COMPARATIVE STUDY OF MAGNESIUM AND ZINC BASED BIODEGRADABLE MATERIALS

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Abstract

Magnesium and its alloys are considered for specific applications in medicine such as fixation devices, screws and stents. However, release of hydrogen gas, pH increase and premature failure of the mechanical integrity of implant material are considered as the main limitations. Zinc-based alloys offer an interesting alternative choice for similar kind of applications, however, some limitations are known. First of all, the human body is able to accept significantly lower daily doses of zinc compared to magnesium. Zinc is also quite heavy metal with density and young modulus highly different from that of bones. In summary, both kinds of alloys intended for applications in medicine behave very differently. In present work Mg-4Y-3RE magnesium-based alloy and Zn-1Mg-0.5Ca zinc-based alloy were selected as representative materials and the most relevant properties of both groups of alloys are specified. Obtained results confirmed that zinc-based alloys can compete magnesium-based alloys in the case of strength and corrosion rate. Unfortunately, plasticity and also biocompatibility of studied Zn-1Mg-0.5Ca were significantly deteriorated compared to the Mg-4Y-3RE alloy.

Keywords: Magnesium, zinc, biodegradable materials, mechanical properties, corrosion

1. INTRODUCTION

Metallic biodegradable materials are intensively considered for applications in medicine like fixation devices as the better choice over polymers and ceramics due to higher strength, hardness, and ductility. Specifically, magnesium, iron, and zinc were widely investigated for such applications [1-2]. Iron exerts slow corrosion rate due to the quite easy passivation of the surface. Contrary, magnesium exhibits insufficiently high corrosion rate [3]. Therefore, both materials have to be properly alloyed in order to obtain acceptable degradation. Zinc is essential element for the human body as it is involved in many biological processes [4]. In addition, the corrosion rate of zinc is in between mentioned Fe and Mg. The upper limit of a recommended daily dose of Zn is 40 mg, however, even higher amounts of it are tolerated by the organism for few days [5]. The cytotoxicity tests have been performed on Zn alloys with positive results [6-7]. Moreover, some in-vitro tests revealed that the implant stained intact at least for four months and the formation of new bone tissue was observed after exposition [5,8].

However, pure Zn has low mechanical properties and the application of alloys is necessary [9-10]. Three main alloying elements are generally considered: Mg, Ca and Sr. Addition of Mg up to 2 wt.% significantly improves mechanical properties [6,9]. Higher contents of Mg lead to the creation of the brittle eutectic phase, which causes a decrease in the strength and plasticity [6]. Calcium is the main component of bone tissue and is involved in mineralization and enzymatic reactions in a human organism [11]. The reason behind the addition of Ca is therefore in the biological application in addition to the improvement of mechanical properties [12]. Liu [13] reported a significant increase of mechanical properties with the addition of 0.1 wt.% of Ca to Mg-1.5Mg alloy.

The preparation of Zn materials is relatively easy due to the low melting point and low reactivity in the molten state compared to Mg. Zn can be, therefore, prepared by simple casting [14]. Different intermetallic phases such as MgZn, $MgZn_2$, Mg_7Zn_3, Mg_4Zn_7, and Mg_2Zn_{11} were observed in as-casted Zn-Mg alloys depending on the preparation process [15]. Ternary Zn-Mg-Ca alloy contains also additional $CaZn_{13}$ intermetallic phase [13]. However, improved mechanical properties are usually associated with thermomechanical processing [16]. Mg-1Zn alloy examined by Gong et al. [17] exerted improvement of strength and elongation after extrusion from 150 MPa and 1 % to 200 MPa and 10 %, respectively. Present work brings some comparison of Zn-1Mg-0.5Ca with one of the most advanced magnesium alloy Mg-4Y-3RE which is similar in composition to the commercial alloy designated as WE43. Materials were prepared in both as-cast and as-extruded states and mechanical and corrosion properties of both alloys are discussed.

