CORROSION AND MECHANICAL PROPERTIES OF BIODEGRADABLE Zn-BASED AND Mg-BASED ALLOYS

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Abstract

Zn and Mg based alloys are promising materials for medical implants because the mechanical characteristics of their alloys are close to human bone and zinc and magnesium are relatively non-toxic. In addition, magnesium is well-known for providing optimum corrosion rates under specific conditions. Therefore, in this paper, the corrosion behaviour of these alloys is compared to that of biodegradable materials. Alloys were prepared by casting without protective atmosphere. The microstructure of prepared alloys was observed by light and scanning electron microscopy (SEM). The mechanical properties of the investigated alloys were determined by Vickers hardness measurements at ambient temperature. The corrosion rates of alloy samples were measured by their exposure in a solution with similar characteristics to the body fluid. Corrosion rates were calculated of the decrease weight of the exposed samples per exposure time. Corrosion products on the surface were analysed using X-ray diffraction analysis. The surface of each alloy after the exposure test was documented by scanning electron microscope (SEM). Due to the heterogeneity of structure of magnesium alloys it is possible to observe micro-galvanic cells with the surrounding matrix in the phase structure. Therefore, homogenization of the structure of magnesium alloys was performed and subsequently the same exposure test of obtained alloys was carried out. It was found that the homogenization treatment led to a decrease of corrosion rates. Magnesium alloys in the as-cast condition and after homogenization treatment have higher corrosion rates than zinc-based alloys.

Keywords: Biodegradable material; zinc; magnesium; corrosion rate

1. INTRODUCTION

Metallic biomaterials are used in medicine for the replacement of damaged or malfunctioning human tissues. Titanium alloys and stainless steel are some of the most important materials used in orthopedics and traumatology for the manufacture of implants and as well as joints the fixing of broken bones. These materials are characterized by high strength and good overall corrosion resistance in body fluids. This resistance is caused by the spontaneous formation of protective passive layers on their surfaces. Due to this fact, these materials corrode very slowly in the body. These materials are developed as permanent replacements.

Biodegradable materials are developed besides metallic biomaterials. They have significantly higher corrosion rates compared to implants intended as a permanent replacement. Biodegradable materials are commonly used in medicine for the manufacture of temporary medical implants. They degrade gradually in the human body, being replaced by healing tissue [1]. When the bone healing process is complete, no second surgery is needed to remove a biodegradable fixation device, which reduces the inconvenience and the health care costs for patients. Moreover, these materials must good biocompatibility. It means that these materials and their products of degradation are neither toxic nor carcinogenic, and don´t cause any allergic reactions in the human body [2]. Currently, polymer materials are commonly used for temporary fixation of bone fractures. Their disadvantages are worse mechanical properties (lower strength, hardness) than metal alloys. Therefore, the metallic biodegradable materials are continuously being developed, whose mechanical properties are significantly better. It is known that large differences in elastic modulus between the implant and the tissue can lead to problems with the correct regrowth of new bone. **Table 1** compares the basic mechanical properties of various biomaterials.

Table 1 Summary of the physical and mechanical properties of various implant materials in comparison to natural bone [3]

Material/ tissue	Density (g/cm^3)	Tensile strength (MPa)	Elastic modulus (GPa)
Natural bone	~2	30-280	5-20
Synthetic hydroxyapatite	3	10-80	70-100
Mg-alloys	~ 2	100-350	45
Zn-alloys	~7	150-400	90
Ti-alloys	~4.5	600-1100	110
Polylactic acid	~1	~30	~2
Stainless steel	~8	600-1000	200

This paper describes two groups of metallic biodegradable materials: magnesium and zinc-based alloys. They have tensile strength and modulus of elasticity similar to human bones. Both magnesium and zinc are considered suitable candidates for the manufacture of biodegradable materials because they have good biocompatibility and low toxicity. Magnesium and zinc are important for the proper biological functions of the human organism [4,5]. In this paper, the microstructures of these alloys are described and the mechanical properties and corrosion behavior are compared.

2. EXPERIMENT

Overview of studied magnesium and zinc alloys is shown in **Table 2**. Their composition was verified by X-ray fluorescence analysis. Zinc is an alloying element in magnesium alloys and magnesium is an alloying element in the zinc alloys.

