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Original Research Article

Impact of Zn and Ca on dissolution rate, mechanical properties and GFA of resorbable Mg–Zn–Ca metallic glasses

Ryszard Nowosielski *, *Katarzyna Cesarz-Andraczke*

Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Gliwice, Poland

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ABSTRACT

This article presents investigations utility of Mg-based metallic glasses for resorbable orthopedic implants. Exploration of biocompatible Mg–Zn–Ca alloys in order to determine Zn and Ca optimum concentration were conducted, based on three criteria: sufficiently high GFA (glass forming ability), sufficiently high tensile strength, microhardness and the suitable dissolution rate (corrosion rate) in Ringer's solution. Fulfillment of these criteria should ensure bone union before implant dissolution. The optimatization of Ca and Zn concentration in the range of 4–6 at.% Ca and 28–32 at.% Zn was executed. The samples in form of ribbons (0.02–0.05 mm thickness) and rods (about diameter up to 4 mm) with amorphous structure were produced. These investigations allowed to determine the GFA. The optimal results for $Mg_{66}Zn_{30}Ca_4$ and $Mg_{64}Zn_{32}Ca_4$ alloys: tensile strength: 191–166 MPa, microhardness: 291–263 HV and volume of released hydrogen 0.04–0.12 $ml/cm^2/h$. The corrosion studies - immersion and potentiodynamic methods were conducted (including measurement specific corrosion current density for Mg alloys). Finally, a comparative analysis was performed, which indicated the impact of Ca and Zn concentration on: GFA, mechanical properties and dissolution rate of studied metallic glasses.

1. Introduction

Due to the biocompatible chemical composition of magnesium based alloys they may be considered as potential biomaterial for medical implants. The magnesium alloys containing Ca and Zn generally are biocompatible with human body, also in crystalline and amorphous form. It motivates attempts of application of these materials for producing resorbable orthopedic implants according to new concept of implants with controlled and predictable resorption [1]. There are results, which indicated that magnesium alloys and their corrosion products are biocompatible for living organism and could lead to bone cell activation. In work [2] was to investigate the degradation mechanism at the bone – implant interface of different degrading magnesium alloys. From the results of [2], there is a strong rationale that in this research model, high magnesium ion concentration could lead to bone cell activation. New bone

* Corresponding author.
E-mail addresses: ryszard.nowosielski@polsl.pl (R. Nowosielski), katarzyna.cesarz@polsl.pl (K. Cesarz-Andraczke).
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was formed around magnesium implant in the work [3]. In work [4] the in vitro and in vivo corrosion suggested that a mixture of $Mg(OH)_2$ and hydroxyapatite formed on the surface of Mg–1Ca alloy with the extension of immersion/implantation time. These results indicated that Mg–1Ca alloy had the acceptable biocompatibility as a new kind of resorbable implant material. In addition, the corrosion products on the surface of Mg–Zn contained hydroxyapatite (HA), Mg(OH) $_2$ and other Mg/Ca phosphates, which could reduce the degradation rate [5].

For biomedical purposes pure Mg and new crystalline Mg-based alloys, including alloying with low toxic elements (Mg-Y, Mg-RE) [6–8] were examined. In work [6] results of mechanical properties have shown that the element Y could improve both tensile strength and elongation. There are results of corrosion study's Mg-Y-RE [7] and Mg-RE [8] alloys, but there is no information that Y or RE elements are biocompatible for living body.

However, amorphous Mg–Zn–Ca, Mg–Zn–Ca–(Cu, Ag) alloys for resorbable implants were also studied [9–11]. In work [9] Mg–Ca–Zn amorphous alloys characterized by high strength and high glass forming ability. In addition, it is found that the addition of Cu decreases the glass-forming ability of Mg–Zn–Ca amorphous alloys [10], but their compressive fracture strength is enhanced by the addition of Cu. Besides, the minor addition of 1% Ag improved strength and corrosion resistance. However, with more Ag addition, both the strength and corrosion resistance were decreased due to the deceasing of the glass forming ability and galvanic corrosion [11]. However, this results is very useful but not sufficient, because it should be concerns the issue multi-criterial optimization of chemical compositions of investigated alloys because of the simulated requirements (criteria of strength and dissolution rate). Therefore, the multicriterial optimization is the foundation of the research concept of this work.