2. MATERIALS AND METHODS

2.1. Materials processing

As-cast ingots of the Mg-4Y-3RE magnesium alloy were obtained from company Magnesium Elektron CZ. Cylindrical billets with 30 mm in diameter were produced from this ingot and processed by extrusion. Extrusion of samples was performed at 400 °C, extrusion ratio 16:1 and at 0.3 $mm \cdot s^{-1}$. Zn-1Mg-0.5Ca was prepared by melting pure Zn (99.95 wt.%), Mg (99.96 wt.%) and Ca (99.96 wt.%) in a resistance furnace in air. To prevent excessive evaporation of volatile zinc, the melting temperature did not exceed 550 °C, and homogenization was ensured by intense mechanical stirring with a graphite rod. After sufficient homogenization, the melts were poured into a cast-iron metal mould to prepare cylindrical ingots of 50 mm in diameter and 120 mm in length. Chemical composition of studied materials was verified by atomic absorption spectrometry (AAS - AGILENT 280 FS AA spectrometer), as shown in **Table 1**.

Table 1 Chemical composition of studied alloys (values are given in wt.%)

Chemical composition	Mg	Ca	Zn	Y	Nd	Gd	Dy	Zr
Zn-1Mg-0.5Ca	0.78	0.48	bulk	-	-	-	-	-
Mg-4Y-3RE	bulk	-	-	3.62	2.24	0.28	0.35	0.43

2.2. Microstructure

The microstructure studies were performed using light microscopy (OM) and scanning electron microscopy (SEM, Tescan Vega 3 LMU). Preparation of the samples consisted of mechanical grinding, polishing and final etching of Mg-4Y-3RE in a solution containing 10 ml of acetic acid, 4.2 g of picric acid, 10 ml of distilled water and 70 ml of ethanol. The Zn-1Mg-0.5Ca alloy was etched in the solution containing 2 ml of nitric acid and 100 ml of ethanol. Phase and chemical composition were characterized by energy dispersion spectrometry (EDS - Oxford Instruments AZtec) and X-ray diffraction (X'Pert Philips, 30 mA, 40 kV, X-ray radiation Cu Kα), respectively.

2.3. Mechanical properties

Tensile tests were performed according to the standard ČSN EN ISO 6892-1 on cylindrical samples in the shape of dog bone with 4 mm in diameter. These tests were carried out at the strain rate 0.001 s^{-1} on the mechanical testing machine (Lab Test 5.250SP1-VM).Tensile yield strength (TYS), ultimate tensile strength (UTS) and Elongation (E) were determined from obtained data.

2.4. Corrosion

Corrosion behaviour was studied by immersion tests that were performed in a simulated body fluid (SBF) environment, whose composition is given in **Table 2**. Samples were first ground with SiC abrasive papers (P4000) and degreased with ethanol. Then, cylinders about 6 mm in diameter and 15 mm high were immersed in the SBF for 168 hours at 37 °C. The ratio of the volume of SBF to the surface area of each specimen was kept at 80 ml·cm^{-2}. After the corrosion tests, corrosion products were removed using a solution of 200 g·l^{-1} CrO^3, 10 g·l^{-1} $AgNO^3$, and 20 g·l^{-1} $Ba(NO^3)^2$ at 25 °C for magnesium-based alloy and at 70 °C for zinc-based alloy. Corrosion rates were calculated from the weight losses measured with the accuracy of 0.1 mg and by the measurement of the total quantity of Mg or Zn ions released during corrosion by AAS. Each immersion test was performed three times.

