COMPOSITION AND MORPHOLOGY OF CALCIUM PHOSPHATE COATINGS FORMED ON PURE MG AND MG-HAP COMPOSITE RESORBABLE SUBSTRATES

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Introduction

Over the resent decades implant surgery has made a great leap both in the methodological approach and in the variety of materials used. Vasodilator, orthopedic implants, including plates, prostheses, screws, etc., as well as implants for the dentistry, can radically differ in the requirements for strength characteristics and surface properties. 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 repeated surgical intervention to remove it, thereby improving the quality of life and treatment of the patient.

Recently, coatings formed on magnesium products with different content of biologically active components, e.g. hydroxyapatite, which is closely resemble of bone and tooth tissues have attracted the greatest interest. The porous coatings applied by the PEO on the surface of a resorbable substrate makes it possible to produce multilayer composite implant materials. Moreover, it could prevents implant rejection, promotes intensive growth of connective tissue and can be used in the osteolysis, osteoporosis treatment. Furthermore, in some cases, there is a need to introduce drugs into the coating that have a long therapeutic effect, which helps *inter alia* to reduce the patient's rehabilitation period.

Results and discussions

The samples studied in this work were obtained by spark plasma sintering (SPS) of magnesium powder and nanosized calcium hydroxyapatite in an amount of 3 wt. % and 7 wt. %. The properties of coatings formed by the PEO method in electrolytes containing osteoinductive components: calcium glycerophosphate and calcium hydroxyapatite were studied in the work (Table 1).

Table 1. *Designation of the samples*

Ca content in the substrate (wt. %)	Sample		
	Bare	with PEO	
		Electrolyte with $CaC_3H_7PO_6$	Electrolyte with $Ca_{10}(PO_4)_6(OH)_2$
0	Mg-0	Mg-0-G	Mg-0-H
3	Mg-3	Mg-3-G	Mg-3-H
7	Mg-7	Mg-7-G	Mg-7-H

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 in the electrolyte with hydroxyapatite – 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 (Fig. 1). The adhesive properties of the coatings are represented by the force L_{C3} – the load at which the coating is rubbed to the metal (Fig. 2). With a similar thickness of PEO layers (110 μm), the L_{C3} force for the coating formed in the electrolyte with HAp is noticeably higher (Fig. 2)

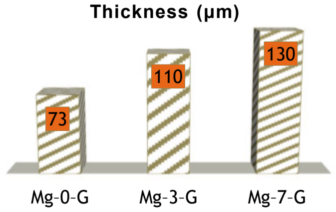

Fig. 1. *Coating thickness dependence on the amount of hydroxyapatite in the substrate*

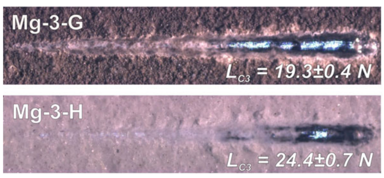

Fig. 2. *The appearance of scratches on the coatings, at a load of 30 N*

Evaluation of the results of electrochemical studies showed that the curves of the samples Mg–0–G, Mg–7–G on the plot of impedance vs. frequency behave the same 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, Fig. 5).

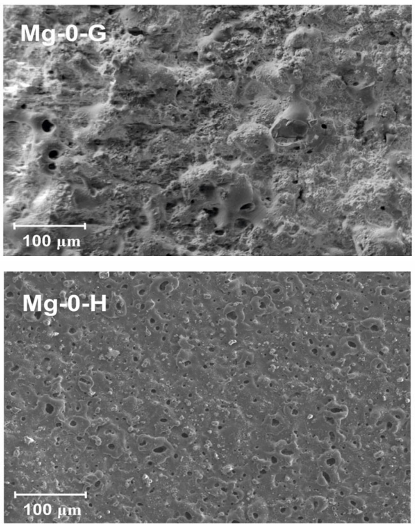

Fig. 3. *Morphology of coatings*

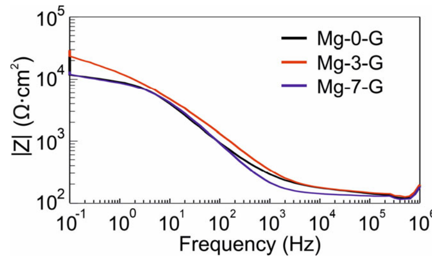

Fig. 4. *Bode diagrams for the studied samples Mg-3, Mg-3-G and Mg-3-H*

Table 2. *Corrosion properties of the uncoated/coated samples*

Sample	E_c (V vs. SCE)	I_c (A·cm^{-2})	R_p (Ω·cm^2)	Z (Ω·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	$6.30 \cdot 10^{-7}$	$1.52 \cdot 10^{5}$	$1.07 \cdot 10^{5}$

The coatings formed on the substrate containing 3 wt. % hydroxyapatite, demonstrated greater corrosion resistance in both electrolytes. But the coatings obtained in an electrolyte with calcium hydroxyapatite on the Mg–3-substrate, have a higher anticorrosion characteristic of the layers, compared with the coatings formed in an electrolyte with calcium glycerophosphate.

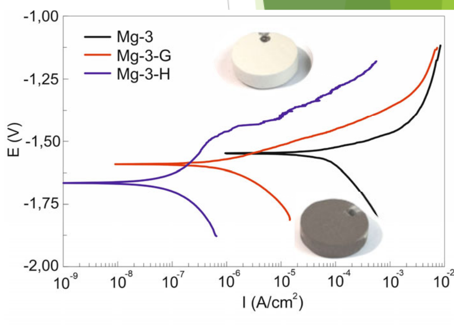

Fig. 5. *Polarization curves for the studied samples Mg-3, Mg-3-G and Mg-3-H*

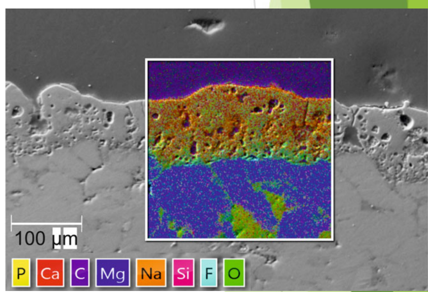

Fig. 6. *Distribution of elements over the thickness of the Mg-7-H coating by the EDX*

Conclusions

Coatings formed by the PEO on a composite material based on 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. The corrosion current density of coatings formed in an electrolyte with calcium glycerophosphate up to 1–2 orders of magnitude than that of bare substrate. Oxidation of composite samples in an electrolyte with calcium hydroxyapatite leads to a decrease in corrosion currents by 2 orders of magnitude, and an increase in polarization resistance and impedance modulus by 2–3 orders of magnitude, against raw samples. It has been established that the best protective properties are exhibited by coatings formed on resorbable substrates with 3 wt. % content of calcium hydroxyapatite in the composition.

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