ZN-BASED ALLOYS AS AN ALTERNATIVE BIODEGRADABLE MATERIALS

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Abstract

Zinc like magnesium has important role in many biological processes in human organism. However, recommended dietary allowance (RDA) for zinc is 15-40 mg per day which is much lower in comparison with 300-400 mg for magnesium. For this reason biodegradable materials based on Zn should be characterized by lower corrosion rate in comparison with magnesium materials. Sufficient mechanical properties especially high strength and medium ductility are required. Poor mechanical properties of pure zinc can be increased by alloying with other elements. In this research magnesium was used as alloying element due to its beneficial effect on bone growth. Binary zinc alloys that contained from 0.5 to 3 wt. % of magnesium were prepared. Mechanical properties of studied alloys in the cast state were determined and compared to pure Mg and Zn. Moreover, corrosion behaviour in physiological NaCl solution and simulated body fluid (SBF) solution was studied by immersion tests and potentiodynamic measurements. Maximum strength of 150 MPa was achieved in the case of Zn-Mg (wt. %) binary alloy. Corrosion rates of Zn-Mg alloys were determined to be significantly lower than that of pure Mg. Both mechanical and corrosion properties are discussed in relation to the structural features of the alloys.

Key words:
zinc alloys, biodegradability, corrosion, mechanical properties

1. INTRODUCTION

Biodegradable materials can be gradually dissolved and absorbed in organism [1, 2, 3]. In this group polymeric, ceramic and metal materials are included. In comparison with polymeric and ceramic ones metallic biomaterials are characterized by higher strength and fracture toughness [4] which mean that they are more suitable for load-bearing applications [5]. Currently, biodegradable metallic materials are based on magnesium. Magnesium is not toxic even in quite high daily doses. His recommended dietary allowance (RDA) for adults is 300 – 400 mg per day [6]. Magnesium itself support some biological processes such as functions of muscles, nerves, heart and has positive influence on the growth of bones [1, 2, 7, 8]. Moreover Young’s modulus of magnesium is close to human bones, which is important to prevent stress-shielding effect [1, 2]. On the other hand pure magnesium is often characterized by high corrosion rate in body fluids. Excessive corrosion rate can lead to formation of hydrogen pockets and disruption of some pH dependant physiological reaction balances [2]. Uniform corrosion, acceptable corrosion rate and improved mechanical properties are main requirements for new biodegradable materials. For this reason different magnesium alloys with rare earth elements, aluminium, zinc, calcium, manganese have been tested recently [9 - 14]. It is considered that suitable alloying with rare earths elements can slow down corrosion process of magnesium alloys, however there is still lack of information about toxicity of members of this group [2, 15, 16]. Other element such as aluminium is still associated in connection with Alzheimer’s disease [9]. Different alloys with zinc as a main constituent were prepared [9 - 14]. It is known that zinc can positively affect the corrosion rate and mechanical properties of magnesium alloys [9]. Moreover it is important element for functions of enzymes, immune functions, wound healing, it supports normal growth and proper sense of taste and smell [9, 15, 16]. Magnesium alloys in the form of metal glasses that contained about 50 wt.% of zinc with excellent...
strength, high corrosion resistance and good biocompatibility have been prepared recently [17, 18]. From this point of view it worth considering the use of Zn-based alloys as a biodegradable material. Although recommended dietary allowance (RDA) of zinc for adults is only 10 - 15 mg per day [19], it may be expected that this value is sufficient due to the much slower dissolution rate of more noble zinc compared to magnesium. Other advantages are the lower melting point, lower chemical reactivity and better machinability of zinc, as compared to Mg. However there is almost no information about behaviour of Zn-based alloys in simulated biological environment. For this reason mechanical properties and corrosion behaviour of Zn-Mg alloys with 1, and 2 and 3 wt.% Mg were investigated and compare to properties of pure Mg and Zn. Magnesium as a main alloying element were choose due to its positive influence on mechanical properties of zinc alloys and promotion bone growth.