Table 2 The chemical composition of the simulated body fluid (SBF)

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO^{3-}	HPO_4^{2-}	SO_4^{2-}
Concentration (g·l^{-1})	142	5.0	1	2.5	109	27	1	1

3. RESULTS AND DISCUSSION

3.1. Microstructure

The microstructure of as-cast materials is displayed in **Figure 1a**. Mg-4Y-3RE alloy is characterized by average grain size of 30 ± 9 µm. It consists of the solid solution of α-Mg, eutectic β-phase ($Mg_{14}Nd_2Y$) and also $Mg_{41}Nd_5$ and $Mg_{24}Y_5$ phases. Similar phases have been often observed in the microstructure of Mg-Y-Nd alloys [18-21]. The as-cast state is characterized by strong dendritic microsegregation with differences in Y and Nd concentrations between dendrite cores and dendrite edges. The concentration of Y and Nd in dendrite cores reached about 1.5 - 2.2 and 0.5 - 1.1 wt.%, respectively. After extrusion of the Mg-4Y-3RE alloy, the microstructure was almost completely recrystallized and intermetallic phases with up to 2 µm in size were rearranged in the rows parallel to the extrusion direction (**Figure 2a**). These phases contained about 28 wt.% of Nd, 12 wt.% of Y, and about 1 wt.% of Gd and correspond to the equilibrium β phase ($Mg_{14}Nd_2Y$). Two additional phases were observed in the microstructure. Specific blocked-shaped particles with edges of 0.2 - 1 µm containing about 48.5 wt.% Y, 8.6 wt.% Nd, 2 wt.% of both Dy and Gd correspond to the $Mg_{24}Y_5$ phase. In addition, $Mg_{42}Nd_5$ phase, which is commonly observed in the as-cast state of WE43 alloy, was observed. The solid solution of α-Mg observed between stringers contained about 2 wt.% Y, 1 wt.% Nd, and about 0.4 wt.% Zr. The grain size of extruded alloy ranged between 0.5 and 7 µm and the average grain size reach 2.6 ± 1.8 µm. Generally, extrusion process led to obvious refinement of the microstructure, rearrangement of intermetallic phases and removing of the dendritic microsegregation. All these phenomena have a strong effect on both mechanical and corrosion properties of the studied material.

The microstructure of the as-cast Zn-1Mg-0.5Ca alloy is composed of primary zinc dendrites and a non-equilibrium eutectic mixture of α-Zn + $MgZn_2$ (**Figure 1a**). Such eutectic mixture is preferentially formed at higher solidification temperatures, which is in our case fulfilled by casting to the non-preheated mould. In addition, huge block-shaped particles of $CaZn_{13}$ can be observed. Based on EDS measurements, primary Zn contains a negligible concentration of alloying elements like Mg and Ca. This is in good agreement with phase diagrams and solubility limits for mentioned two elements in Zn which are near zero at laboratory temperature [22]. The microstructure of the hot-extruded Zn-1Mg-0.5Ca alloy is illustrated in **Figure 2b**. $CaZn_{13}$ phases, which have remained in their original state are seen as sharp-edged particles with size up to 10 µm. Also, eutectic mixture is preserved (**Figure 2b**). The extruded material was characterized by completely recrystallized microstructure without observable deformation texture suggesting that dynamic recrystallization was completed during the hot extrusion process.

