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### **Composition and morphology of calcium phosphate coatings formed on resorbable substrates based on pure Mg and Mg-HAp composite**

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**Abstract:** We considered coatings obtained on a magnesium based substrate with a different content of a bioactive component, nanosized hydroxyapatite (HAp). The properties of coatings formed by plasma electrolytic oxidation (PEO) in electrolytes containing calcium compounds were compared. Coatings obtained in the electrolyte with HAp demonstrated higher strength characteristics compared to coatings obtained in the glycerophosphate electrolyte. It can be explained by the hardness of the components included in the coating ( $\text{Mg}_2\text{SiO}_4$ ) as well as by the presence of hydroxyapatite nanoparticles. Oxidation of composite samples in an electrolyte with HAp leads to a decrease in the corrosion current density by 2 orders of magnitude compared to this parameter for uncoated samples.

**Keywords:** bioresorbable composite, magnesium, hydroxyapatite, PEO, adhesion

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Материалы конференции

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### **Состав и морфология кальций-фосфатных покрытий, сформированных на резорбируемых подложках на основе чистого Mg и композита Mg-HAp**

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**Аннотация.** В данной работе были исследованы ПЭО-покрытия для нужд имплантационной хирургии, полученные на магнии с различным содержанием биоактивного компонента — наноразмерного порошка гидроксиапатита кальция. Было проведено сравнение свойств покрытий, сформированных методом ПЭО в электролитах, содержащих соединения кальция. Покрытия, сформированные в электролите с гидроксиапатитом, демонстрируют более высокие прочностные характеристики и антикоррозионные свойства, по сравнению с покрытиями, полученными в электролите с глицерофосфатом.

**Ключевые слова:** биорезорбируемый композит, магний, гидроксиапатит, ПЭО, адгезия

**Финансирование:** Исследование выполнено при поддержке гранта № 22-23-00915.

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## Introduction

Over the recent decades, implant surgery has made a great leap both in the methodological approach and in the variety of materials used [1]. Stents, orthopedic implants, including plates, prostheses, screws, etc., as well as bone substitute materials, can radically differ in the requirements for strength characteristics and surface properties [2–4]. An important role in the orthopedics of cortical bones is played by the implant resorption, which, in the case of restoring the functionality of the bone, excludes secondary surgical intervention to remove it, thereby improving the quality of life and health of the patient [4–6]. Biodegradable magnesium and its alloys evincing huge potential to be used as a new class of implant materials [7, 8] due to outstanding features of biodegradation [9], antibacterial [10], osteogenesis inductivity and some other biofunctional properties [11]. Among plenty techniques aimed to reducing the corrosivity of magnesium and its alloys the plasma electrolytic oxidation (PEO) is a powerful method for application an oxide coating on the metal substrate [12], which significantly reduces the tendency of the metal to corrode and wear out. Mg-PEO-coatings can ensure a stable composition, excellent adherence to the substrate and controllable surface roughness [13]. Wherein poor bioactivity due to moderation the adsorption and reproduction of osteoblast, remaining a disadvantage [14]. Calcium phosphorus compounds (specifically, hydroxyapatite – HAp) presence can activate bioactivity of implants [15] and enhance the healing process of wound in body fluid environment. A number of approaches have been used with combined PEO technology or as a preliminary step to fabricate calcium phosphate protective coatings on the implant surface [16]. It is well known that coating morphology and properties of PEO-coating is greatly dependent on the electrolyte and polarization mode. Incorporating nanoparticles into PEO-coatings is recognized as a promising and effective method for pores filling and introducing some functional properties to PEO-coatings. In present work, a versatile approach is proposed to form a PEO-CaP composite coating on Mg-HAp composite substrate using in-situ suspending synthesized HAp nanoparticles into the basic sodium silicate electrolyte as well as an electrolyte with calcium-phosphate salts (glycerophosphate) at the stage of forming a PEO-coating. The influence of hydroxyapatite nanoparticles concentration and processing parameters on the dynamics of the growth of the coating, its morphology and composition were evaluated and studied with SEM and EDS, respectively. Evaluating the corrosion performance of the coatings was held by electrochemical impedance spectroscopy (EIS).

