CALCIUM-PHOSPHATE COATING ON AZ91D MAGNESIUM ALLOY PREPARED VIA RF MAGNETRON SPUTTERING

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КАЛЬЦИЙ-ФОСФАТНЫЕ ПОКРЫТИЯ НА МАГНИЕВОМ СПЛАВЕ AZ91D, СФОРМИРОВАННЫЕ МЕТОДОМ ВЧ МАГНЕТРОННОГО РАСПЫЛЕНИЯ

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Аннотация. *В исследовании представлены результаты научной работы, посвященной изучению структурных и поверхностных свойств биокомпозита на основе магниевого сплава AZ91D с кальций-фосфатным покрытием, сформированным методом ВЧ магнетронного распыления.*

Nowadays attention of many scientific groups is devoted to the development of magnesium implants in biomedicine area [1]. Magnesium is a lightweight metal with physical properties similar to that of bone. In recent years, there are several studies reported the investigation towards the magnesium alloys with the aim to decrease the degradation rate of the material in body fluids [1]. Due to the fact that magnesium alloys are actively corroded in the body one needs to improve its corrosion resistance. Calcium phosphate (*CaP*) coating on magnesium is a prospective way to enhance corrosion rate of alloy, furthermore *CaPs* are widely used in orthopedic and dental surgery because of their biocompatibility and high osteoinductivity [2].

A coating prepared via *RF*-magnetron sputtering is an attractive way because of its ability to prepare uniform, dense pore-free coating; high-purity films; ability to regulate structure of the coating (amorphous or crystalline) and the *Ca/P* ratio; ability to fabricate coating with a strong adhesion to the substrate (bonding strength 30 *MPa*) [3].

The aim of the study was to investigate the structure, chemical composition and wettability of *CaP* coating sputtered via RF magnetron on magnesium alloys.

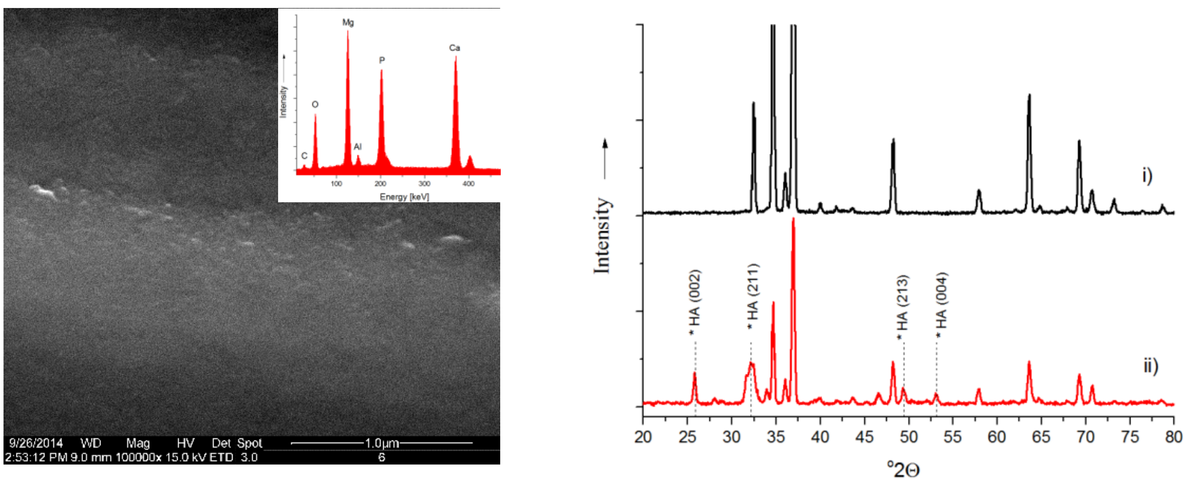
The thickness of the prepared coating was investigated by optical ellipsometry (Ellipse 1891-*SAG*, Institute of Semiconductor Physics, *RAS*, Siberian Branch). Morphology of the surface was estimated using *SEM* with an ESEM Quanta 400 FEG instrument combined with an energy-dispersive X-ray analysis (*EDX* analysis system Genesis 4000, SUTW-Si(Li) detector) operated in high vacuum. The samples were coated with platinum for 30 s before the *SEM* study, with the deposited *Pt* layer thickness equaled 5 nm. The *EDX* spectra were collected for 60 s with a dead time of 30% and an electron beam energy of 15 keV. The presence of *Ca*, *P*, *O* and *Ca/P* ratio in the coating was determined by *EDX*.

