Properties of Biodegradable Alloys Usable for Medical Purposes

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Magnesium alloys are promising materials for production of biodegradable implants that may be used for fixation of fractured bones. Magnesium itself is an essential element that plays important roles in many biological processes. However, some common alloying elements of magnesium alloys such as aluminium or copper may cause health problems to the organism. A major problem is the high corrosion rate of magnesium and its alloys in physiological environment that contains chloride anions. Currently, the research focuses on alloys doped by rare-earth elements and zinc. All these elements affect corrosion resistance and mechanical properties of magnesium alloys. This work was dealing with the study of Mg–Gd binary alloy and Mg–Gd–Y, Mg–Gd–Zn ternary alloys that were prepared from pure metals by melting in induction furnace. Various alloy compositions were tested. Corrosion behaviours in 9 M NaCl saline environments (exposure tests, potentiodynamic measurements) were studied on alloys in the cast state. Good corrosion resistance and uniform corrosion were observed in the case of binary Mg–Gd alloy. The influence of the addition of Y or Zn to the Mg–Gd system is discussed.

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1. Introduction

Magnesium is a suitable candidate for the preparation of biodegradable implants due to its non-toxicity and very important role in biological processes [1–3]. Recommended dietary allowance (RDA) for adults is 300–400 mg/day [2, 3]. A significant advantage of magnesium based alloys is the modulus of elasticity that is around 45 GPa [1]. That is much closer to the modulus of elasticity of bones in comparison with other metal materials such as stainless steels or titanium based alloys. For example the modulus of elasticity of cortical bone is in the order of 3–20 GPa, however the stainless steel may be characterized by 200 GPa. Big differences in modulus of elasticity can lead to the stress shielding effect and negatively affect the healing process [1, 2].

Mechanical properties of magnesium and its alloys are closer to human bones in comparison with currently known materials. It supports good healing process [1, 2]. However, the corrosion resistance of magnesium in physiological environment that contains especially chloride anions is quite poor. Excessive corrosion rate can lead to formation of hydrogen pockets and local alkalization which may affect the pH-dependent physiological reaction equilibrium [2]. Both mechanical properties and corrosion behaviour may be improved by alloying with other metals (Al, Mn, Zn, Ca, RE = rare-earth elements) but some of these elements may be connected with medical complications of various nature [3]. Recently, the re-

search has been focused on magnesium alloys containing especially Gd, Y and Zn [4–8], although many results are connected more with applications in automotive industry than in medicine.

In this work corrosion behaviour of Mg3Gd, Mg3Gd1Y and Mg2Gd7Zn was examined. The influence of Zn or Y addition on structure and corrosion behaviour of binary MgGd is discussed.

2. Experimental

Cylindrical ingots of Mg, Mg3Gd, Mg3Gd1Y and Mg2Gd7Zn were prepared by melting of pure Mg (99.9 wt%), Gd (99.9 wt%), Y (99.9 wt%) and Zn (99.9 wt%) in vacuum induction furnace under protective argon atmosphere of technical purity (99.9 wt%). The melt was homogenized for 15 min at 750 °C and casting into cast-iron metallic mould with 100 mm in length and 20 mm in diameter. These moulds were not pre-heated. The chemical composition of these ingots was verified in the middle of cylindrical ingot by X-ray fluorescence spectrometry (Table I). Vickers hardness with a load of 5 kg (HV5) was measured on samples grinded on abrasive papers P800. The microstructure of alloys was observed by light microscopy and scanning electron microscopy (Tescan Vega 3 LMU). For this purpose, the samples were grinded using SiC abrasive papers P180–P4000, polished by diamond pastes with 2 and 0.7 µm particles and etched in 2 ml HNO₃ + 100 ml H₂O solution.

Phase and chemical composition were studied by energy dispersion spectrometry (Oxford Instruments Inca

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TABLE I

Chemical composition of investigated magnesium alloys (wt%).