## Materials and Methods

Magnesium powder (Mg, purity  $\geq 99.9\%$ , size  $\leq 40 \mu\text{m}$ , Merck) and pre-synthesized hydroxyapatite were used as the basis for biodegradable substrate design. Hydroxyapatite nanoparticles (HAp, size  $\leq 80 \text{ nm}$ ) were obtained by preparing an aqueous solution of  $(\text{NH}_4)_2\text{HPO}_4$  (Merck) and  $\text{Ca}(\text{OH})_2$  (Merck) through gradual pouring until a suspension was formed. Aging of the suspension were followed by microwave radiation. Resulting precipitate was centrifuged, washed and then dried at 343 K overnight. The final powder was subjected to sequential screening through sieves with a mesh size of 100–75–20  $\mu\text{m}$  (Cisa, Italy). Magnesium and obtained hydroxyapatite powders were mixed in ratios of 97:3 and 93:7 (wt.), dispersed in solvent (ethanol), followed by

evaporation of the solvent followed by continuous stirring. The resulting mixture as well as source magnesium powder were proceed using spark plasma sintering on an SPS-515S unit (Dr. Sinter-LABTM, Japan) at a temperature of 823 K under a constant pressure of 25 MPa at a heating rate of 373 K/min. Sintering was carried out in a graphite mold in vacuum (10–5 atm), the samples were held at the maximum temperature for 5 min and then cooled for 45 min to room temperature.

The formation of calcium-phosphate PEO-coating on magnesium samples was carried out by the PEO in various electrolytes using bipolar modes as described in our previous works [17, 18]. The composition of the electrolyte containing calcium glycerophosphate,  $C_3H_7CaO_6P$  (25 g/l), NaF (5 g/l) and  $Na_2SiO_3$  (8 g/l) described in [18]. Electrolyte containing HAp nanoparticles (20 g/l) also included sodium fluoride (5 g/l) and silicate (20 g/l) as well as sodium dodecylsulfate (used as a stabilizer) in the amount of 0.5 g/l.

The phase composition of the surface layers was determined on a Rigaku X-ray diffractometer (XRD) (SmartLab, Japan), using  $CuK\alpha$ -radiation. Bragg-Brentano geometry focusing was used in the  $2\theta$  angle range from  $10^\circ$  to  $80^\circ$ . Adhesive properties were studied on three samples with the same type of coating using Revetest Scratch Tester (CSM Instruments, Switzerland). The experiments were carried out at a track length of 5 mm with a gradual increase of the applied load from 1 to 30 N (Mg–7–H sample up to 60 N) using a Rockwell diamond indenter. The load, at which abrasion of the coating to the substrate occurs were determined, average value and error were calculated, the measurement error was up to 3%. The electrochemical tests were carried out using VersaSTAT MC (Princeton Applied Research, USA). EIS and potentiodynamic polarization were performed at room temperature using three-electrode K0235 Flat Cell (PAR, USA) in 0.9 wt.% NaCl solution. The platinized niobium grid was used as a counter electrode, the saturated calomel electrode (SCE) was used as a reference electrode. The area of contact of the sample with electrolyte was equal to 1 cm<sup>2</sup>. The cross sections of the coated specimens were prepared using EpoxySet epoxy resin (NA) by cold pouring into a mold with a diameter of 30 mm, then polished using a Tegramin-25 polishing machine. The morphology of the cross sections as well as sample's surface were studied by SEM measurements (Carl Zeiss EVO 40 Series and Hitachi S5500). Element mapping by means of SEM-EDS measurements were performed by Carl Zeiss EVO 40 Series using the AZtec 3.0 SP2 program (Oxford Instruments, USA).

