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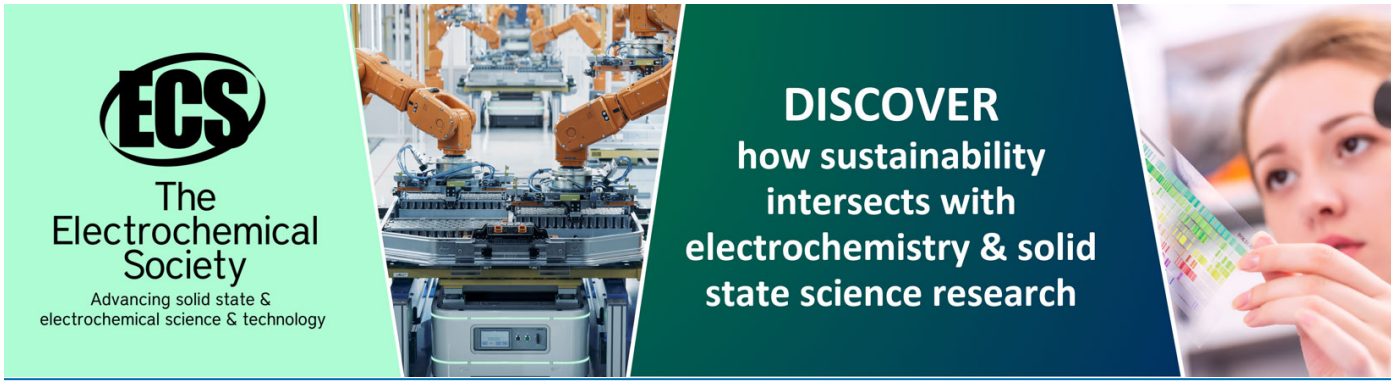

Thin hydroxyapatite coating on AZ91D magnesium alloy fabricated via RF-magnetron sputtering

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Abstract. In this study the morphology, composition, structure and wettability of radio-frequency (RF) magnetron sputter-deposited hydroxyapatite (HA) coating deposited on the surface of AZ91D magnesium alloy were investigated. The results revealed that the fabricated coating is uniform, homogeneous with the structure of the stoichiometric HA. The deposition of the HA coating did not change significantly the surface wettability of the bare alloy, however water contact angle dynamics in the case of the HA coated substrates revealed a lower rate of a droplet spreading over the surface.

1. Introduction

The development of biodegradable materials for bone injuries repair is an attractive scientific topic [1-5]. Biodegradable materials allow to avoid the problems associated with non-resorbable implants for example long-term complications like restenosis, thrombosis [6]. The concept is based on the idea to use implants inserted into the human body which are slowly degraded and gradually replaced by natural bone [6].

Nowadays attention of researchers is devoted to the development of magnesium alloy implants [7]. Magnesium alloys have been applied as implants since 1930s and possess good biocompatibility. Over the last years, magnesium alloys have been proposed for applications as biodegradable implants for bone repair along with cardiovascular stenting [1, 8-10]. Magnesium is degradable in physiological environment and has no toxic effect. Moreover, magnesium is an essential microelement for human metabolism Magnesium is also necessary for bone strength and can intensify bone tissue growth [5]. In addition Young's modulus and density of the alloy are closer to that of bone which allows to reduce stress-shielding effect and thus induce bone growth and improve implant stability [11].

