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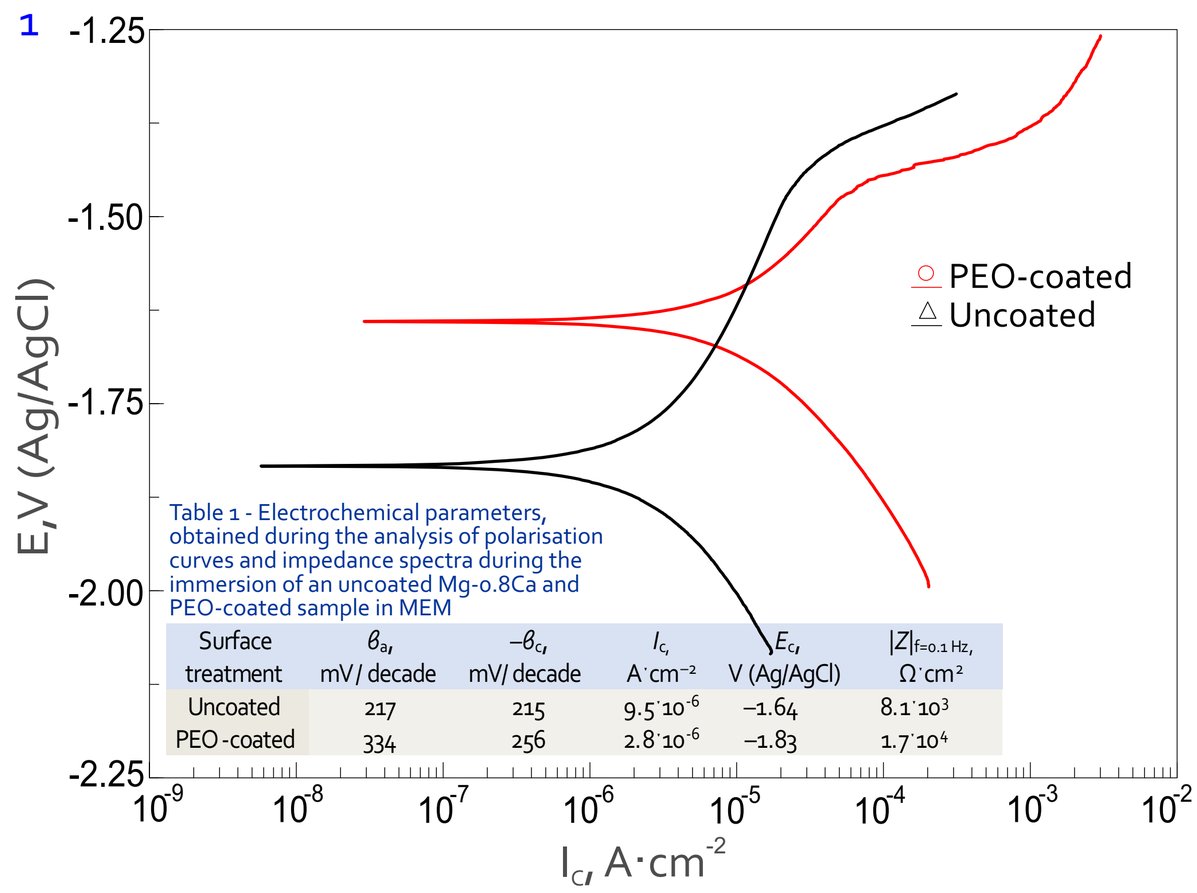

Table 1 - Electrochemical parameters, obtained during the analysis of polarisation curves and impedance spectra during the immersion of an uncoated Mg-0.8Ca and PEO-coated sample in MEM

Surface treatment	β_a, mV/ decade	$-\beta_c$, mV/ decade	I_c, A·cm^{-2}	E_c, V (Ag/AgCl)	$\lvert Z\rvert_{f=0.1\ Hz}$, Ω·cm^2
Uncoated	217	215	$9.5\cdot10^{-6}$	−1.64	$8.1\cdot10^{3}$
PEO-coated	334	256	$2.8\cdot10^{-6}$	−1.83	$1.7\cdot10^{4}$

