Formation on magnesium alloy MA8 bioactive coatings containing nanosized hydroxyapatite

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Abstract. Calcium hydroxyapatite (HAp) in the form of rounded nanoparticles 100–150 nm in diameter was produced by chemical synthesis. Coatings were formed on the surface of the MA8 magnesium alloy by plasma electrolytic oxidation in an electrolyte containing HAp nanoparticles. The modes of oxidation, electrolyte concentration and oxidation time were optimized, it allows to obtain coatings with high adhesion to the substrate. The morphology of the coatings, the phase and elemental composition were estimated.

1. Introduction

Applied conventional metal implants are made of titanium and stainless steel. This materials possess a high strength, wear resistance and corrosion resistivity. However the stresses arising between the bone and the titanium implant due to the difference in the modulus of elasticity (~105 GPa and 27 GPa, respectively [1, 2]) leads to osteopenia and osteoporosis [3–6]. Furthermore, the inert of titanium cause the occurrence of inflammatory processes at long-term implantation [7, 8], which, in turn, often leads to revision surgery and extracting the implant [9, 10]. This factor plays a special role in maxillofacial surgery, as a secondary intervention can lead to an increase of scarring and the impossibility of using aesthetic surgery.

Currently, magnesium and its alloys are widely used in aviation, development of high-tech devices and other areas of human activity. In the past decades, there has been an explosion of interest to magnesium alloys as implant material due to their physiological and mechanical properties. Advantages of magnesium are its plasticity, low density, high strength-weight ratio [11, 12]. The application of magnesium in orthopedics can be regarded as a revolutionary event for biodegradable materials, in particular, metals. The elastic modulus of Mg (45 GPa) is the closest to bone indexes in comparison with the metals used today in implantation medicine. In addition, the possibility of controlled dissolution of the magnesium implant [13, 14] eliminates the need for secondary surgical intervention, thereby reducing the health risks and costs of healing. Recent evidence indicates that magnesium corrosion products can be beneficial to the patient's health, in contrast to the products of the destruction of other metals [15].

Hydroxyapatite (HAp) is the basic mineral component of bones (50% of the total bone mass) and teeth (95% in enamel). As a component of coating HAp may promote the growth of a new bone [16]. The brittle nature of the ceramic restricts the clinical orthopedic and dental applications despite ones excellent biocompatibility. In addition to providing the protective function of internal organs and levers...
for muscle action, human bones also provide a natural reservoir for cells and mineral ions that play an important role in maintaining the biochemical balance within the body. For example, calcium, whose level in the body is closely monitored and regulated by a process called homeostasis is an important element involved in muscular action and nerve conduction [17, 18]. Thus, the development of a composite material based on a magnesium alloy coated with HAp acting as a protective / bioactive layer [14, 16, 18] is a unique finding for many tasks of implantology and orthopedic surgery.

In the present study, a coating with incorporated nanoparticles of calcium hydroxyapatite on the surface of the MA8 magnesium alloy has been formed. The composition, morphology, and structure of the obtaining layers on the surface of a magnesium alloy were studied.

2. Materials and methods

In the present paper, calcium hydroxyapatite was obtained by maturation (7 days) in aqueous solution (0.1 М Ca(OH)2 and 0.1 М H3PO4) followed by filtration, drying and annealing of the resulting precipitate at 800°C for 3 h. The procedure for obtaining HAp is similar to [19], slightly increased addition time of orthophosphoric acid. The single-phase nature of the obtained HAp was confirmed by X-ray diffraction using Bruker D8 ADVANCE diffractometer with CuKα−radiation.

The coatings were formed on the surface of a MA8 magnesium alloy (mas. %): 1.5–2.5 Mn, 0.15–0.35 Ce, balance – Mg). For the deposition of coatings, the method of plasma electrolytic oxidation (PEO) was used. Preliminary for the surface standardization samples of Mg alloy (15x20x1 mm3) underwent mechanical treatment by grinding paper of different grain sizes (600, 800, and 1200), cleaned and degreased with acetone in an ultrasonic bath for 90 s. The electrolyte containing sodium fluoride (5 g/l) and silicate (15 g/l) was selected to treat samples using the PEO-method. The obtained hydroxyapatite nanopowder with the particle size of 50–100 as a component of the electrolyte for PEO was used to produce the composite coating. PEO-coatings on the MA8 magnesium alloy were formed at the concentration of 10 g/l HAp particles in the working electrolyte. Since at the plasma electrolytic oxidation the coating growth proceeds, as a rule, during the sample anodic polarization, to ensure the maximal incorporation of particles into the coating, an anionic surfactant (sodium dodecylsulfate) was used as a stabilizer of the dispersed system. Its concentration in the final electrolyte was equal to 0.5 g/l. Formation of coatings occurred in the two-stage bipolar PEO-mode as described in [20]. After PEO process, the samples were cleaned with de-ionized water to remove the remained electrolyte and then dried in air. All the samples were sealed by waterproof silica gel, just leaving an exposed area of 1 cm2 for the electrochemical tests.