### Results and Discussion

The properties of coatings formed by the PEO in electrolytes containing osteoinductive components: calcium glycerophosphate and hydroxyapatite were studied in the work (Table 1).

Using X-ray phase analysis, it was found that the coatings formed in the electrolyte with glycerophosphate contain Mg, MgO,  $Ca_5(PO_4)_3F$ ,  $Mg_3(PO_4)_2$ , and those formed in the electrolyte with hydroxyapatite contain Mg, MgO,  $Mg_2SiO_4$ .

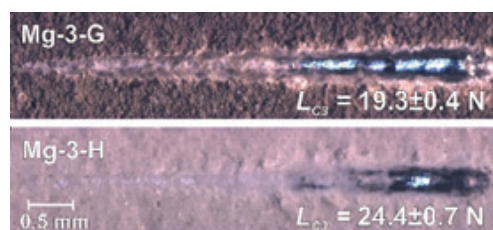
It has been established that the thickness of the oxide PEO-layers increases with a growth of calcium hydroxyapatite content in the composition of the substrate (Table 1). The adhesive properties of the coatings are represented by the parameter  $L_{C3}$ , which is the load at which the coating is abraded to the metal (Fig. 1). With almost the same thicknesses of the Mg–3–G and Mg–3–H-coatings, the  $L_{C3}$

Table 1

Designation of the samples

Ca content in the substrate (wt.%)	Sample/coating thickness*, $\mu m$		
	Bare	+PEO obtained in the electrolyte	
		with glycerophosphate	with HAp
0	Mg–0	Mg–0–G / $73 \pm 5$	Mg–0–H / $47 \pm 8$
3	Mg–3	Mg–3–G / $110 \pm 8$	Mg–3–H / $110 \pm 7$
7	Mg–7	Mg–7–G / $130 \pm 10$	Mg–7–H / $186 \pm 12$

Note. The asterisk corresponds to eddy current measurements.



**Fig. 1.** Appearance of scratches on the coatings at a load of 30 N

values differ significantly and amount to 19.3 N and 24.4 N, respectively. Composition of the substrate has a great influence on the adhesion properties of coatings. In the absence of calcium phosphate compounds in the substrate composition, the adhesive properties of the Mg-0-G and Mg-0-H PEO-layers are nearly identical, despite a significant (almost 2 times) difference in thickness. The Mg-7-G-coating with the maximum content of calcium hydroxyapatite in the substrate reaches a thickness of 130  $\mu\text{m}$ , while the thickness of the PEO-layer obtained in the electrolyte with HAp nanoparticles is even greater and reaches 186  $\mu\text{m}$  (Mg-7-H-sample). It should be taken into account that the data obtained by the eddy current measurements are somewhat overestimated, but the analysis of SEM-images of cross sections confirms the indicated trend (see below). This effect can be associated with the electrophoretic deposition of Hap-particles during the formation of the oxide layer, which provides a significant thickness of the coating, not excluding, at the same time, the variation of the thickness. Comparing the thickness of the PEO-layers and the  $L_{C3}$  load, it can be concluded that coatings formed in the electrolyte with hydroxyapatite have higher adhesive characteristics. It can be explained with the hardness of the components including in the coating as well as HAp nanoparticles. On the Mohs scale, fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), contained in the sample Mg-3-G has a hardness of 5, while the forsterite ( $\text{Mg}_2\text{SiO}_4$ ) detected in Mg-3-H sample has a hardness value of 7.

During the formation of PEO-coatings on composites obtained by the spark plasma sintering, there are differences in the behavior of the current and voltage curves vs treatment time compared to traditional curves for wrought magnesium alloy [18]. There is an initial voltage rise with a steepness of  $\sim 1 \text{ V s}^{-1}$ , and the slope is much smaller, while it is “smeared” over the processing time (Fig. 2). That process occurs when a barrier film forms on the surface during conventional anodizing stage and, according to the absence of a drop in the current density curves, the anodizing process continues throughout the treatment. Depending on the surface area and concentration of non-metallic additives, modes were selected as increased current density from  $0.59 \text{ A/cm}^2$  to  $0.97 \text{ A/cm}^2$  (Mg-0  $\rightarrow$  Mg-7).