Table 2 Chemical composition of the investigated alloys (in wt. %)

Alloys designation	Element (wt. %)			
	Zn	Mg	Si	Ca
Mg	0.05	99.72	0.04	0.01
Mg-1.5Zn	1.54	92.62	0.49	0.05
Mg- 3.8Zn	3.79	95.81	0.06	0.01
Mg-5.7Zn	5.69	94.0	0.05	0.01
Zn	99.96	0	0.02	0.01
Zn-0.8Mg	99.10	0.86	0.02	0.02
Zn-1.6Mg	98.37	1.59	0.02	0.01
Zn-2.6Mg	97.35	2.61	0.03	0.01
Zn-3.5Mg	96.49	3.49	0.01	0.01
Zn-5.4Mg	93.64	6.32	0.02	0.01
Zn-8.3Mg	91.64	8.34	0.01	0.01

They were prepared by melting pure metals without protective atmosphere. After melting and sufficient homogenization of the melt, alloys were cast into a brass mold. All alloys were studied in the as-cast state. Magnesium alloys have been studied also in the condition after homogenization. This heat treatment was carried out at 300 °C for 150 hours.

The structure of the materials was observed using a light metallographic microscope (Olympus PME-3) and TESCAN VECA 3 LMU scanning electron microscope with an EDS analyzer (Oxford Instruments). Basic mechanical properties were determined by Vickers hardness (HV5). The corrosion rate of alloys were measured using exposure tests (ASTM standard G-31-72) for three times for selected alloys. As the corrosion environment model physiological solution (aqueous solution of 9 g/l sodium chloride) was chosen, which is similar to blood plasma containing chloride ions. The samples (5 mm in diameter, 5 mm in height) intended for exposure were weighed before inserting it into the solution. Exposure testing was carried out at 37 °C for 168 hours in 500 ml solution. These tests were carried out in closed containers. After the exposure tests, corrosion products were chemically removed (aqueous solution of 200 g/l CrO_3 at 80 °C according to ISO 8407). Subsequently, the samples were exactly weighed. The corrosion rates in mm/year were calculated from weight losses.

3. RESULTS AND DISCUSSION

3.1 Structure

Microstructures of prepared alloys are morphologically similar. Therefore only some of them were selected. **Fig. 1** presents the microstructure of pure Mg. It consists of relatively large grains whose size is caused by slow cooling during solidification. This samples contained grains elongated in the direction of heat transfer.

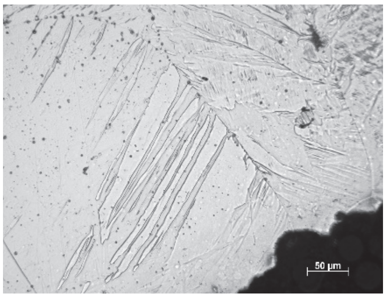

Fig. 1 Pure Mg

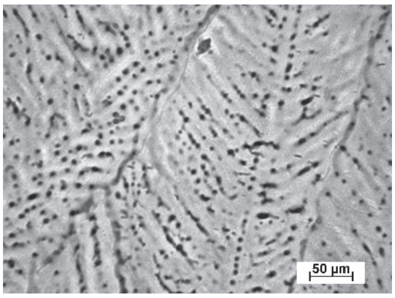

Fig. 2 Mg-3.8Zn in the as-cast condition

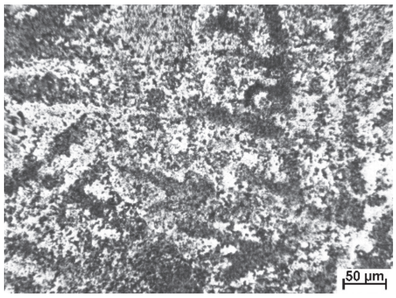

Fig. 3 Mg-3.8Zn after homogenization 300 °C/150 h

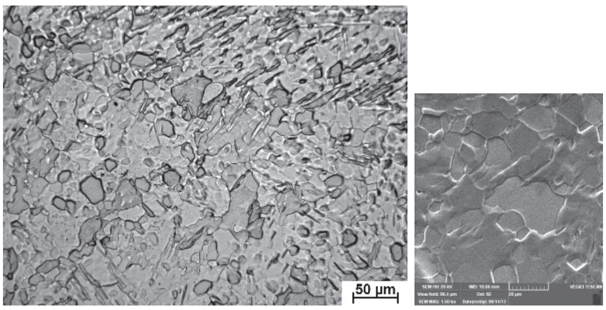

Fig. 4 Microstructure of pure Zn and detail (SEM)

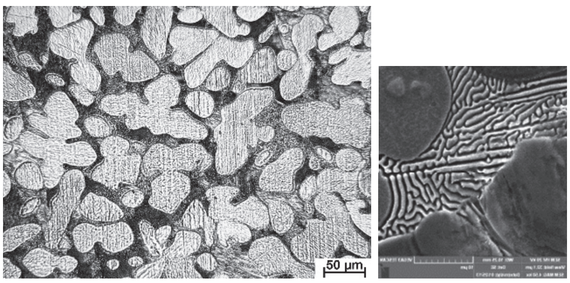

Fig. 5 Microstructure of hypoeutectic alloy Zn-1.6Mg and detail (SEM)

