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Influence of phenol red in Earle's solution on corrosion properties of coated and uncoated Mg alloy

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Abstract: Metallic biomaterials are widely used for clinical purposes due to their excellent mechanical properties and good biocompatibility. Inspired by the functional surface of natural biological systems, many new designs and concepts have recently emerged to create multifunctional surfaces with great potential for biomedical applications. In present study, bioactive coatings were formed on Mg alloy by plasma electrolytic oxidation (PEO). Morphological features and composition of formed layers were studied by SEM and EDS. It was revealed that PEO-coatings have in their composition Ca and P, which can increase biocompatibility. Moreover, obtained coatings demonstrated high corrosion properties: corrosion current density substantially decreased compared to bare alloy.

Keywords: metallic biomaterials, bioactive coatings, plasma electrolytic oxidation

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Влияние фенолового красного в растворе Эрла на коррозионные свойства сплава магния с покрытием и без покрытия

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Аннотация. Металлические биоматериалы широко используются в клинических целях благодаря их превосходным механическим свойствам и хорошей биосовместимости. В последнее время появилось много новых подходов и концепций для создания многофункциональных поверхностей с большим потенциалом для биомедицинских приложений, которые вдохновлены функциональной поверхностью природных биологических систем. В данной работе биоактивные покрытия были сформированы на сплаве магния МА8 методом плазменного электролитического оксидирования (ПЭО). Установлено, что ПЭО-покрытия имеют в своем составе Ca и P, которые могут повышать биосовместимость. Кроме того, полученные покрытия продемонстрировали высокие коррозионные свойства: плотность тока коррозии существенно снизилась по сравнению со сплавом без покрытия.

Ключевые слова: металлические биоматериалы, биоактивные покрытия, плазменное электролитическое оксидирование

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Introduction

The current advances in technologies make it possible to create safe implants that are biocompatible with the human body. Developing new materials for implants requires a deep knowledge of the chemical, physical and mechanical properties of natural bone tissue, the qualitative and quantitative characteristics of implant materials. Recently, the possibility of natural regeneration has been actively studied, when the implant material biodegrades and dissolves in body fluids, and the process of healing of damaged tissues occurs with the replacement of the implant with the body's own tissue. This property of bioresorption is exhibited by magnesium and magnesium alloys. Early clinical studies, as well as in vivo and in vitro studies shown that magnesium-based implants are highly biocompatible. It has also been reported that magnesium-based implants can stimulate the bone tissue heals [1].

The unique mechanical properties of Mg alloys also make them desirable for fabrication of load-bearing implants. Magnesium has been tested as non-allergenic and stimulates new bone formation in vivo and in vitro tests [1]. However, the high electrochemical activity of magnesium and low wear resistance of this material can lead to early failure of the implant, which in turn can significantly affect to the patient's healing [2]. As result, magnesium needs additional protection to improve corrosion resistance and reduce wear.

Alloying of metals is a widely used method for improving the functional characteristics of a material, including in the field of protection against corrosion damage. This method of protection is laid down at the stage of creating a certain brand of alloy. The essence of alloying is the addition of certain impurity substances to the composition of metals that improve the mechanical or physico-chemical properties of these compositions.

A suitable alloy composition can improve corrosion resistance, mechanical properties and facilitate the production of magnesium (Mg) based materials. The two main groups of Mg-based alloys are those containing 2–10 wt.% aluminum (Al) with trace additions of zinc (Zn) and manganese (Mn), they show moderate corrosion resistance and improved mechanical properties [3], and those that use a mixture of rare earth elements in combination with another metal such as zinc, yttrium, and a small amount of zirconium, which gives a fine-grained structure and improved mechanical properties [3]. Because these materials are used in the body, non-toxic alloying elements must be selected. However, it is well known that aluminum is harmful to neurons and osteoblasts and also associated with dementia and Alzheimer's disease [4]. The introduction of rare earth metals (Pr, Ce, Y, etc.) can lead to hepatotoxicity. Excess yttrium ions (Y^{+3}) have been shown to alter the expression of several rat genes and adversely affect DNA transcription factors.

One of the possible ways to solve this problem is formation of coating on the surface of a magnesium implant by the plasma electrolytic oxidation (PEO) [5]. Note that this method gives

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opportunity creating surface layers of a purposeful structure and composition; thus, the use of PEO makes it possible to form coatings similar in composition to mineral component of human bone tissue [1].