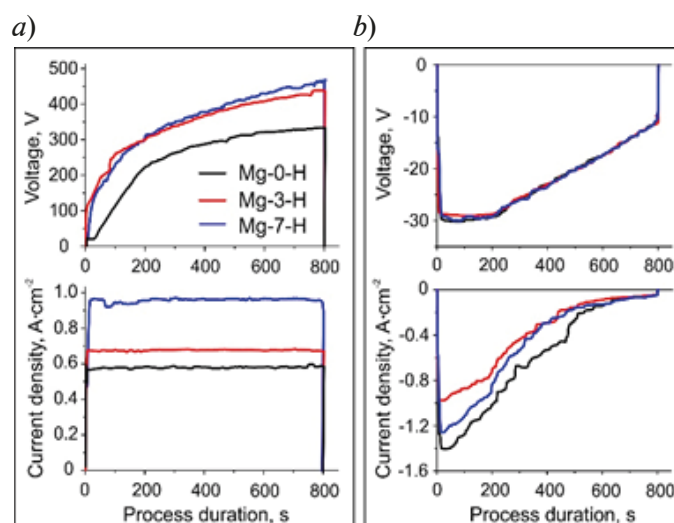
The difference in the strength characteristics of the studied coatings is also probably associated with different surface morphology of the layers. The coatings formed in the electrolyte with hydroxyapatite have a more uniform dense structure, while the coating obtained in glycerophosphate electrolyte is characterized by a more “fungous” structure (Fig. 3).

Table 2

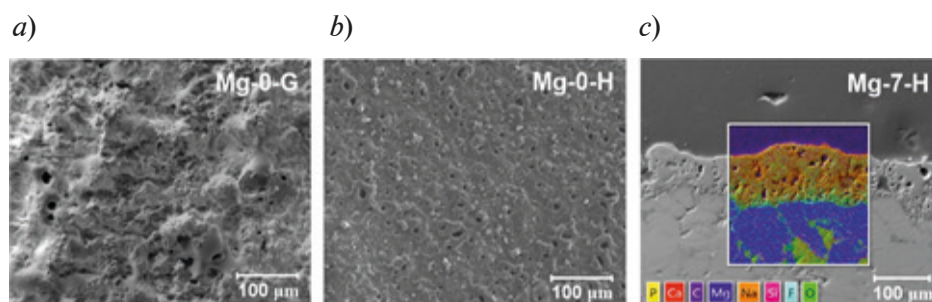
**Corrosion properties of the uncoated/coated samples**

Sample	$E$ (V vs SCE)	$I$ ( $\text{A} \cdot \text{cm}^{-2}$ )	$R_p$ ( $\Omega \cdot \text{cm}^2$ )	$ Z $ ( $\Omega \cdot \text{cm}^2$ )
Mg-0	-1.61	$1.06 \cdot 10^{-5}$	$1.61 \cdot 10^2$	$1.77 \cdot 10^3$
Mg-3	-1.55	$1.21 \cdot 10^{-5}$	$4.21 \cdot 10^2$	$3.90 \cdot 10^2$
Mg-7	-1.57	$2.88 \cdot 10^{-5}$	$5.67 \cdot 10^2$	$8.48 \cdot 10^2$
Mg-0-G	-1.58	$1.25 \cdot 10^{-6}$	$1.07 \cdot 10^4$	$1.26 \cdot 10^4$
Mg-3-G	-1.59	$9.80 \cdot 10^{-7}$	$2.29 \cdot 10^4$	$2.96 \cdot 10^4$
Mg-7-G	-1.57	$1.33 \cdot 10^{-6}$	$1.46 \cdot 10^4$	$1.33 \cdot 10^4$
Mg-0-H	-1.54	$7.37 \cdot 10^{-7}$	$7.06 \cdot 10^4$	$4.71 \cdot 10^4$
Mg-3-H	-1.66	$1.27 \cdot 10^{-7}$	$4.05 \cdot 10^5$	$3.32 \cdot 10^5$
Mg-7-H	-1.69	$6.30 \cdot 10^{-7}$	$1.52 \cdot 10^5$	$1.07 \cdot 10^5$