Fig. 1 - Polarization curves, obtained during electrochemical measurements in MEM

Results. As a result of the PEO process, ceramic-like coatings with high heterogeneity of surface relief were obtained on the surface of a Mg-0.8Ca bioresorbable magnesium alloy. XRD analysis showed that the main component of PEO-coating was hydroxyapatite. The other component of protective layer was periclase. According to data obtained by potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) methods, the formation of a PEO-layer provides the material an advanced corrosion resistance. The corrosion current density (I_C) values for a coated sample (I_C = $2.8\cdot10^{-6}$ A·cm^{-2}) are more than 3 times lower than the ones for an uncoated Mg-0.8Ca (I_C = $9.5\cdot10^{-6}$ A·cm^{-2}) (Fig. 1, Tab. 1). The results of the analysis of electrochemical impedance spectroscopy data also make it possible to confirm the higher corrosion resistance of the sample with a PEO-coating, compared to the material without a protective layer (Fig. 2). The values of the impedance modulus measured at a low frequency ($|Z|_{f=0.1\ Hz}$) during exposure to MEM for a sample with a PEO layer are more than 2 times higher ($|Z|_{f=0.1\ Hz}$ = $1.7\cdot10^{4}$ Ω·cm^2) than the value for an uncoated Mg-0.8Ca ($|Z|_{f=0.1\ Hz}$ = $8.1\cdot10^{3}$ Ω·cm^2) (Tab. 1). For the coated sample during 42 h of exposure to MEM there is an increase both in the diameter of the half-cycle on the complex plane of Nyquist plot and the values of $|Z|_{f=0.1\ Hz}$ (Fig. 3). This is due to the formation of a Ca-P film of corrosion products (including PEO-layer, substrate material and components of MEM), which leads to sealing the pores of the PEO-layer [1,2]. This is also confirmed by the analysis of calculated data obtained as a result of fitting the impedance spectra, representing the evolution of barrier properties of thePEO-coated sample in MEM medium over time (Table 2). For comparison, uncoated material is characterized by an increase in these parameters only during the first 30 h of exposure, then protective properties of the surface layer decrease noticeably, which is associated with the intensification of the corrosion process, leading to the destruction of the Ca-P compounds film [2].

Conclusions. The way to improve the corrosion resistance of bioresorbable magnesium alloy Mg-0.8Ca was obtained during the presented study. Formation of the hydroxyapatite-containing oxide layers leads both to a significant increase in the values of I_C and a decrease in $|Z|_{f=0.1\ Hz}$. Based on the analysis of the obtained data, the prospects for use of calcium-phosphate PEO-coatings on a bioresorbable magnesium alloy for the needs of implant surgery were established.

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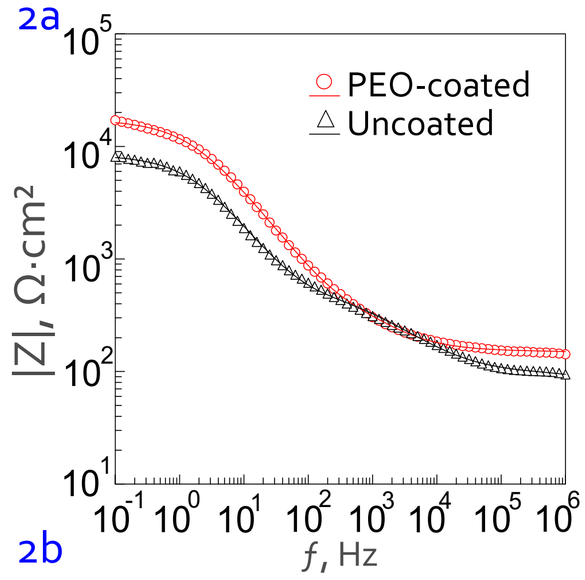
2a