Materials and Methods

Samples. The samples were prepared from rectangular sheets made of MA8 magnesium alloy (Mg–Mn–Ce system, wt.%: 1.30 Mn; 0.15 Ce; Mg to balance), $8\times8\times1$ mm^3 and $30\times20\times2$ mm^3 in size. Before the coatings were produced, all samples were treated with sandpaper, washed with distilled water, and degreased with alcohol.

Coating formation. In accordance with the previously developed principles of directed plasma electrochemical synthesis of coatings on the surface of metals and alloys [6, 7] and conclusions drawn from the analysis of literature data [6,7], plasma electrolytic oxidation was carried out in bipolar mode: in the anode component the voltage 400 V, while in the cathode component, the current decreased from 5 to 3 A at a sweep rate of 0.04 A/s. PEO of the samples was carried out in an electrolyte containing 25 g/l calcium glycerophosphate ($C_3H_7CaO_6P$), 5 g/l sodium fluoride (NaF), and 7 g/l sodium metasilicate (Na_2SiO_3). The duration of the process was 100 s. After the coatings were formed, all samples were washed with distilled water, degreased with alcohol, and dried with warm air.

Coating characterization. To evaluate the morphology and chemical composition of the obtained samples the scanning electron microscopy and energy dispersive spectroscopy were used. EVO 40 scanning electron microscope (SEM, Carl Zeiss, Germany) equipped with INCA X-act instrument (Oxford Instruments, UK) for energy dispersive spectroscopy (EDS) was used for surface characterization [2].

Study of electrochemical properties. The electrochemical parameters of the samples were studied by potentiodynamic polarization using VersaSTAT MC electrochemical system (Princeton Applied Research, USA) in accordance with the technique described in [2].

The measurements were carried out in a three-electrode cell at a temperature of 37 °C in Earle's solution with and without phenol red, which are similar in ionic composition to human blood plasma (Table 1). The concentration of phenol red in Earle's solution was 0.02 g/L. Thus, phenol red is a pH indicator, its often used in medicine and microbiology for determination of metabolic products of bacteria. However, the presence of this substance in solution can directly affect the corrosion of such an electrochemically active material as magnesium/magnesium alloy. In this regard, and due to the fact that solutions with and without phenol red can be used in the course of research on implantation materials, it is of great interest to study the effect of this

Table 1

Ionic concentration (mmol/L) in Earle's solution and human blood plasma

Ion concentration, mmol/L	Human blood plasma	Earle's solution
Na^+	142	143.5
Cl^-	103	123.5
HCO^{3-}	27	26.2
K^+	5.0	5.4
Ca^{2+}	2.5	1.8
Mg^{2+}	1.5	0.8
PO_4^{-3}	1.0	0.9
SO_4^{-2}	0.5	0.8
Glucose, g/L	1.1	1.0

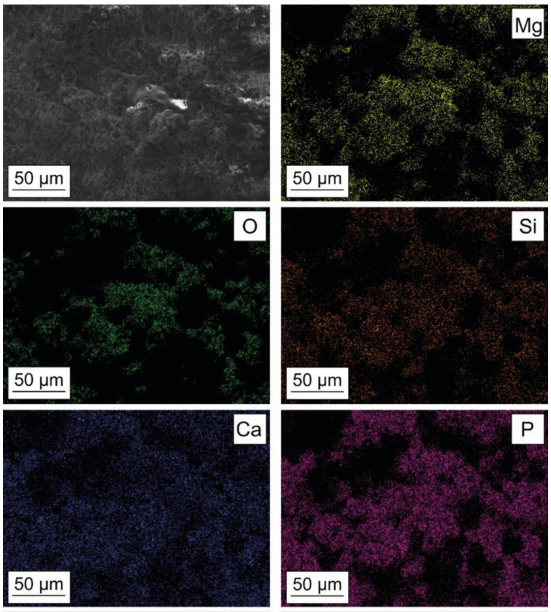

Fig. 1. SEM-image of the PEO-coating and EDS map of the element distribution

substance on the corrosion of Mg alloy, including those with protective PEO-layers.

Results and Discussion

It can be concluded from SEM analysis that the PEO-coating formed has a typical surface morphology with crater-like pores (Fig. 1). This is the result of sharp cooling of the breakdown zone down to the electrolyte temperature after the attenuation of the plasma discharge as well as gas evaporation during the PEO. According to [6], such a developed surface can positively affect cell proliferation and improve bone-to-implant contact.

