

# Porous magnesium scaffolds with biodegradable polycaprolactone coating

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**Abstract.** The results of the synthesis of magnesium matrices with a porous structure have been presented. The cavities sizes vary from 10 microns to hundreds of microns. It has been obtained porous magnesium samples coated by spin-coating with biodegradable polycaprolactone. It has been shown that a dense layer of biodegradable polymer more than 50  $\mu\text{m}$  thickness can be formed on the sample surface. Study of the electrochemical properties of the obtained coatings has been carried out. Obtained results suggest that porous magnesium metals with protective coatings can be used as degradable bone substitute implants.

## 1 Introduction

Advances in the medical materials science and tissue engineering led to a reorientation of views on the treatment of bone defects and the production of bone implants. Design and development of modern tissue-compatible frameworks (scaffolds) imitating the structure of bone tissue, as well as a bioresorbable composite materials enable one to completely correct a bone defect or restore of vascular patency [1–7]. Bioresorbable implant's implementation can provide not only musculoskeletal functionality, but also regenerate metabolic functions, which traditional corrosion-resistant metals are not acceptable [8–10]. Eliminating the need for re-surgery reduces the risk of inflammation and the final cost of treatment. In addition, the controlled degradation rate of bioresorbable implants makes it possible to expand the circle of young patients.

The application of magnesium for the manufacture of implants eliminates the disadvantages inherent in traditional metal implants (significant difference between the elastic modulus of bone tissue and alloy, inflammation [5, 9]) and polymer scaffolds (insufficient mechanical strength and inconvenient degradation rate [11, 12]). Magnesium differs favorably in mechanical characteristics close to bone tissue, high biocompatibility, hardness and density, comparable with these parameters for cortical bone. In addition, bone tissue is one of the main accumulators of Mg, furthermore this element itself contributes to the calcium absorption [13, 14]. The problems of design a novel implant materials implies a multidisciplinary integrated approach. It includes the application of both traditional and additive technologies in the production of required implant material. This allows

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manufacturing the products with the required strength and controlled porosity. The main disadvantage of magnesium products is the high rate of degradation in the human body. This drawback is eliminated by the additional operation of forming a multifunctional coating on the implant [15–17]. One way to form a protective coating on alloys, including magnesium, is plasma electrolytic oxidation (PEO) characterized by high adhesion and composition variability of the formed layers [18–20]. The presented method of formation a magnesium-based composites can be implemented in laboratory studies. At the same time, to use the material in real medicine, additional research is needed. It can be noted that design of resorbable biocomposites with a controlled rate of degradation and functioning of the implant is very critical issue. This paper presents the results of the formation of multifunctional materials based on magnesium for the needs of implant surgery. The synthesis of porous materials for implantation has already been carried out, including the use of magnesium [4, 21, 22]. However, protection of such materials from premature and uncontrolled dissolution in the human body is required. In this regard, we have synthesized and investigated the properties of composite materials based on magnesium foam and a protective coating consisting biodegradable polyester.

## 2 Materials and methods

### 2.1 Material production

Porous magnesium matrix was prepared by the cold pressing technique using the powders of magnesium (several tens of micrometers, Merck) and urea,  $(\text{NH}_2)_2\text{CO}$  (few microns in size, Merck). Magnesium and urea powders (30 and 50 % vol. urea) were previously thoroughly mixed in zirconia bowls at a rotation speed of 120 rpm for 30 minutes (Pulverisette 7 premium line, Germany). The mixed powders were uniaxially pressed at a pressure of 1.7 tons per  $\text{cm}^2$  into compacts. The obtained compacts in the form of tablets with a diameter of 15 mm and a thickness of 2-6 mm were then heat treated to burn out spacer particles and to sinter into the porous magnesium foam. The annealing procedure was carried out in two stages: 250 °C for 4 h and following 500 °C for 2 h in a vacuum atmosphere (medium vacuum at residual pressure 10-30 Pa). Resulting green compacts were machined with grinding paper of 600-1200 grain size using ethanol as lubricant.

Spin-coating solutions were prepared by adding a certain amount of polycaprolactone (PCL) granules to acetone. Calculations of the amount of polymer in the solvent were made according to the formula:

$$\omega = \frac{m}{m + \rho V} \times 100\%, \quad (1)$$

where is  $\omega$  - mass fraction of solute (%),  $m$  – is solute mass (g),  $\rho$  – solvent density (g/ml),  $V$  – solvent volume. In this work, solutions were prepared with a concentration of 8 and 12 wt.%.

The phase composition of the porous magnesium specimens were analyzed with X-ray powder diffractometer (XRD, Bruker D8 ADVANCE) with  $\text{CuK}_\alpha$  radiation. Electron microphotographs of the sample surfaces were obtained using a Carl Zeiss EVO 40 electron microscope (Carl Zeiss, Germany).