However, magnesium reveals a high degradation rate in physiological environment [12, 13]. In recent years, there are several studies reported the investigation on the degradation behavior of the magnesium alloys in body fluids [7, 12, 14]. Due to the fact that magnesium alloys actively corrodes in the body there is a need to improve its corrosion resistance. Biocompatible coatings such as calcium phosphates (CaP), in particular HA, are prospective ways to enhance the corrosion resistance of

magnesium alloys. Furthermore CaPs are widely used in orthopedic and dental surgery due to their biocompatibility and high osteoinductivity [15]. There are different techniques to deposit HA coatings [16]. Radio-frequency (RF) magnetron sputtering allows to deposit thin uniform, dense, high-purity films. It is possible to tailor the structure (amorphous or crystalline) and the Ca/P ratio of the coating. Moreover, the coating has a strong adhesion to the substrate [15, 18].
The corrosion resistance of magnesium alloys was improved [2, 4, 5, 7, 12, 13, 17, 18], though RF magnetron sputtering, to the best of our knowledge, was not applied for this purpose. Therefore, the aim of this study was to investigate the structure, morphology, chemical composition and wettability of the HA coating deposited via RF magnetron sputtering on AZ91D magnesium alloy.

2. Materials and methods

The AZ91D magnesium alloy (DSM, Israel Chemicals Ltd) with the composition of 91% Mg, 8% Al and 1% Zn was used. The substrates were ultrasonically cleaned in acetone for 30 min. Then the samples were rinsed in distilled water and ultrasonically cleaned in ethanol for a second time.

Synthesized via mechanochemical activation pure HA powder (Ca10(PO4)6(OH)2 was used as a precursor-powder to prepare a target for sputtering. The uniaxially pressed powder was sintered in air at 1100 °C for 1 h according to the study [19]. The thickness of the prepared coating was investigated using optical ellipsometry (Ellipse 1891-SAG, Institute of Semiconductor Physics, RAS, Siberian Branch). Surface morphology was estimated using scanning electron microscopy (SEM) via ESEM Quanta 400 FEG instrument combined with an energy-dispersive X-ray analysis (EDX analysis system Genesis 4000, SUTW-Si (Li) detector) operated under high vacuum. The EDX spectra were collected for 60 s with a dead time of 30 % and electron beam energy of 15 keV. The structure and phase composition of the HA films were determined using X-ray powder diffraction (D8 Advance, Bruker, Germany) with Cu-Kα radiation (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°/2θ at 40 kV and 40 mA). As reference for the pattern of HA ICDD database #9-0432 was used. The contact angle analyses and water hysteresis were investigated (OCA 15 Plus Data Physics Instruments GmbH, Germany) using an SCA20 software (Data Physics Instruments GmbH, Germany). The calculations of the water contact angle and hysteresis were performed using 10 droplets (5 μL) to reveal an average θ value.

3. Results and discussion

The thickness of the deposited coating was estimated to be of 800±50 nm. Representative SEM-micrograph of the surface of HA coating is shown in Fig. 1.a. The coating is shown to be uniform, and dense, no cracks were observed.

One of the most important characteristics of CaP compounds is molar Ca/P ratio [15, 20]. A lower Ca/P ratio leads to a higher solubility of the HA coating. The Ca/P ratio of the coatings deposited for 8 h as determined by EDX (Fig. 1.b) was 1.6±0.1, which is close to the Ca/P ratio typical for stoichiometric HA.

Based on the XRD results (Fig. 2) it was found that main diffraction peaks at 25.8° (002), 53.1° (004), 31.8° (211), 32.2° (112), and 32.9° (300) are attributed to crystalline HA with the lattice parameters a=b=9.46 Å, and c=6.88 Å.

The wettability of the biomaterial surfaces was assessed by contact angle measurements. Wettability allows us to estimate possible mechanisms of protein absorption and cell adhesion [21, 22]. The average values of water contact angle, water contact angle change in dynamics, and contact angle hysteresis for bare substrate and the HA coating are given in Table 1. All the measurements were carried out at the temperature of 23 ± 1 °C and 45 ± 5% humidity. Water contact angle of the coated substrates was lower compared with the bare alloy. Contact angle hysteresis slightly increased in the case of the HA coating [23, 24].