Analysis of the EDS data indicates the presence of Mg, Si, O, Ca, P in the coating composition (Fig. 1). The presence of Si, Ca, P and O is due to their incorporation from the electrolyte during PEO. Mg is a substrate element. Formed layer is enriched with Ca and P, as result of transfer of these elements in the plasma discharge channel form the electrolyte to the surface of substrate. The presence of Ca and P can significantly increase the biocompatibility of PEO-coatings, because these elements are the main components of bone tissue.

Potentiodynamic polarization data indicate an improvement in the corrosion properties of the samples after coatings formation on their surface. Based on analysis of the potentiodynamic measurements, it can be concluded that the corrosion current density, i_{corr}, decreased after application of PEO-coating on Mg alloy (Table 2).

Table 2

Electrochemical parameters of samples in Earle's solution with and without phenol red

Electro-chemical parameters	Earle's solution without phenol red		Earle's solution with phenol red	
	Bare magnesium alloy	With PEO-coating	Bare magnesium alloy	With PEO-coating
E_{corr} (V vs. SCE)	–1.75	–1.62	–1.82	–1.63
i_{corr} (A/cm^2)	8.6×10^{-6}	6.7×10^{-6}	1.0×10^{-5}	6.9×10^{-6}

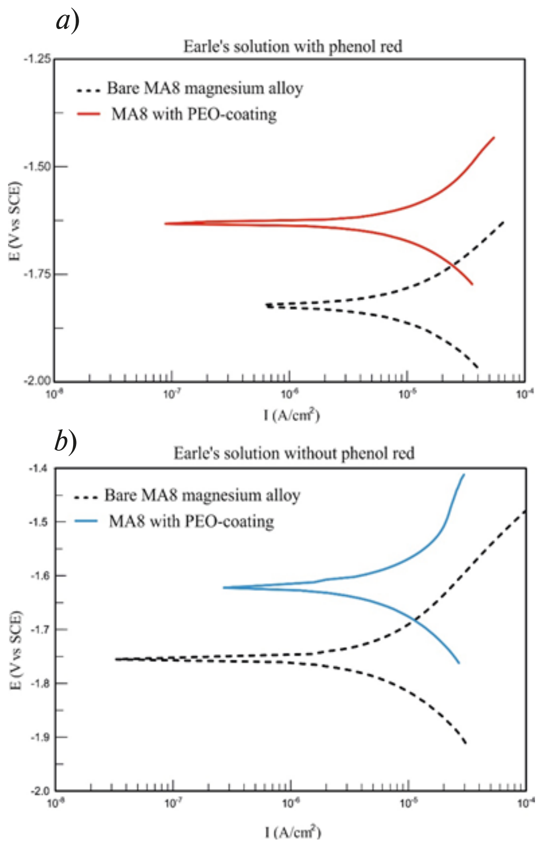

Fig. 2. Polarization curves obtained for MA8 alloy samples with and without PEO-coating in Earle's solution without (*a*) and with (*b*) phenol red

There are no significant differences between the coatings studied in Earle's solution without phenol red and with this compound (Fig. 2, Table 2). This fact is related to the features of the formed coatings. It is known that the PEO-coating consists of an outer porous layer, which mainly determines the mechanical properties, and an inner, practically non-porous sublayer, which is responsible for corrosion resistance [7]. Since the formed sublayer consists of poorly soluble magnesium compounds, in particular, MgF_2 [8], the probability of reactions occurring between it and the substances present in the Earle's solution is extremely low probability. However, for bare Mg alloy, with the addition of phenol red the corrosion current density increased. According to the analysis of the polarization curves, the presence of phenol red leads to a shift in the corrosion potential to more negative values compared to a solution that does not contain this substance (Fig. 2). Accordingly, this leads to an intensification of the magnesium alloy corrosion process. It is known that corrosion of magnesium materials proceeds with alkalization of the medium, which, apparently, leads to reactions between phenol red and evolving hydrogen. In addition, Earle's solution with phenol red has a higher electrical conductivity (14.41 mS/cm) compared to Earle's solution without phenol red (5.67 mS/cm).

Of interest are the details of this interaction, considering the complex composition of Earle's solution, the presence in it of not only phenol red, inorganic compounds, but also organic matter: glucose. The features of the occurring reactions will be the subject of study in our next works.

Conclusion

Coatings containing Ca/P were obtained on MA8 Mg alloy by plasma electrolytic oxidation. Obtained coatings have high corrosion resistance compared to bare alloy. Differences in the results of electrochemical studies showed that the phenol red in Earle's solution affects the course of reactions on the surface of the samples without coatings. However, PEO-coatings demonstrated high protective properties regardless of presence phenol red in Earle's solution, which additionally confirms the high corrosion resistance of the formed surface layers.

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