## 2.2 Corrosion resistance and mechanical properties

The electrochemical properties of the magnesium specimen were studied by potentiodynamic polarization test and electrochemical impedance spectroscopy. Measurements were performed using a VersaSTAT MC device (Princeton Applied Research, USA) in 0.9 % aqueous solution of NaCl used as an electrolyte. The sample working area was about to 1 cm<sup>2</sup>†. Samples were held in the electrolyte for 30 minutes previously, to achieve the electrochemical equilibrium. To perform impedance measurements, a sinusoidal signal with the 10 mV (rms) amplitude was used. The spectra were recorded at an open circuit potential in the range 0.01 Hz – 1 MHz in logarithmic sweep 7 points per decade. During the impedance measurements, the free corrosion potential was stabilized potentiostatically (steady state conditions). Potentiodynamic polarization was carried out at sweep rate of 1 mV/s. The samples were polarized in the anodic direction from the potential of  $E_C - 200$  mV up to  $E_C + 0.5$  V. The processing of the potentiodynamic and impedance data were carried out using CorrView/ZView software. The tests were repeated on three samples for the reliability and reproducibility. The measurement error was not exceed 5%. The Levenberg-Marquardt (LEV) method was used to fit the measured polarization curve (values of potential,  $E$ , and current density,  $I$ ) to the following equation:

$$I = I_C \left( 10^{\frac{E-E_C}{\beta_a}} + 10^{-\frac{(E-E_C)}{\beta_c}} \right), \tag{2}$$

which produced the best fit values of corrosion potential,  $E_C$ , corrosion current density,  $I_C$ , the slope of the cathodic polarization curve,  $\beta_c$ , and the slope of the anodic polarization curve,  $\beta_a$ . The polarization resistance ( $R_p$ ) was determined as the inverse of the slope of the  $I$  vs.  $E$  plot recorded at potentiodynamic polarization in the potential range of  $E_C \pm 0.015$  V at a sweep rate of 0.167 mV/s in a separate experiment.

Studies of mechanical properties, in particular, determination of microhardness and elasticity modulus of the coatings material were carried out using a DUH–W201 dynamic ultramicrohardness tester (Shimadzu, Japan). Measurements of the universal microhardness ( $H_\mu$ ) were carried out on a cross-section using a Vickers indenter at a load of 100 mN. The obtained universal microhardness and elasticity was mean of three tests for 15 points per sample.

## 3 Results and discussion

As it can be seen from cross-section (Fig. 1a,b) there are open interpenetrated pores and smaller isolated pores distributed within the wall of big cavities. The first one is in the size range 100–500 μm and the isolated pores have size about few micrometers. As we have shown earlier, it is possible to coat such magnesium matrices using the PEO method. In this case, the formed layer evenly covers both the surface of the sample and the inner space of the pores, narrowing their diameter (fig. 1c).

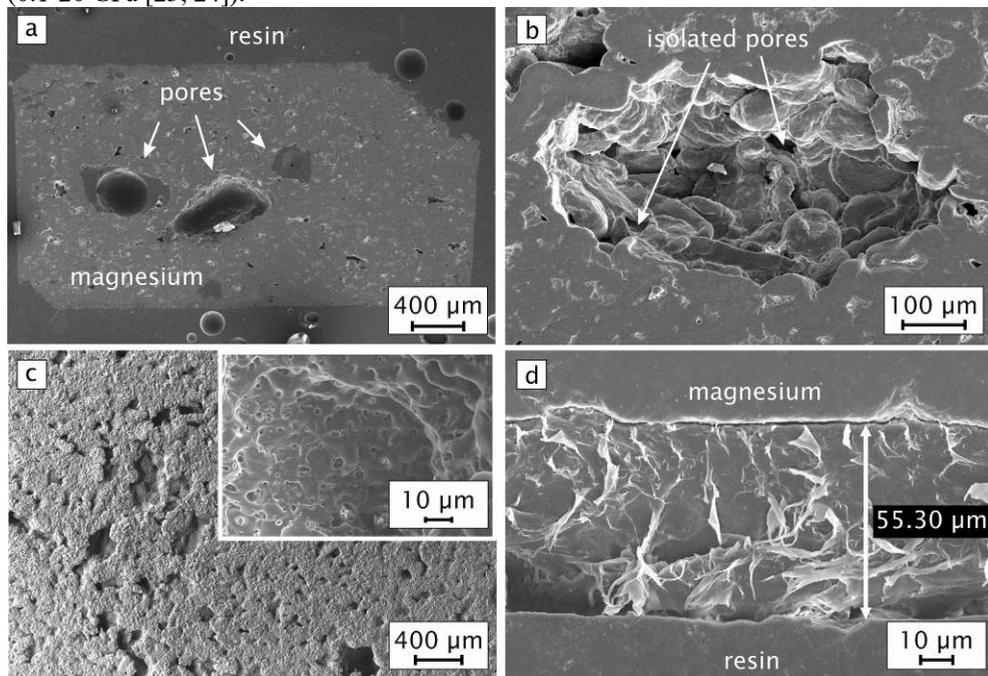
X-ray diffraction analysis of the original magnesium powder and sintered sample indicates the presence of magnesium (not shown).