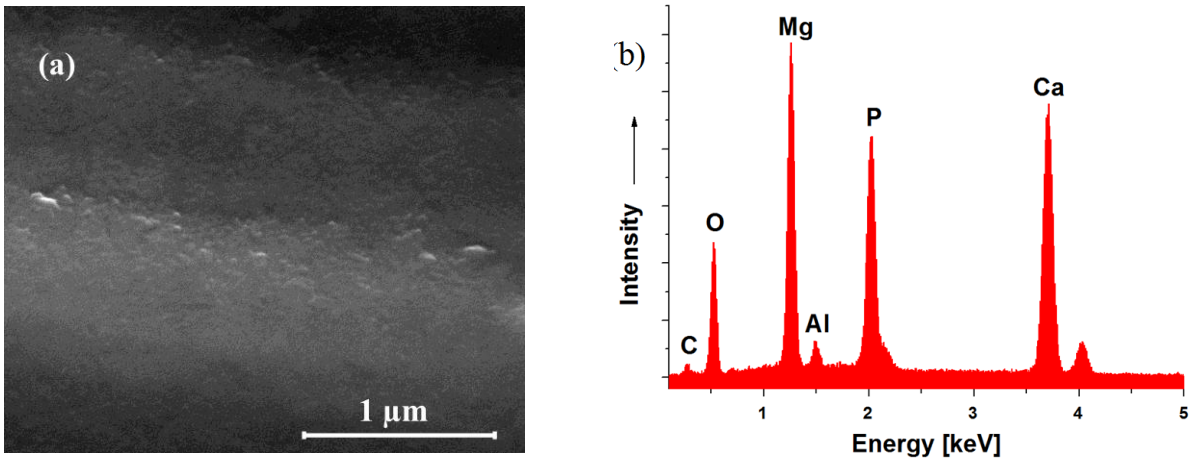

Figure 1. SEM image (a) and EDX spectrum (b) of the HA coating deposited on the surface of AZ91D magnesium alloy.