	Mg	Mg3Gd	Mg3GdY	Mg2Gd7Zn
Mg	99.9	96.99	96.08	90.9
Gd	< 0.01	2.8	3.03	1.94
Y	< 0.01	< 0.01	0.89	< 0.01
Zn	0.01	< 0.01	< 0.01	6.91
Fe	< 0.004	< 0.004	< 0.004	< 0.004
Ni	< 0.004	< 0.004	< 0.004	< 0.004
Cu	< 0.004	< 0.004	< 0.004	0.11
Si	0.03	< 0.01	< 0.01	0.02
Al	0.04	< 0.01	< 0.01	0.024
Mn	< 0.01	0.03	< 0.01	0.03

350) and X-ray diffraction (X'Pert Philips, 30 mA, 40 kV, X-ray radiation Cu K_{α}). The corrosion behaviour was studied by immersion tests that were performed in aerated physiological solution (9 g/l NaCl) at initial pH = 6.5. Before the tests, the samples were grinded on SiC abrasive papers and degreased with ethanol. Samples with approximately 20 mm in diameter and 3 mm in thickness were clamped at two points in plastic mounts and immersed in a physiological solution for 336 h at 25 °C. The ratio of the volume of the physiological solution and surface area of the specimen was kept on the value of 36 ml/cm².

After exposure tests, corrosion products were removed by pickling for 5 min in a solution containing 200 g/l CrO₃. Corrosion rates were calculated from weight losses after pickling in 200 g/l CrO₃ measured with an accuracy of 0.1 mg. Moreover, potentiodynamic curves were measured with SCE (Ag/AgCl/KCl — 3 mol/l) as reference electrode and platinum wire as counter electrode from -0.2 V/Eocp to +0.8 V/Eocp. The scanning rate was 2 mV/s. The pH changes were recorded during exposure experiments.

3. Results and discussion

3.1. Structures and mechanical properties

Structures of alloys with RE elements that were observed by optical microscope are displayed in Fig. 1. These alloys were characterized by dendritic structure with substantial dendritic microsegregations. The solubility of Gd and Y at the eutectic temperature in binary Mg–Gd and Mg–Y system is 23.49 and 12.47 wt%, respectively [9].

Although concentrations of Gd or Y in studied alloys are significantly lower in comparison with their solubility at eutectic temperature, structure of studied Mg–Gd and Mg–Gd–Y alloys was composed of a solid solution of α -Mg (white areas in Fig. 1) and eutectic Mg₅Gd phase in the form of cuboid-shaped compounds with size in the range between 0.5 and 1 μ m (Fig. 2). These phases were preferentially distributed at the interface of dendrites in the areas with the highest dendritic microsegregation (dark areas in Fig. 1a, b). In both systems, 20

Fig. 1. Microstructure of alloys: (a) Mg3Gd, (b) Mg3Gd1Y, (c) Mg2Gd7Zn.

measurements of energy dispersive spectroscopy (EDS) analyses confirmed the presence of Mg₅Gd phase with average composition of 48.2 ± 6.3 wt% of Gd for Mg₅Gd and 51.6 ± 4.9 wt% of Gd for Mg₅Gd1Y. Moreover, in the case of Mg–Gd–Y system, from 2 up to 4 wt% of Y was provided in this phase. The reason for this may be in the small size of eutectic phases, so the results are influenced by composition of solid solution adjacent to Mg₅Gd phases. Differences in the contents of Gd in Mg–Gd, Mg–Gd–Y solid solution due to the dendritic microsegregation were in the range from 1 wt% up to 4 wt% inside the dendrites. However, it may be assumed higher content of Gd at the interface of dendrites. These values cannot be measured directly by EDS due to the large influence of eutectic phases with higher content of Gd. Yttrium concentrations were in the range from 0.5 to 1.5 wt%.

Fig. 2. Mg_5Gd phase in Mg_3Gd binary alloy.

The microstructure of $\text{Mg}_2\text{Gd}_7\text{Zn}$ was composed of solid solution of $\alpha\text{-Mg}$ (white areas in Fig. 1c), Mg_5Gd and Mg-Gd-Zn ternary phase that were distributed at the interface of dendrites (black areas in Fig. 1c). Due to the interaction of Zn and Gd, the solubility of these elements in matrix is decreased. It is the reason why the ternary phases are formed. Moreover, it is known that Zn/Y or Zn/Gd weight ratio influence the phase formation [10–12]. Zn/Gd ratio in $\text{Mg}_2\text{Gd}_7\text{Zn}$ corresponds to Mg_3GdZn_6 phase (*I*-phase).

Fig. 3. *I*-phase in $\text{Mg}_2\text{Gd}_7\text{Zn}$ alloy.

TABLE II

Vickers hardness and corrosion rate of investigated alloys.

