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

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Abstract: The paper presents the results of the study of corrosion performance of HAp-containing coating obtained on the Mg-0.8Ca bioresorbable magnesium alloy using plasma electrolytic oxidation (PEO). Electrochemical measurements were carried out in minimal essential medium (MEM) using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) and monitoring of open circuit potential (OCP) techniques. It was established that the PEO treatment of Mg-0.8Ca leads to a significant increase in corrosion resistance of the material. Formation of heterooxide layer on magnesium alloy contributes to a decrease in corrosion current density (IC) more than three times. The impedance modulus measured at low frequency ($|Z|_{f=0.1\ \mathrm{Hz}}$) for a coated material increased by two times compared to an uncoated one.

Keywords: Magnesium, magnesium alloys, corrosion protection, plasma electrolytic oxidation (PEO), hydroxyapatite

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Коррозионное поведение биорезорбируемого Mg-Ca сплава с гидроксиапатитсодержащим защитным покрытием *in vitro*

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Аннотация. В работе представлены результаты исследования уровня защиты от коррозии гидроксиапатитсодержащих покрытий, полученных на поверхности биорезорбируемого магниевого сплава Mg-0,8Ca методом плазменного электролитического оксидирования (ПЭО). Электрохимические измерения проводились в среде для культивирования клеток млекопитающих minimal essential medium (MEM) с использованием методов электрохимической импедансной спектроскопии (EIS), потенциодинамической

поляризации (PDP), а также мониторинга электродного потенциала (OCP). Установлено, что обработка поверхности сплава Mg-0,8Ca методом ПЭО способствует значительному повышению коррозионной стойкости материала. Формирование гетерооксидного слоя на поверхности магниевого сплава способствует снижению значений плотности тока коррозии (IC) более, чем в 3 раза. Повышение значений модуля импеданса, измеренного на низкой частоте ($|Z|_{f=0,1}$), для материала с покрытием составило 2 раза по сравнению с материалом без защитного слоя.

Ключевые слова: Магний, магниевые сплавы, коррозионная защита, плазменное электролитическое оксидирование (ПЭО), гидроксиапатит

Финансирование: Исследование выполнено в рамках проекта «Многофункциональные биодеградируемые покрытия нового поколения для контроля процессов резорбции материалов на основе магния: механизм самозалечивания, персонализированная медицина» (№ 21-73-10148).

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Introduction

Features of magnesium degradation process determines its great prospects in application as an implant material. Unfortunately, rapid and heterogeneous degradation as well as an alkalization of a surrounding area obstruct the expansion of magnesium scope [1–7]. Improving the corrosion resistance of bioresorbable magnesium-based materials will make it possible to control the degradation process of the material in the human body in order to ensure matching the rates of implant resorption and osteogenesis [8]. The most common way to improve both corrosion resistance and bioactivity of magnesium is to form protective coatings, containing Ca, P, Mg and their compounds, including hydroxyapatite (inorganic components of a bone) [9, 10]. According to [11], magnesium has a positive effect on the activity of osteoblasts and osteoclasts, and therefore on bone growth. In turn, the release of calcium ions and phosphates from surface layer compounds forms a saturated ionic solution at the interface. In this case, there is an ion exchange between the implant material and the patient's bone. Some of these ions can deposit on the bone matrix, forming new bone tissue. One of the easiest and technological ways to improve the corrosion resistance of valve metals (including Mg) is plasma electrolytic oxidation (PEO) [12, 13]. The PEO processing allows to create on magnesium surface protective layers of various morphology and composition, including hydroxyapatite-containing ones [14–18].

Materials and Methods

The experiments were carried out on Mg-0.8Ca alloy samples (0.8 wt.% Ca, balance Mg) with a size of 15×30×1 mm. Samples were ground with Si-C abrasive paper with gradual reduction of a grain size to 14–20 μm (P1000) with following rinsing in isopropyl alcohol and drying in air. Plasma electrolytic oxidation (PEO) coating was formed in a combined bipolar mode with the current density below 0.75 $A \cdot cm^{-2}$. Duty cycle was equal to 1, total oxidation time reached 120 s. The composition of the formed coating was studied via XRD using a SmartLab diffractometer (Rigaku, Japan). The measurements were carried out in the range $2\theta = 4°–90°$ with a step of 0.01°. To evaluate the corrosion resistance of formed samples, electrochemical measurements (including potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and monitoring of open circuit potential (OCP) change) were realized. Experiments were carried out using a Versa STAT MC electrochemical system (Princeton Applied Research, USA) and the electrolyte was minimal essential medium (MEM) solution (a synthetic mammalian cell culture medium).