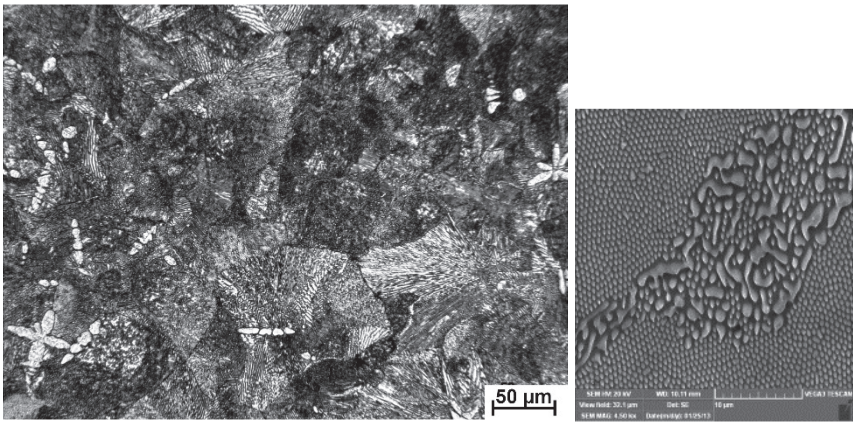

Fig. 6 Microstructure of eutectic alloy Zn-3.5Mg and detail (SEM)

The as-cast Mg-3.8Zn alloy (**Fig. 2**) contains primary α- Mg dendrites (light) surrounded by inter-dendritic regions rich in zinc (dark). The inter-dendritic regions in Mg-1.5Zn, Mg- 3.8Zn, Mg-5.7Zn contain MgZn phase (black particles) whose volume fraction increases with increasing zinc content in the alloy. **Fig.3** shows the influence of solution heat treatment at 300 °C/150 h on the Mg-3.8Zn alloy. The dendritic morphology and inter-dendritic network in Mg-Zn alloys vanished during the heat treatment. Apparently, despite the long annealing time (150 h), the resulting structures were not fully homogeneous, suggesting that a small part of the inter-dendritic MgZn phase remained undissolved in the α-Mg. This phase appeared as small dark particles. Structure of zinc-based alloys can be seen in the micrographs below. **Fig.4** presents the microstructure of pure zinc. With increasing content of alloying elements (Mg), the eutectic phase (α-Zn and Mg_2Zn_{11}) formed. This phase occurs at the grain boundaries of the α-Zn solid solution (dark, **Fig. 5**, Zn). **Fig. 6** shows the Zn-3.5Mg eutectic alloy. The emerging eutectic phases can be seen in the detail taken by SEM.

3.2 Mechanical properties

The values of Vickers hardness are summarized in **Fig. 7**. As expected, the hardness of Mg-based alloys increased slightly with increasing Zn content. The emerging phase MgZn causes strengthening of the alloys. The values of hardness of Zn-based alloys significantly grow with increasing magnesium contain due to the formation of Mg_2Zn_{11} hard eutectic phase.

Fig. 8 demonstrates the effect of annealing on the hardness is negligible. The differences between the as-cast and heat-treated Mg-based alloys are only a few units of HV5.

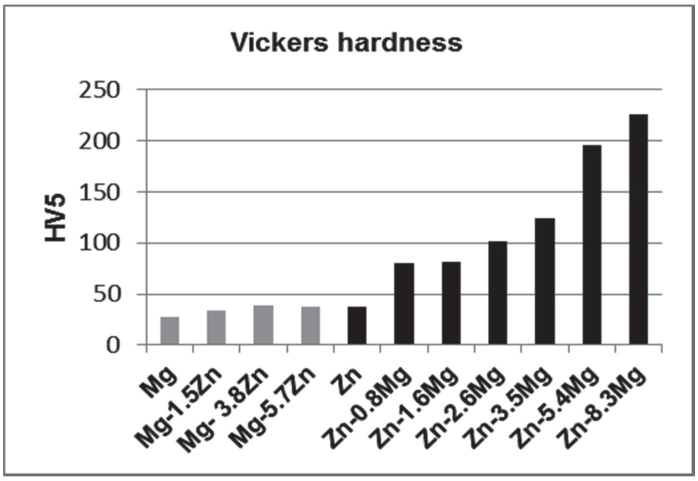

Fig. 7 The values of hardness of Mg-based alloys and Zn-based alloys in the as-cast state