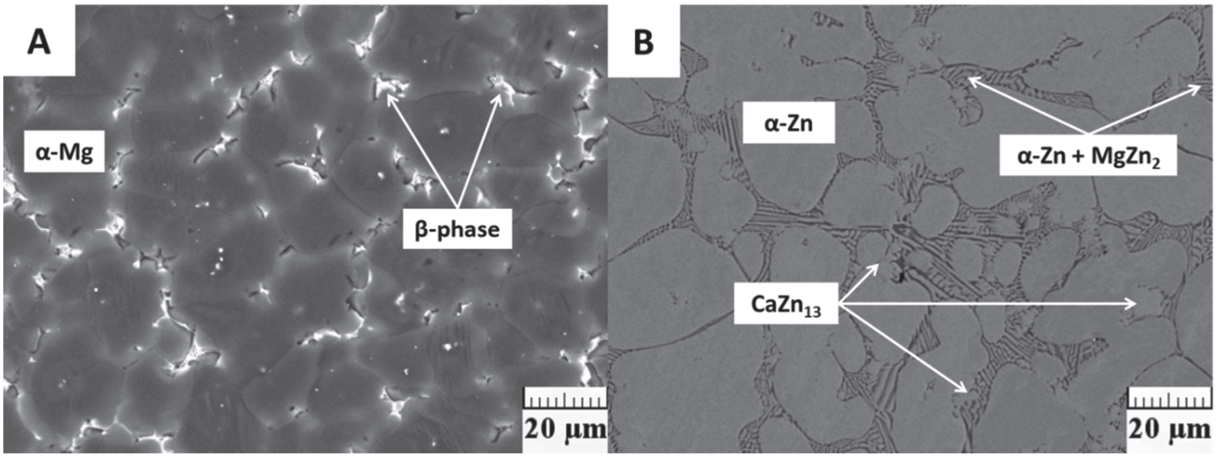

Figure 1 Microstructure of the as-cast alloys (SEM): a) Mg-4Y-3RE, b) Zn-1Mg-0.5Ca

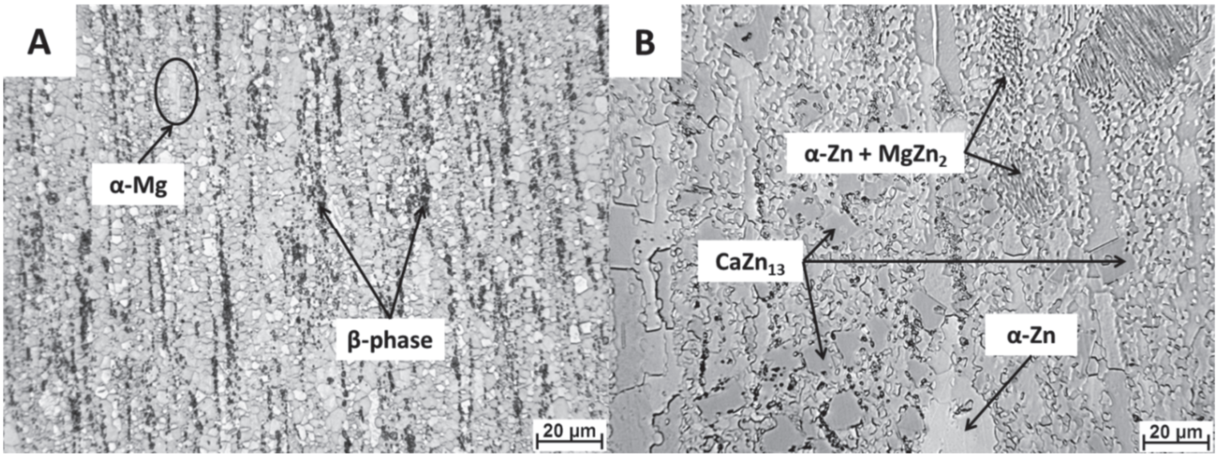

Figure 2 Microstructure of the as-extruded alloys (OM): a) Mg-4Y-3RE, b) Zn-1Mg-0.5Ca

3.2. Mechanical properties

Mechanical properties of studied materials are depicted in **Figure 3**. The Mg-4Y-3RE and Zn-1Mg-0.5Ca alloys in the as-cast state are characterized by TYS/UTS values about 140/215 and 175/235 MPa, respectively. These values are significantly improved after extrusion process up to 250/300 MPa for Mg-4Y-3RE and 315/325 MPa for Zn-1Mg-0.5Ca. However, elongation to fracture is decreased for extruded specimens up to 1.6 and 0.5 % for Mg-4Y-3RE and Zn-1Mg-0.5Ca, respectively. It is worth to mention that also elongations of the as-cast materials are quite poor and reaches at maximum of about 7 %. The main factors which are responsible for mechanical behaviour are different for both kinds of materials.