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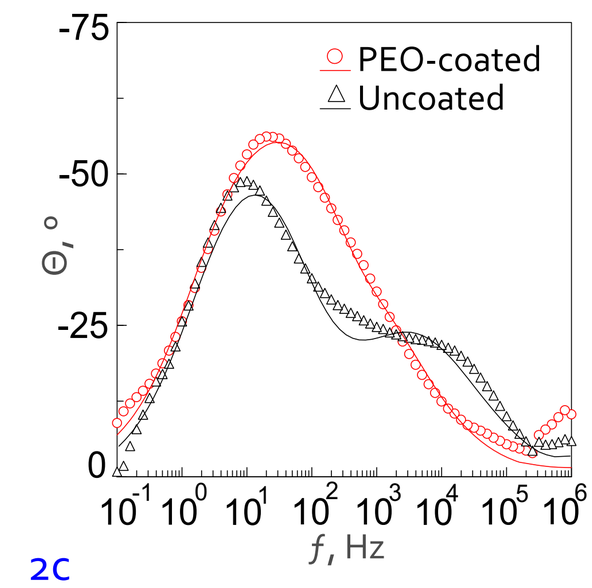

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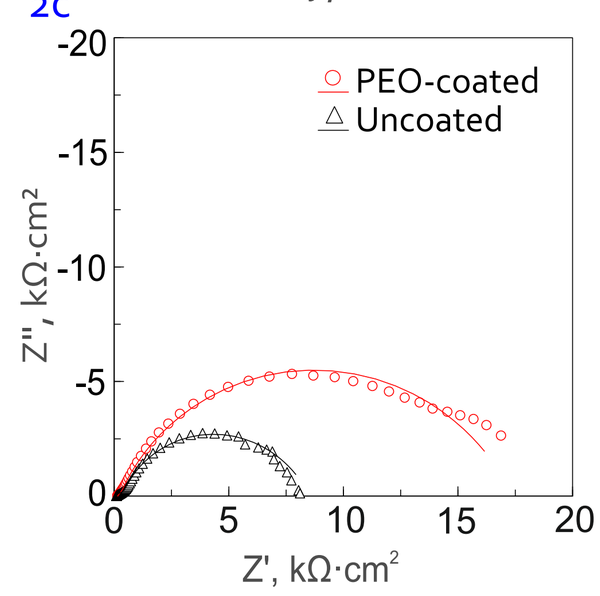
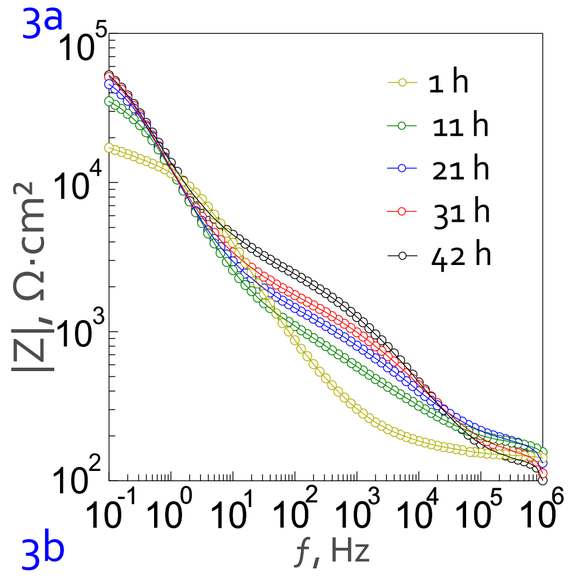


Fig. 2 - Impedance spectra, presented in the form of Nyquist (2a, 2b) and Bode (2c) plots, obtained after the immersion of the samples in MEM for 1 h