The electrochemical properties of the coatings were studied using the VersaSTAT MC electrochemical system (Princeton Applied Research, USA). The measurements were carried out in a three-electrode cell at room temperature in a 0.9% wt. % NaCl solution. The niobium mesh covered with platinum was used as a counter electrode. The saturated calomel electrode (SCE) was used as a reference electrode. The exposed area of the sample was equal to 1 cm2. The samples were kept in a solution for 30 min prior the start of the electrochemical tests to achieve steady state. The potentiodynamic polarization measurements were carried out at a scan rate of 1 mV s−1.

3. Results and Discussion

To reduce the number of agglomerates and increase the dispersion the HAp powder was subjected to milling in a ball mill in isopropyl alcohol medium. X-ray diffraction patterns of the compound after milling in isopropyl alcohol medium (fig. 1) showed no differences in the phase composition of compounds. The particle size of the HAp lies in the range of 50–100 nm, as evidenced by the SEM data (fig 2).
Fig. 1. XRD patterns of HAp powder and one subjected to wet-milling.

Fig. 2. SEM image of HAp powder obtained from an aqueous solution after wet milling.

Analysis of data obtained by the XRD method for formed coating indicates that there is no HAp on the surface of the coating in an amount sufficient to identify. The element analysis of cross-section obtained on the MA8 alloy indicates the presence of Mg, Na, O, F, Si, C, Ca and P elements (fig. 3). In the near-surface layer of the coating mainly contain Ca and P elements (fig. 4).

The data obtained by the EDX method make it possible to describe the structure of the coating formed on the alloy surface. The inner layer adjacent to the surface of the metal consists predominantly of MgO and MgF – dense, substantially nonporous layer with a thickness of ~ 5-10 μm. Further, in the thickness of the coating, pores appear, on the walls of which higher concentrations of Ca and P (fig 4).

Electrochemical studies indicate that coatings formed on the surface of magnesium alloy MA8 have a protective properties. Moreover, the coating formed with the use of calcium hydroxyapatite nanoparticles makes it possible to enhance the protective properties of the PEO coating against corrosion (table 1). The polarization resistance increased by more than threefold in comparison with the PEO coating and by two orders of magnitude compared to the uncoated alloy. The suggested mechanism for
increasing the protective properties of a coating formed in an electrolyte containing nanoparticles is reducing the porosity due to their filling with HAp nanoparticles. In addition, the chemical stability of nanoparticles in the oxidation process is of great importance. As SEM data shown the HAp particles do not form agglomerates and do not appear in the structure of cross-section at any given magnification. Near the surface, the concentration of the elements increased, reaching a maximum in the near-surface layer (~ 10 μm).

Table 1. Electrochemical parameters for samples of alloy MA8 with and without coatings

| Sample         | \( E, \text{ V} \) | \( I_{\text{cor}}, \text{ A cm}^{-2} \) | \( R_p, \Omega \cdot \text{cm}^2 \) | \( |Z|_{f=0 \text{ Hz}}, \Omega \cdot \text{cm}^2 \) |
|----------------|------------------|-----------------|-----------------|-----------------|
| MA8           | -1.56            | 1.42·10^{-5}    | 2.16·10^{3}     | 2.0·10^{3}      |
| MA8 PEO       | -1.45            | 6.70·10^{-7}    | 1.03·10^{5}     | 1.1·10^{5}      |
| MA8 PEO/HA    | -1.46            | 2.40·10^{-7}    | 3.79·10^{5}     | 2.6·10^{5}      |

4. Conclusion

Calcium hydroxyapatite was synthesized by maturation from an aqueous solution in the form of a round shaped nanoparticles. The presented method of formation of composite coatings on magnesium alloy MA8 demonstrated flexibility of the application regime, improved resistance to corrosion, successful filling of pores in PEO coating with calcium hydroxyapatite. Compared to the uncoated metal the corrosion current density for the sample PEO/HA are reduced by more than two orders of magnitude, and impedance module at low frequencies increased by more than two orders of magnitude (up to \( 10^5 \Omega \cdot \text{cm}^2 \)). The abovementioned factors indicate that the PEO/HA composite is promising in surface modification of biodegradable magnesium-based implants for orthopedic application.

Acknowledgments

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