In the case of Mg-4Y-3RE, three different strengthening mechanisms can be considered (1. strengthening by grain boundaries (Hall-Petch relation), 2. strengthening by secondary phases and 3. solid solution strengthening). Due to the low grain size of both as-cast and as-extruded Mg-based alloy, grain boundaries are considered as the main strengthening factor. Alloying elements like Nd and especially Y are dissolved in magnesium solid solution. Solid solution strengthening is related to the difference in the atomic radii and shear modulus of the elements dissolved in the solid solution and the magnesium. Atoms of Y and Nd reach a comparable size of 0.18 nm. Compared to the atomic radius of magnesium (0.16 nm), this is a 12 % difference. Therefore, it can be assumed that the presence of a higher concentration of these elements in the solid solution has a direct effect on mechanical properties. In addition shear modules of Nd, Y and Mg are 16.3, 25.6 and 17 GPa [23]. Therefore the dominant strengthening effect of Y in the solid solution is assumed. Precipitation strengthening is also generally considered in magnesium-based alloys. However, Mg-4Y-3RE was processed by extrusion at 400 °C, which is a quite high temperature and stable β phases are preferentially formed. These phases have only miner strengthening effect [24], therefore expected contribution to measured values of TYS and UTS is low.

Mechanical properties of Zn-1Mg-0.5Ca are affected by the slightly different way. Firstly, secondary dendrite arm spacing or grain boundaries have also the dominant effect on observed values of TYS in the as-cast (C) and as-extruded (E) conditions. However, the effect of solid solution strengthening is expected to be very low because the solubility of Ca or Mg in primary Zn is almost zero at 25 °C. This is the main reason, why the microstructure of the as-cast and also as-extruded material contains the high fraction of eutectic $MgZn_2$ phase and coarse particles of $CaZn_{13}$. Both these phases are considered to have strengthening effect but they also highly deteriorate plasticity of the alloy (**Figure 3**).

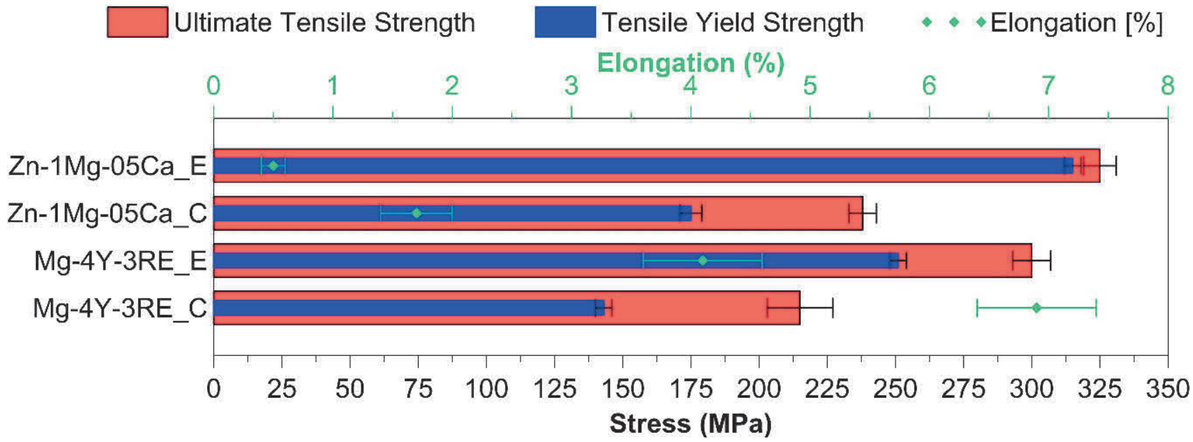

Figure 3 Tensile mechanical properties of Mg-4Y-3RE and Zn-1Mg-0.5Ca alloys

3.3. Corrosion

Corrosion rates of Mg-based and Zn-based alloys are displayed in **Figure 4**. Although from the perspective of corrosion rate, Zn-1Mg-0.5Ca is characterized by about one third corrosion rate compared to the extruded Mg-4Y-3RE, the corrosion mechanism is highly different. The anodic reaction of both kinds of materials is the dissolution of matrix elements and release of Zn^{2+} or Mg^{2+} ions. Such anodic reaction must be accompanied by the cathodic reaction, which is **equation (1)** in the case of Mg and **equation (2)** in the case of Zn [14]. Therefore, magnesium corrosion is accompanied by hydrogen release, which is known complication during healing of damaged tissue. On the contrary, no hydrogen is generally produced during corrosion of Zn-based materials. This is one of the main advantages of zinc.