2. EXPERIMENTAL
Cylindrical ingots of pure zinc and three binary Zn-Mg alloys with 20 mm in diameter and 130 mm in length were prepared by melting of pure Zn (99,9 %) and Mg (99,9 %) in resistance furnace in air at 500 °C. The melts were poured into a cast-iron mould preheated to 50 °C. Mg ingot with the same parameters was prepared in induction furnace at 740 °C under protective atmosphere of argon. The melt was poured into non-preheated steel mould. Composition of studied alloys (Tab. 1) was determined by X-ray fluorescence spectrometry (XRF). Structures of all investigated alloys were observed under optical microscope and transmission electron microscope Tescan Vega 3 – LMU equipped with EDS analyzer (Oxford Instruments Inca 350). Phase composition was studied using both EDS analyzer and X-ray diffraction analyses (XPert Philips, 30 mA, 40 kV, X-ray radiation Cu Kα). Vickers hardness with loading of 5 kg was measured. At least ten measurements were performed for each sample for statistic evaluation. Tensile tests were performed on Heckert FPZ 100/1 machine with deformation rate of 1 mm/min. Ultimate tensile strength (UTS), yield strength (YS) and elongation (E) of all alloys were established. Corrosion behaviour was studied on immersion tests and potentiodynamic measurements in aerated simulated body fluid (SBF) at pH 6,5 and 37 °C. Composition of solution is shown in Tab. 2. Immersion test were performed on samples with 20 mm in diameter and 3 mm thick for 336 hours. Before tests, surface of samples was grinded on abrasive SiC papers up to P4000 and degreased in ethanol. After immersion test, morphology and composition of corrosion products were analyzed on SEM equipped by EDS analyzer, XRD and X-ray photoelectron spectroscopy (XPS, ESCA Probe P, pressure in the analytical chamber of 2 × 10⁻⁸ Pa, monochromatic Al Kα, X-ray source, binding energy calibration with respect to the energy of Au 4f7/2 peak). Corrosion rates were calculated from weight changes before exposure and after removing the corrosion products in 200 g/l CrO₃ solution. Finally potentiodynamic curves were measured in SBF with SSCE (Ag/AgCl/KCl – 3 mol/l) as a reference electrode, platinum wire as a counter electrode and sample as working electrode. Potentiodynamic measurements were performed at scanning rate 2 mV/s from -0,2 V/Eocp to +0,8 V/Eocp.

<table>
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<th>Mg</th>
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<th>Simulated body fluid solution (SBF)</th>
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<td>compound</td>
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<td>Concentration [g/l]</td>
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3. **RESULT AND DISCUSSION**

3.1 **Structures**

Structures of investigated alloys are shown in Fig. 1. Pure zinc was consisted of large equiaxed grains with an average size of 500 µm. Some elongated grains in a direction parallel to heat removal were observed. Pure magnesium was consisted of elongated grains with about 300 – 500 µm in thickness and 1 – 1,5 mm in length. Both Zn-1Mg and Zn-1.5Mg alloys are hypoeutectic. Microstructure is consisted of primary dendrites of Zn (white areas) and Zn + Mg$_2$Zn$_{11}$ eutectic mixture (dark areas). Detailed view on the eutectic phase at the interface of dendrites is shown on Fig. 2a. Volume fraction of eutectic mixture is increased with higher content of Zn. In both alloys concentration of Mg in solid solution was about 0,2 wt.%. From 5 to 6 wt.% of Mg were analysed by EDS in eutectic mixture. Mg-3Zn alloy were composed of very fine eutectic mixture of Zn and Mg$_2$Zn$_{11}$ phases. This mixture created colonies up to 500 µm in size that differ in spatial orientation of intermetallic phases (Fig. 2b). This is in good agreement with phase diagram Zn-Mg, where eutectic point is approximately at 3,5 wt.% of magnesium.

Fig. 1 Structure of studied materials (optical microscope):
- a) Mg, b) Zn, c) Zn-1Mg, d) Zn-1.5Mg

Fig. 2 Detailed structure of studied alloys (SEM): a) Zn-1Mg, b) Zn-3Mg
3.2 Mechanical properties

Mechanical properties of studied alloys are compared in Fig. 3. The lowest ultimate tensile strength (UTS) and very poor elongation (E) were measured for pure Zn which can be attributed to coarse-grained structure. Binary Zn-Mg alloys with 1 and 1.5 wt.% of magnesium were characterized by much higher UTS 153 MPa and 147 MPa respectively. This is connected with presence of fine dendritic structure and network of eutectic mixture (Zn + Mg$_2$Zn$_{11}$). Both fine grains and eutectic mixture can prevent crack growth. Zn-3Mg alloy was characterized by low UTS similar to pure Zn and the lowest elongation only about 0.2 %. This is caused by presence of high volume fraction of brittle eutectic mixture and coarse-grained structure. As a consequence fracture crack growth resistance is very low. Compared to zinc, pure magnesium was characterized by higher UTS about 96 MPa and the highest elongation (2.9 %) from studied alloys. In this case magnesium was composed of finer grains in comparison with pure zinc and probably some plastic deformation accompanied fracture. Only in the cases of pure Mg and Zn-1Mg alloy yield strength value 49 and 108 MPa respectively were obtained. In other alloys fracture occurred before the onset of plastic deformation. Vickers hardness of studied alloys depends on the Mg content in Zn-Mg. The lowest values about 30 HV5 were measured for pure zinc and magnesium. However HV5 of Zn-1Mg alloy increased to nearly 65 and in the case of Zn-3Mg to 206 HV5. It is due to increasing amount of hard and brittle Mg$_3$Zn$_{11}$ intermetallic phase in microstructure as a consequence of higher Mg content in alloy.