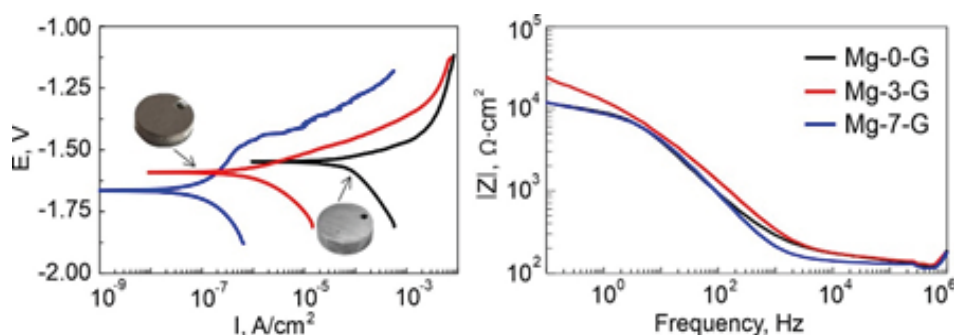


**Fig. 2.** Evolution of current and voltage with time for bipolar PEO-process in electrolyte with HAp; anodic (a) and cathodic (b) phases are presented separately



**Fig. 3.** SEM images of the surface of Mg-HAp composites coated with PEO, obtained in various electrolytes (a, b) and cross-section of Mg-7-H-sample (c)

Evaluation of the results of electrochemical studies showed that the spectra for the samples Mg-0-G, Mg-7-G on the Bode plot (impedance modulus vs frequency) exhibit the same  $|Z|$  at low frequencies, while the Mg-3-G-sample shows a greater value of the impedance modulus (Fig. 4). The same trend can be traced in the values of the corrosion current density and polarization resistance (Table 2). Both PEO-coatings formed on the substrate containing 3 wt.% hydroxyapatite in two used electrolytes, demonstrated greater corrosion resistance. But the coatings obtained in an electrolyte with hydroxyapatite on the Mg-3-substrate, have a higher anticorrosion characteristic, compared to the coatings formed in the electrolyte with calcium glycerophosphate.



**Fig. 4.** Polarization curves and Bode plot for the studied samples

## Conclusion

Coatings formed by the PEO on a composite material containing magnesium and hydroxyapatite obtained by spark plasma sintering have been studied. The phase composition of the PEO-layers is established, which explains their mechanical properties. It has been established that the strength of the PEO-layer obtained in an electrolyte with hydroxyapatite (Mg–3–H) is 20% higher than the strength of coatings formed in an electrolyte with glycerophosphate (Mg–3–G). This mechanism is mainly due to the formation of the silicon-containing forsterite phase with high hardness. Coatings formed in an electrolyte with glycerophosphate allows to reduce the corrosion current density by 1 order of magnitude compared to untreated samples (from  $1.1 \cdot 10^{-5}$  to  $1.3 \cdot 10^{-6} \text{ A} \cdot \text{cm}^{-2}$ ). Protective layers obtained in an electrolyte with hydroxyapatite nanoparticles further reduce corrosion currents by 2 orders of magnitude: up to  $6.30 \cdot 10^{-7} \text{ A} \cdot \text{cm}^{-2}$ . Oxidation of composite samples in electrolyte with hydroxyapatite leads to increase in polarization resistance and impedance modulus by 3 orders of magnitude against uncoated samples. In addition, it has been demonstrated that the uncoated composites sintered with HAp demonstrate better protective properties than magnesium samples.

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