$$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^- \qquad (1)$$

$$2\ H_2O + O_2 + 4\ e^- \rightarrow 4\ OH^- \qquad (2)$$

It is evident from **Figure 4** that corrosion rate of Mg-4Y-3RE is decreased after corrosion, which is caused by more homogenous microstructure an also lower grain size. However, the as-cast and as-extruded Zn-1Mg-0.5Ca corrodes by similar corrosion rate. Corrosion starts by dissolution of eutectic phase enriched by Mg and intermetallic phase enriched by Ca because these elements are less noble than zinc. Generally, such behaviour is contradictory to Mg-based materials, where the majority of alloying elements is nobler than magnesium, and therefore, intermetallic phases containing these elements work as cathodic sites and stimulate the dissolution of magnesium matrix. Therefore, the presence of intermetallic phases has a negative impact especially on corrosion of magnesium-based alloys.

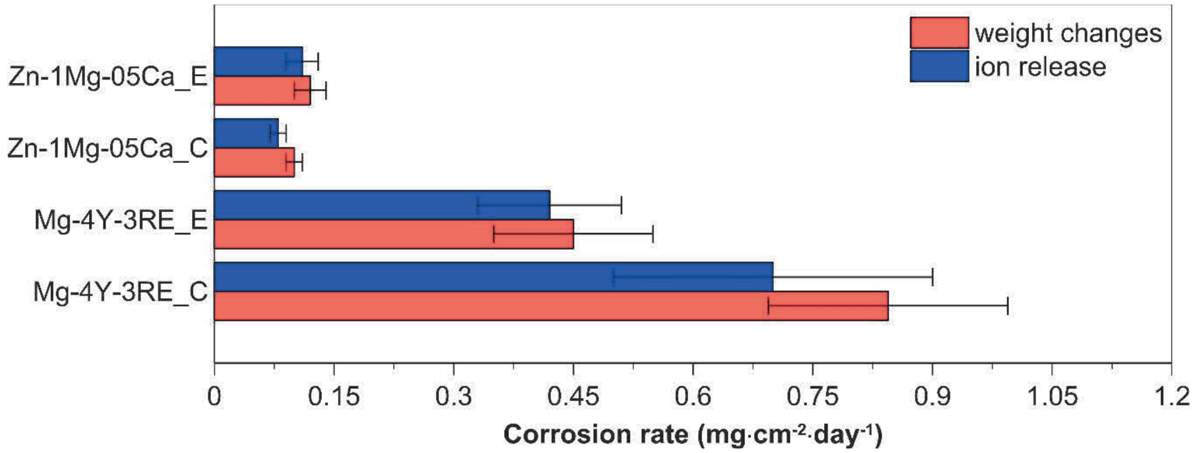

Figure 4 Corrosion rates of Mg-4Y-3RE and Zn-1Mg-0.5Ca alloys

4. CONCLUSION

Present paper deals with the comparison of two different materials considered for application in medicine as biodegradable materials. The Mg-4Y-RE alloy is well known commercial materials which are characterized by a good combination of mechanical and corrosion properties. On the contrary, the Zn-1Mg-0.5Ca alloy is material specifically developed for applications in medicine. Over the low concentration of alloying elements, this alloy can reach TYS and UTS values between about 315 and 325 MPa, which is slightly higher compared to the extruded Mg-4Y-3RE. Also, the corrosion rate of the Zn-based alloy is really promising because it represents about one-third of the corrosion rate of Mg-4Y-3RE. Unfortunately, Zn-1Mg-0.5Ca is a really brittle material with almost no signs of plasticity during tensile loading, which is unacceptable for various applications in medicine.

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