3.3 Corrosion behavior

From Fig. 4 it is evident that corrosion rates of Zn and Zn-based alloys are much lower in comparison with pure magnesium. This is in good agreement with the fact, that Zn is much more noble metal than magnesium. This fact is confirmed by corrosion potentials of studied Zn alloys that are higher by about 0.6 V compared to pure Mg (Fig. 4 b). Basic corrosion reaction for Mg and Zn take place according to the equation (1) and (2) respectively.

$$\text{Mg} + 2 \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{H}_2 + 2 \text{OH}^- \quad (1)$$

$$\text{Zn} + 2 \text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + \text{H}_2 + 2 \text{OH}^- \quad (2)$$

$$\text{Mg(OH)}_2 \text{ (insoluble)} + 2 \text{Cl}^- \rightarrow \text{MgCl}_2 \text{ (soluble)} + 2\text{OH}^- \quad (3)$$

Corrosion process of both metals is accompanied by hydrogen release a pH increase. According to the Pourbaix diagram magnesium is passivated in strongly alkaline liquids by Mg(OH)$_2$ [20]. On the contrary zinc can be passivated by Zn(OH)$_2$ even at neutral or slightly alkaline liquids [20]. However SBF solution contains some dyhydrogenphosphate, hydrogenphosphate and hydrogencarbonate ions. These ions stimulate creation of insoluble corrosion products on magnesium at lower alkaline pH values and decrease the corrosion rate. Moreover the same products may improve the protective character of passive layers on the surface of Zn and its alloys. After exposure tests the surfaces of Mg, Zn and zinc alloys were covered by quite compact layers of corrosion products that were locally detached due to the internal stress. In addition some spherical particles of corrosion products precipitated on these layers. Surfaces of all alloys after immersion tests looked very similar. No pits were observed on the surface of zinc alloys although many intermetallic phases were precipitated in structure. Mg$_2$Zn$_{11}$ phase contain high amount of zinc and the corrosion potential of this phase is probably close to pure Zn. As a consequence galvanic cell formation is suppressed. Composition of corrosion products measured by EDS is given in Tab. 3. Although XPS analyses indicate the presence of Ca$^{2+}$, Mg$^{2+}$, Zn$^{2+}$ and P$^{5+}$ oxidation states in these products, XRD analyses did not confirm any new phases. The reason may be in thin layers of corrosion products that cannot be detected by XRD. From EDS and XPS analyses it can be assumed that corrosion products on pure Mg and zinc alloys contain calcium-magnesium phosphates that are enriched by some zinc in the case of zinc alloys and magnesium or zinc hydroxides. Moreover some carbonates can be presented on the surface after exposures in SBF solution, however this element could not be quantificated due to the danger of contamination by carbon. Insoluble compounds are able to decrease corrosion rate due to the formation of
protective layers on the surface of alloys. These layers work as barrier for transport of ions especially chloride anions that facilitate dissolution of magnesium according to the equation (3).

**Fig. 3** Mechanical properties of studied materials

**Fig. 4** Corrosion rate (a) and potentiodynamic curves (b) of studied materials

**Tab. 3** EDS analysis of alloy surfaces after exposure in SBF (composition in wt. %)

<table>
<thead>
<tr>
<th>alloy</th>
<th>Mg</th>
<th>Zn</th>
<th>P</th>
<th>Ca</th>
<th>Na</th>
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<td>63,6</td>
<td>15,9</td>
<td>14,1</td>
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4. **CONCLUSION**

Studied Zn-Mg alloys were characterized by excellent corrosion resistance and good mechanical properties in the cast state. Additional improvement in strength could be achieved by suitable combination of
mechanical and thermal treatment. Based on these facts Zn-Mg alloys can be considered as a suitable materials for biodegradable implants. Due to the very low corrosion rates of Zn-based alloy, estimated doses of zinc ions released from implants should not exceed tolerable limit of Zn daily intake.

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REFERENCES