Measured universal microhardness for annealed porous magnesium specimen with 50% volume content of carbamide varied from 24 to 112 MPa; the average value was 55 MPa.

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† The area of the sample in contact with the sodium chloride solution was limited to 1 cm<sup>2</sup>, the rest of the sample was varnished. Nevertheless, we are aware that the real contact area is larger due to the porosity of the sample.

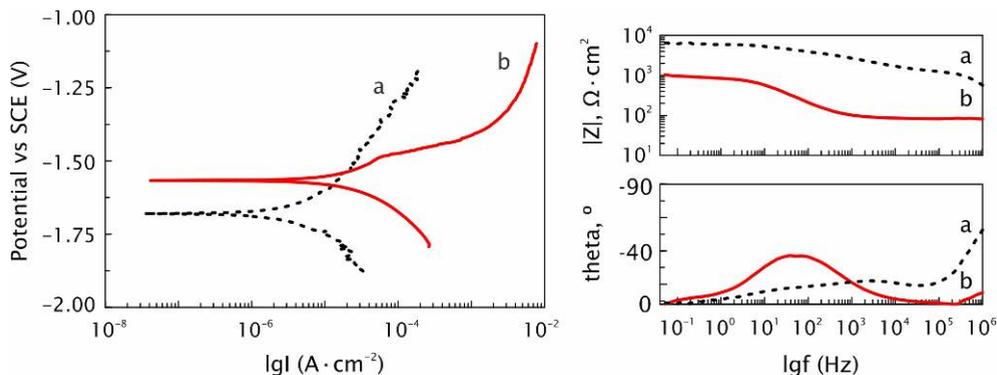
The elastic modulus was an average of 5.8 GPa, varying from 3.4 to 11 GPa. The achieved values of the modulus of elasticity are in a very close range of values of the natural bone (0.1-20 GPa [23, 24]).



**Fig. 1.** SEM images of cross-section of porous magnesium specimen (Mg-PCL 50%) at various magnifications (a, b), porous magnesium matrix surface coated with PEO (c) and d) layer of polycaprolactone applied by spin-coating

The dripping mode of the solution (1 ml) included the application to the surface of a sample rotating at 400 rpm for 50 s. Following, in the second stage, a solution was dropped onto the sample rotating at 4000 rpm for 60 s. During the spin-coating process, it has been shown that a less viscous solution forms a coating that is too thin. At the same time, a more viscous solution (12 wt.%) allows to apply a layer of polycaprolactone 50 and more micrometers thickness (fig. 1d). Resulting layer of biodegradable polyester forms a dense, non-porous homogeneous coating penetrating into surface pores (Fig. 1d).

Investigation of the electrochemical properties of the deposited polycaprolactone layer indicates a significant protective properties. This is evidenced by a decrease in the corrosion current by 2 orders of magnitude in comparison with untreated porous magnesium (Table 1, Fig. 2a) and calculated values of polarization resistance.



**Fig. 2.** Polarization curves (left) and impedance spectra (right) of porous magnesium samples with coating (a) and without coating (b)

**Table 1.** Corrosion properties for bare sample and coated with polycaprolactone

Sample	$E_c$ (V vs. SCE)	$I_c$ ( $A \cdot cm^{-2}$ )	$R_p$ ( $\Omega \cdot cm^2$ )	$\beta_a$ (mV)	$\beta_c$ (mV)
Porous magnesium	-1.57	$1.59 \cdot 10^{-5}$	$1.6 \cdot 10^3$	127	105
Porous magnesium+PCL	-1.68	$2.57 \cdot 10^{-6}$	$9.3 \cdot 10^3$	112	106

## 4 Conclusions

Porous magnesium specimens with an open-cellular structure in the range of 100–500  $\mu m$  including pores in the range of several micrometers have been fabricated. The obtained samples were coated with biodegradable polycaprolactone by two-stage spin-coating. The electrochemical properties (such as corrosion current density, polarization resistance) of the porous magnesium specimens increase after coating formation.

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