COVERSION AND POLYMER-BASED COATINGS AS STRATEGIES TO INCREASE CORROSION RESISTANCE OF BIODEGRADABLE MAGNESIUM-CALCIUM ALLOYS

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Introduction

Currently, magnesium and its alloys are considered to be one of the most promising metallic biomaterials. They are biocompatible, biodegradable, bioactive, have density similar to that of cortical bone and Young's modulus significantly lower than e.g. titanium-based materials [1,2]. Mg-based biomaterials with desired properties can be obtained by purification or alloying with Ca, Zn, Mn or other elements. Among those alloying elements, calcium is of particular interest due to its crucial role in natural bone and some evidence that co-release of Mg and Ca ions might be advantageous to the bone healing. Magnesium and its alloys are beneficial in many aspects, nevertheless one cannot forget about the need to strictly control their degradation behaviour since rapid corrosion in physiological environment can lead to serious cell and tissue damage [1-4].

The aim of this study was to combine two different approaches to slow down corrosion rate of binary MgCa alloy - appropriate surface treatment and polymer-based coatings. Conversion coatings, beside reducing the degradation rate, were used to increase the surface roughness of Mg alloy samples, and hence improve the adhesion of the polymer-based coating.

Materials and Methods

Magnesium-calcium alloys were produced in the light metal foundry (Institute of Non-Ferrous Metals in Gliwice, Light Metals Division). Conversion coatings were prepared on the alloys by an electrochemical treatment in the KOH+KF solution at 20°C, at a current density of 5 A/dm^2 within 5 minutes. Conversion interlayer was characterized by surface roughness (Hommel-Etamic W10 profilometer) and thickness measurements (Dualscop MP-20), as well as by scanning electron microscopy (SEM) and immersion test in Ringer's solution. Polymer-based coatings were used in the next step. MgCa samples were coated either with pure poly(ε-caprolactone) (PCL, Sigma-Aldrich, Mn = 80 000) or a composite system in which polymer matrix was modified with tricalcium phosphate (TCP, Sigma-Aldrich®) ($Ca_3(PO_4)_2$ ≥96.0%)) and zinc oxide (ZnO, Avantor Performance Materials Poland S.A.). Tested samples were incubated in phosphate buffered saline (PBS, Sigma-Aldrich) and simulated body fluid (SBF) in 37°C. SEM with EDS, FTIR, pH measurements, release of Mg ions and release of H_2 were used to test the samples.

Results and Discussion

In order to protect magnesium alloy substrates from rapid degradation and enhance its biological performance two strategies were combined. In the first step, conversion coatings were created on the surface of the MgCa alloy samples. Next, biodegradable polymer-based coatings were applied, in which TCP was introduced to the PCL matrix to improve bioactivity, while ZnO was added to ensure antibacterial properties.

The coating produced in the KOH+KF solution uses potassium, fluorine, oxygen and magnesium. All these elements are beneficial to the human body and most importantly, they are not dangerous.

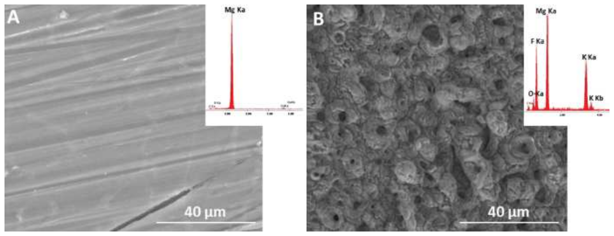

FIG. 1. SEM images with EDS analysis of (A) MgCa and (B) MgCa sample with conversion interlayer.

SEM analysis (FIG. 1) confirmed successful fabrication of conversion coatings on the surface of the MgCa samples (with EDS showing Mg, F, K and O). Surface treatment affected microstructure resulting in higher surface roughness. MgCa samples were further successfully coated with homogenous layer of polycaprolactone alone or composite system with TCP and ZnO particles that were uniformly distributed in the polymer matrix.

Hydrogen release studies showed significant reduce in the amount of H_2 released when the composite PLA/TCP/ZnO coating was used. Both chemical composition of the polymer coating and pretreatment of magnesium alloy (conversion coating) influenced morphology and composition of precipitates observed on the surface of the samples incubated in simulated biological fluids (PBS and SBF). Deposition of magnesium oxide on the surface of all the incubated samples and formation of calcium-phosphate or magnesium-phosphate precipitations was observed. It points to potential bioactivity of the conversion- and polymer-coated MgCa samples.

Conclusions

It was proven that combination of conversion coating with polymer-based coating reduces resorption rate of the MgCa binary alloy and improves their biologically relevant properties. The conversion coating increased the surface roughness of the Mg elements, thus increasing the adhesion of the polymer-based layer. Further studies, including bacterial activity and in vitro biocompatibility assays (with appropriate cell cultures) are needed.

Acknowledgments

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