Table 1

Equivalent electrical circuit parameters, obtained during the fitting the impedance spectra for PEO-coated sample exposed to MEM for 42 h

Immersion time, h	CPE_1		R_1, Ω·cm²	CPE_2		R_2, Ω·cm²
	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

Results and Discussion

As a result of the PEO process, ceramic-like coating with high heterogeneity of the surface relief were obtained on the surface of a Mg-0.8Ca bioresorbable magnesium alloy. XRD analysis showed that the main component of the 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) for a coated sample (I_C = $2.8\cdot10^{-6}$ A·cm^{-2}) is more than 3 times lower than the one for an uncoated Mg-0.8Ca (I_C = $9.5\cdot10^{-6}$ A·cm^{-2}) (Fig. 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 bare alloy. The values of the impedance modulus measured at a low frequency ($|Z|_{f=0.1\ Hz}$) after 1 h exposure to the MEM for a sample with a PEO-layer are more than 2 times higher ($|Z|_{f=0.1\ Hz}$ = $1.7\cdot10^4$ Ω·cm²) than the value for uncoated Mg-0.8Ca ($|Z|_{f=0.1\ Hz}$ = $8.1\cdot10^3$ Ω·cm²) (Fig. 2). For the coated sample the increase in the diameter of the half-cycle on the complex plane of Nyquist plot due to increase both the values of resistance of outer (porous, R_1) and inner (nonporous, R_2) layers of the PEO-coating (Figs. 2,*d*, 3, Table 1) is observed during the whole immersion time (42 h). This is due to the formation of a Ca-P film composed of corrosion products of the sample (including PEO-layer and substrate material) and components of the MEM, which leads to sealing the pores of the PEO-layer. 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 [4].

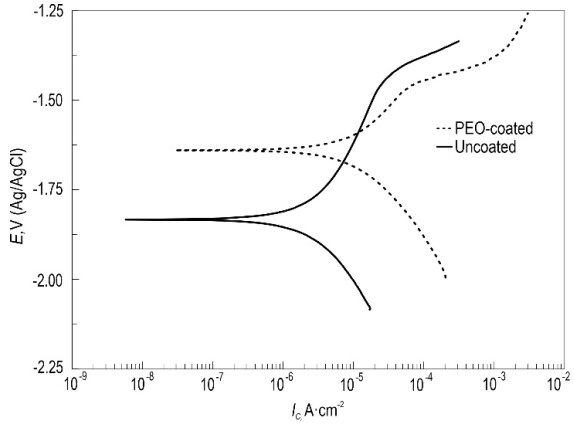

Fig. 1. Polarization curves obtained as a result of electrochemical tests (PDP measurements) in MEM

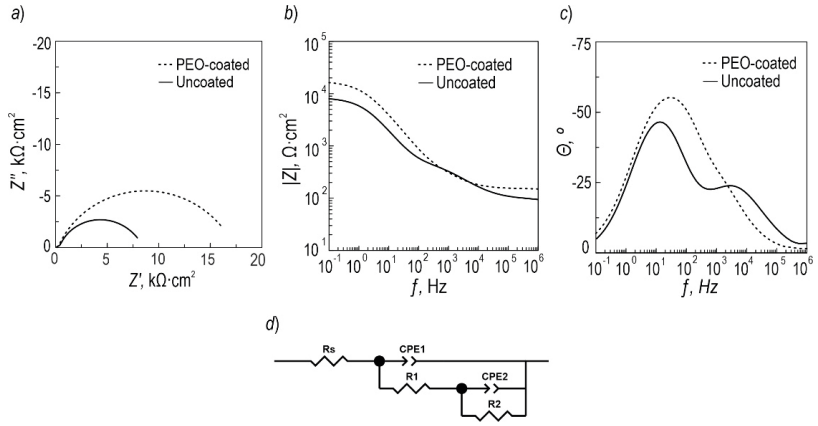

Fig. 2. Impedance spectra presented as Nyquist (*a*) and Bode (*b*, *c*) plots after 1 h of exposure of the samples to the MEM and an equivalent electrical circuit (EEC) used for fitting the impedance spectra (*d*)

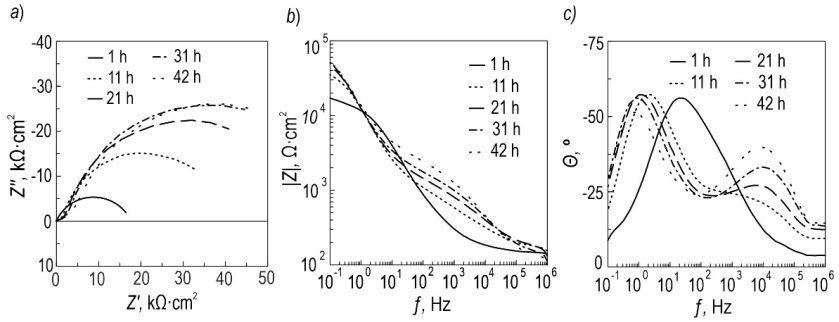

Fig. 3. Impedance spectra presented as Nyquist (*a*) and Bode (*b*, *c*) plots during 42 h of exposure of the PEO-coated sample to MEM

Conclusion

The way to improve the corrosion resistance of bioresorbable Mg-0.8Ca magnesium alloy was obtained during the presented study. Formation of the hydroxyapatite-containing oxide layers leads both to a significant decrease in the values of I_C and increase 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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