In present work amorphous Mg-based alloys were chosen for research due to theirs single-phase structure, which characterizes a reduced susceptibility to local corrosion (pitting) [12,13]. Resorbable materials should be assessed by following criteria: the sufficiently large GFA, mechanical properties and the suitable dissolution rate. Mechanical strength determinate the bearing capacity of implant. On the other hand the strength determines the implants' dimensions. GFA decides on dimensions, mainly diameters and thickness of the implants. Released hydrogen rate may be reflected by corrosion rate. Based on the literature, for Mg–Zn–Ca metallic glasses the largest GFA is 5 mm [14] compression strength is in the range 550–894 MPa [1,15] and corrosion rate is up to 0.5 mm/year [12]. In the literature there are a few attempts, which aim to optimize chemical composition for choosing the best amorphous Mg-based

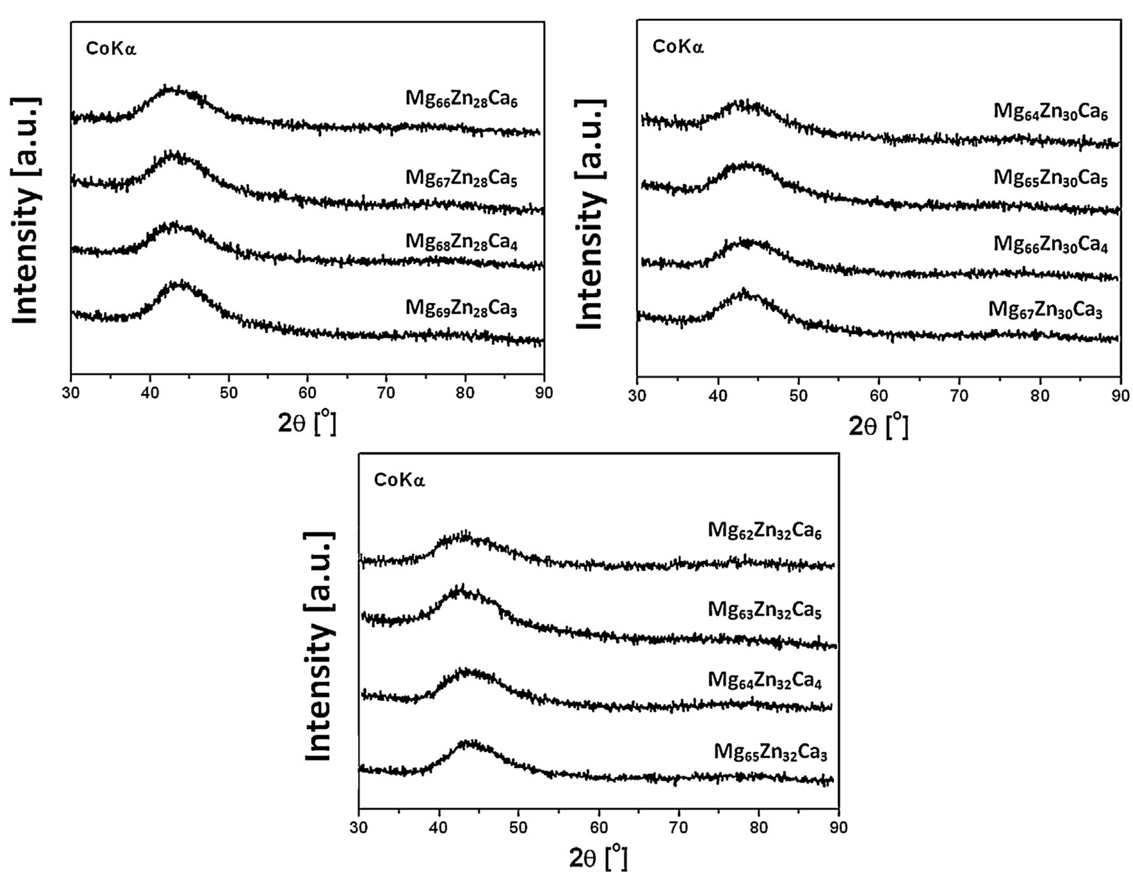

Fig. 1 – X-ray diffraction patterns of $Mg_{69-x}Zn_{28+y}Ca_{3+x}$ (x = 0, 1, 2, 3; y = 0, 2, 4) alloys in the form of ribbons with a thickness of 0.02 mm.