The structure and phase composition of the *CaP* films were determined by X-ray powder diffraction (D8 Advance, Bruker, Germany) with *Cu-Kα* radiation (l = 0,154 *nm*). The surface of the samples was irradiated using grazing incidence X-ray diffraction (incident beam angle was 1° and step size of 0.01°/2*Θ* at 40 *kV* and 40 *mA*). The ICDD database was used as reference for the pattern of hydroxyapatite (HA) and magnesium.

Contact angle analyses were conducted by applying the sessile drop method using an optical contact angle equipment (OCA 15 Plus Data Physics Instruments GmbH, Germany) using an SCA20 software (Data Physics Instruments GmbH, Germany. Calculations of water contact angle and water hysteresis were performed using 10 droplets (5 *μL*) for each to reveal an average *Θ* value.

The thickness of the coating was estimated to be 800±50 *nm*. Representative *SEM*-micrographs of the surface of *CaP* coating are shown in Fig.1. a. The coating corresponded uniform, homogeneous, dense layer and no cracks were observed.

One the most important characteristic is the molar *Ca/P* ratio of *HA* film [2, 4] . The lower the Ca/P molar leads to the more soluble condition of the *CaP*. *HA* is represented with the chemical formula: $Ca_{10}(PO_4)_6(OH)_2$, and the stoichiometric *Ca/P* atomic ratio close to that of natural bone (1,67). The *Ca/P* ratio of the coatings deposited for 8h as determined by *EDX* was 1,6 which was very close to the natural *Ca/P* ratio (measurement error was below 7%).



a) b)

Fig.1. a) Typical SEM images and chemical composition of CaP coating on AZ91D magnesium alloy
b) *Representative XRD patterns of the HA coating deposited at 500W for 8 hours on AZ91D magnesium alloy: i) bare substrate, ii) CaP coating. "*" denotes the peaks attributed to hydroxyapatite. The peaks of hydroxyapatite (ICDD card number 09-432) is shown by vertical lines.*

Based on the *XRD* results (Fig. 1.b) it is found that main diffraction peaks at 25,8° (002), 53,1° (004), 31,8° (211), 32,2° (112), and 32,9° (300) belong to crystalline *HA* with parameters of hexagonal lattice a=9,46, b=9,46, c=6,88.

Information on the wettability properties of a biomaterial is provided by the contact angle measurements. Protein absorption and cell behavior depended on the surface wettability [5, 6]. The initial osseointegration depended on the surface wettability. It influenced on the cell behavior during implantation. [6] The average values of water contact angle, surface free energy and coating water hysteresis for bare substrate and *HA* coating are given in Table 1. It is observed that contact angle had a lower value compared to the bare alloy. On the other hand contact angle hysteresis increased in the case of the coating. These both tendencies reported an improvement of surface conditions for cells adhesion. In this investigation, wettability results have shown that the contact angle decreased (hydrophilic behavior) with the three liquid probes for the coated samples.

Table 1

Contact angle values for CaP coating on AZ91D magnesium alloy

Surface type	Average contact angle [°] - water, ethylene glycol, diiodomethane n = 10	Surface free energy (mJ/m^2), n = 10	Contact angle hysteresis [°]	Image of water droplets
Bare substrate	103±2 81±4 73±4	21,67	40,5	
CaP coating	92±2 85±2 71±5	21	44,1	

CaP coatings were fabricated onto AZ91D magnesium alloys via *RF*-magnetron sputtering. Surface morphology and structure results suggested that the coating is crystalline *HA* with the uniform, homogeneous, dense layer. Investigations showed improvement of the surface wettability of the *CaP* coated samples compared to the bare alloy.

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REFERENCES

1. Zheng Y.F., Gu X.N., and Witte F. Biodegradable metals // Materials Science & Engineering R-Reports. – 2014. №77. – P. 1–34.
2. Surmenev R.A., Surmeneva M.A., Ivanova A.A. Significance of calcium phosphate coatings for the enhancement of new bone osteogenesis – A review // Acta Biomaterialia. – 2014. №10 (2) – P. 557–579.
3. Surmenev R.A. A review of plasma-assisted methods for calcium phosphate-based coatings fabrication // Surface & Coatings Technology. – 2012. № 206 (8–9). – P. 2035–2056.
4. ASTM F1185 – 03(2009). Standard specification for composition of hydroxylapatite for surgical implants.
5. Nishizawa K. Effects of the surface wettability and zeta potential of bioceramics on the adhesiveness of anchorage – dependent animal cells // Journal of Fermentation and Bioengineering. – 1993. №75(6). – P. 435–437.
6. Bodhak S., Bose S., Bandyopadhyay A. Role of surface charge and wettability on early stage mineralization and bone cell – materials interactions of polarized hydroxyapatite // Acta Biomaterialia. – 2009. – № 5(6). P. 2178–2188.