3a



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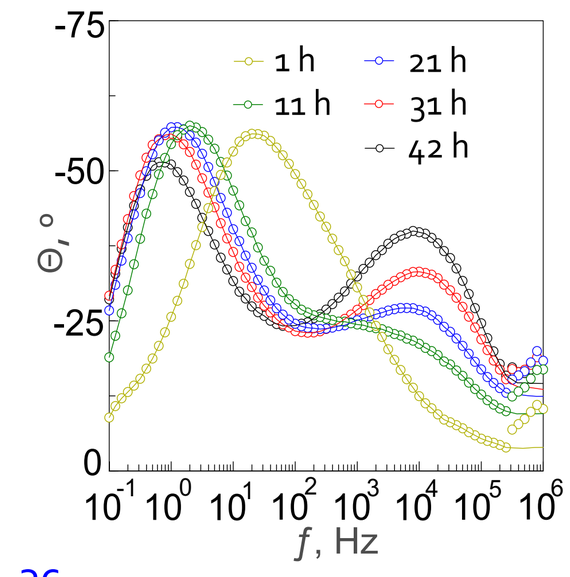

3c

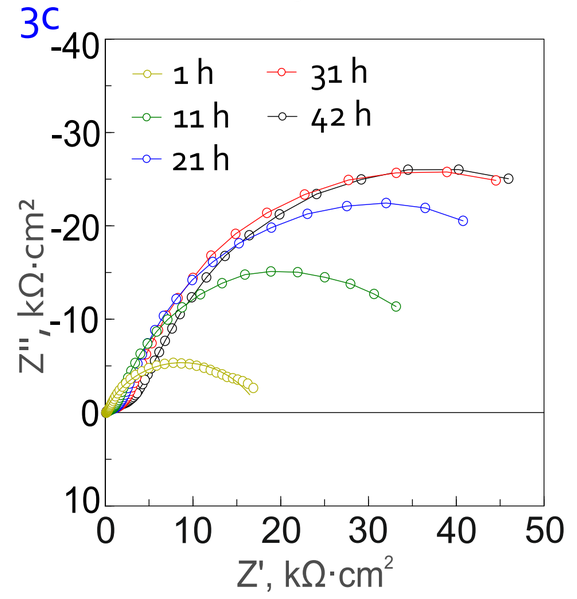

Fig. 3 - Impedance spectra, presented in the form of Nyquist (3a, 3b) and Bode (3c) plots, obtained during the immersion of the PEO-coated sample in MEM for 42 h

Table 2 - Equivalent curcuit parameters, obtained during the fitting of impedance spectra for PEO-coated sample exposed to MEM for 42 h

Immersion time, h	CPE_1		R_1, Ω·cm^2	CPE_2		R_2, Ω·cm^2
	Q_1, Sm·cm^{-2}·s^n	n_1		Q_2, Sm·cm^{-2}·s^n	n_2	
1	$1.00\cdot10^{-5}$	0.69	678	$1.90\cdot10^{-6}$	0.86	16641
11	$1.19\cdot10^{-5}$	0.57	1100	$9.05\cdot10^{-6}$	0.86	45776
21	$9.89\cdot10^{-6}$	0.54	1760	$1.08\cdot10^{-5}$	0.85	76060
31	$7.32\cdot10^{-6}$	0.54	2156	$1.28\cdot10^{-5}$	0.82	89374
42	$3.61\cdot10^{-6}$	0.59	3307	$1.53\cdot10^{-5}$	0.76	87448

References

[1]A. S. Gnedenkov, D. Mei, S. V. Lamaka, S. L. Sinebryukhov, D. V. Mashtalyar, I. E. Vyaliy, M. L. Zheludkevich, S. V. Gnedenkov Corr. Sci 170 (2020)
[2]A.S.Gnedenkov, S.L.Sinebryukhov, V.S.Filonina, V.S.Egorkin, A.Yu.Ustinov, V.I.Sergienko, S.V.Gnedenkov Journal of Magnesium and Alloys (2021) in press.