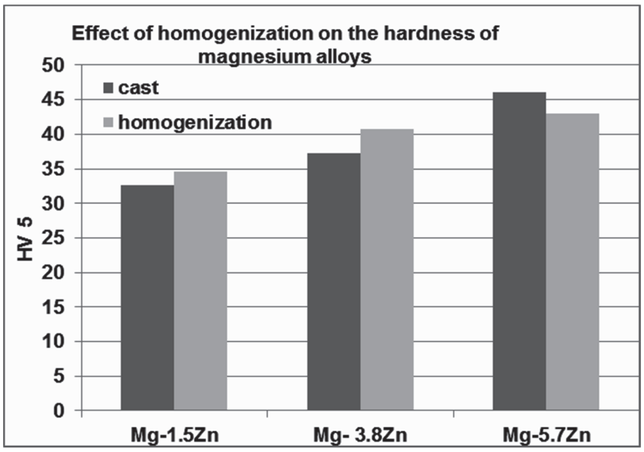

Fig. 8 Effect of homogenization on the hardness of Mg alloys

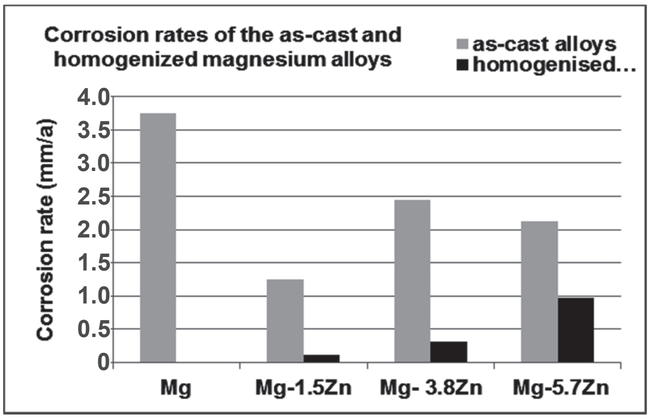

Fig. 9 Corrosion rates (in mm per year) of Mg-based alloys in the simulated physiological solution

3.3 Corrosion behavior

Fig. 9 shows the corrosion rates of the as-cast and heat- treated Mg-based alloys. It is clear that corrosion rate of alloys significantly depends on the zinc concentration. The reason is that zinc is more noble than magnesium. The positive influence of homogenization of the Mg-based alloys is evident.

Corrosion behavior of Zn-based alloys is evaluated in **Fig. 10**. The corrosion rates of these alloys are significantly lower than Mg-based alloys.

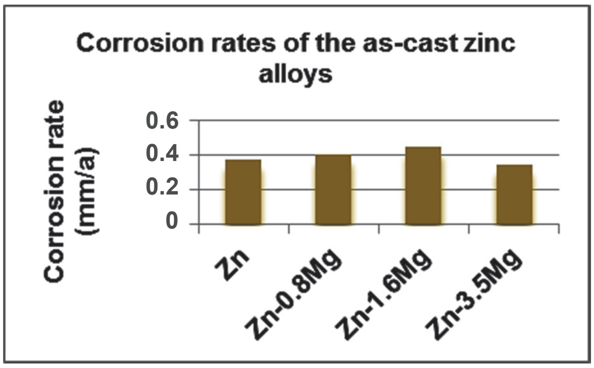

Fig. 10 Corrosion rates (in mm per year) of Zn-based alloys in the simulated physiological solution

CONCLUSIONS

In the paper, the results achieved in the development of new biodegradable metallic materials for medical applications are presented. Chosen types of magnesium alloys and zinc alloys were described. Both of these metals are characterized by a relatively good biocompatibility. Magnesium alloys alloyed by zinc and zinc alloys alloyed by magnesium were investigated. Of the studied Mg-based alloys, Mg-3.8Zn alloy seems to be the most appropriate. Of the studied Zn-based alloys, alloys Zn-0.8Mg and Zn-1.6Mg can be recommended. This conclusion is based on the evaluation of the mechanical properties of alloys and their corrosion behavior in simulated body fluid. It can be assumed that there is a large space for improvement of their mechanical properties by suitable thermo-mechanical treatment.

ACKNOWLEDGEMENTS

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REFERENCES

[1] VOJTĚCH, D., KUBÁSEK, J., ŠERÁK, J., NOVÁK, P. Mechanical and corrosion properties of newly developed biodegradable Zn-based alloys for bone fixation. *Acta Biomaterialia*, 2011, Vol. 7, pp. 3515-3522.

[2] WITTE, F. The history of biodegradable magnesium implants. *Acta Biomater.*, 2010, Vol. 6, pp. 1680-1692.

[3] DAVIS, J.R. *Handbook of Materials for Medical Devices*. ASM International, 2003.

[4] GRAY-MUNRO, J.E., SEGUIN, Ch., STRONG, M. Influence of surface modification on the in vitro corrosion rate of magnesium alloy AZ31. *J. Biomed. Mater. Res., Part A*, 2009, Vol. 91, pp. 221-230.

[5] KUBÁSEK, J., VOJTĚCH, D. Zn-based alloys as an alternative biodegradable materials. In *Conference Proceedings Metal* 2012.