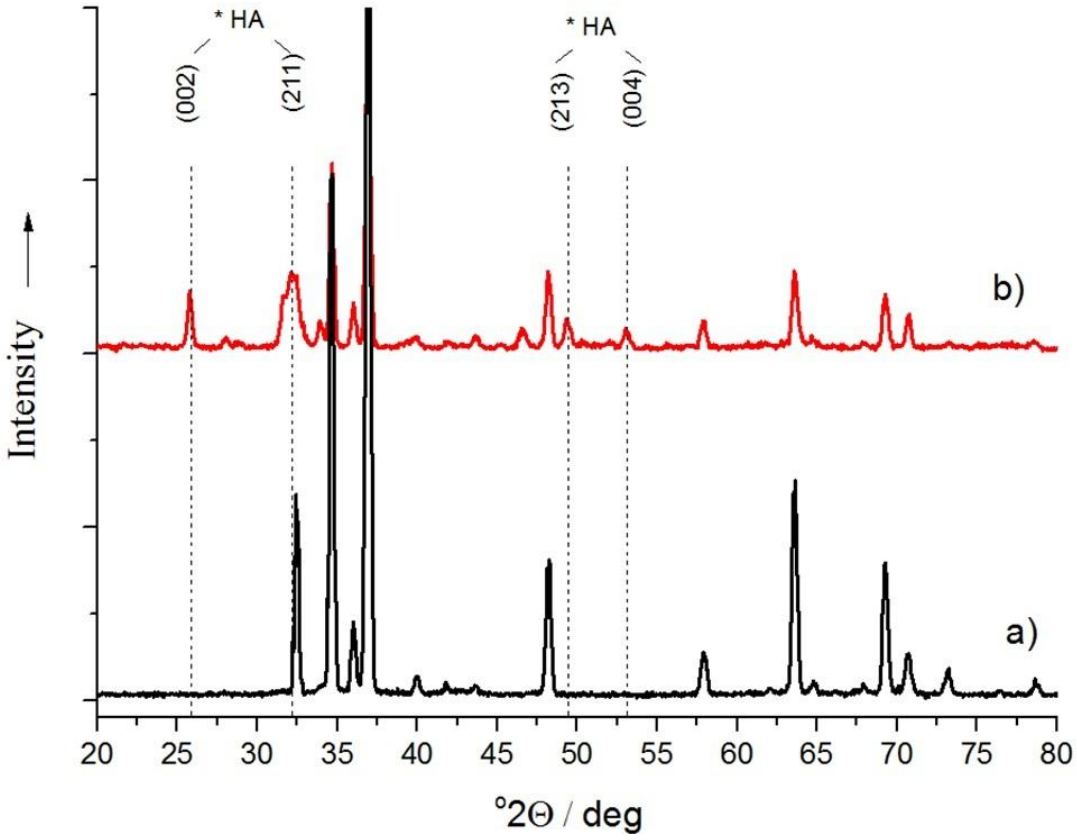

Figure 2. XRD patterns of the HA coating deposited at 500 W for 8 h on AZ91D magnesium alloy: a) bare substrate, b) HA coating on the substrate. "*" denotes the peaks attributed to HA. The peaks of HA (ICDD card number 09-432) are shown using vertical lines.

Table 1. Water contact angles and hysteresis for the HA coating on AZ91D magnesium alloy

Surface type	Water contact angle (°, n = 10)	Contact angle hysteresis (°)
Bare substrate	104±5	40
HA coating	100±3	44

In spite of the some decrease in the water contact angle it was observed that the surface of the HA coating still revealed hydrophobic behaviour [25]. It was reported that wettability of the surface can change over the time [23, 24]. For this reason dynamic contact angle measurements were performed and the results are presented in Fig. 3.

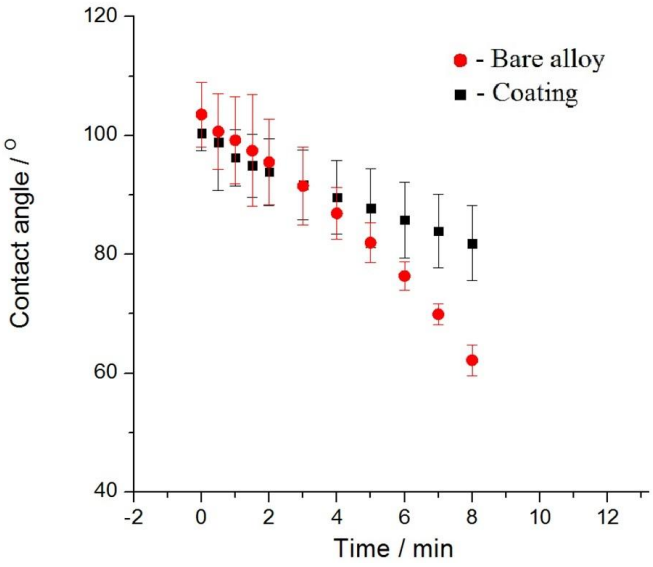

Figure 3. Water spreading behavior of a single droplet on the surface of the HA coating and bare alloy.

The wettability of the bare alloy and HA coating deposited on Mg alloy was monitored. It was revealed that after only 8 min of water droplet spreading over the surface a significant decrease in the water contact angle (from 100° to 66°) was observed. A significantly higher water spreading rate was observed in the case of bare alloy compared with that of the HA coated samples. The observed changes in the surface wettability over time indicated a strong time-dependent tendency to turn initially hydrophobic behavior to hydrophilic.

Conclusion

In this study, fabrication process and the properties of the HA coating deposited onto AZ91D magnesium alloys via RF-magnetron sputtering are described. Surface morphology and structure results suggested that the coating is crystalline HA with the uniform, homogeneous, and dense structure. Investigations did not reveal improvement of the surface wettability of the HA coated samples compared to the bare alloy, however water contact angle dynamics in the case of the HA coated substrates revealed a lower rate of a droplet spreading over the surface. The initially hydrophobic surface of the HA coating tend to be more hydrophilic with time.

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