	Mg	Mg_3Gd	Mg_3GdY	$\text{Mg}_2\text{Gd}_7\text{Zn}$
HV5	29.7 ± 3	42.5 ± 2.4	45.6 ± 1.9	49.8 ± 2.6
corrosion rate [mm/y]	3.61 ± 0.32	0.29 ± 0.02	3.20 ± 0.38	3.13 ± 0.65

This phase was proved by diffraction analyses (Fig. 3). Due to the obvious dendritic microsegregations it may be considered that the increase of the Vickers hardness in comparison with pure Mg was probably caused by solid solution strengthening and not only by the presence of intermediate phases in the structure. Average values of HV5 (Table II) were calculated from 20 measurements on the specimen.

3.2. Corrosion behaviour

Magnesium is a non-noble metal. It corrodes in acidic, neutral and slightly alkaline environments but in strongly alkaline environment a passive $\text{Mg}(\text{OH})_2$ layer is formed. The presence of other phases that are more noble than Mg may lead to microgalvanic corrosion. This kind of

corrosion behaviour was described in different magnesium alloys such as AZ, AE, WE, WZ, etc. It was shown that higher amount of β phase in structure of AZ91 alloy may act as a barrier and increase corrosion resistance. On the contrary, a lower amount of β phase acts as a cathode and increases the corrosion rate by microgalvanic corrosion between $\alpha\text{-Mg}$ and β phase [13]. Similar behaviour may be expected in other types of magnesium alloys. Corrosion rates of Mg, Mg_3Gd , Mg_3GdY and $\text{Mg}_2\text{Gd}_7\text{Zn}$ alloy are shown in Table II. It is evident that the addition of 3 wt% of Gd to pure Mg rapidly decreases the corrosion rate to nearly 0.29 mm/y. Although addition of Y and Zn is considered to have a positive effect on corrosion resistance of magnesium alloys, corrosion rates of Mg–Gd–Y and Mg–Gd–Zn were much higher in comparison with binary Mg_3Gd . Moreover, these values were only slightly lower in comparison with the corrosion rate of pure Mg. The reason may be attributed to higher content of intermetallic phases and more significant structure inhomogeneity as a consequence of higher concentration of alloying elements. In this case Mg_5Gd phase acts as a cathode while $\alpha\text{-Mg}$ is preferentially dissolved due to the anodic process. Corrosion reaction is spread especially from the interface between solid solution and intermetallic phases. Due to the dissolution of matrix, intermetallic phases may be released from the surface. In $\text{Mg}_2\text{Gd}_7\text{Zn}$ alloy, *I*-phase is considered to have bad effect on corrosion resistance of Mg–Y–Zn or Mg–Gd–Zn alloys [10, 11]. It is evident from potentiodynamic measurements (Fig. 4) that $\text{Mg}_2\text{Gd}_7\text{Zn}$ alloy is characterized by a higher corrosion potential. Zinc increases the corrosion potential of the alloy but the majority of this element is concentrated in intermetallic phases. Although the corrosion potential of this alloy is more positive in comparison with Mg_3Gd , the difference between corrosion potentials of solid solution and intermetallic phases with zinc significantly increases the corrosion rate by microgalvanic cell.

Fig. 4. Potentiodynamic curves of investigated alloys in 9 g/l NaCl solution.

Fig. 5. Diffraction pattern of Mg3Gd binary alloy after an immersion test.

Fig. 6. SEM images of surfaces after exposures in physiological solution (a) Mg3Gd; (b) Mg3Gd1Y.

After corrosion exposures, surfaces of all samples were covered by $\text{Mg}(\text{OH})_2$ that was identified by XRD measurements (Fig. 5). However, regular and compact layer

was observed only on the surface of Mg3Gd binary alloy (Fig. 6a). Mg3GdY and Mg2Gd7Zn alloys were characterized by irregular disturbed layers with significant pits as a consequence of galvanic corrosion (Fig. 6b).

4. Conclusion

The structures of Mg–Gd, Mg–Y–Gd and Mg–Gd–Zn alloys were quite inhomogeneous containing dendritic microsegregations and intermetallic phases. The corrosion resistance of investigated alloys was influenced by galvanic cell between solid solution and Mg_5Gd or Mg_3GdZn_6 phases. Compact and protective surface layers of magnesium hydroxide were formed only on the surface of Mg3Gd binary alloy. The remaining alloys significantly suffer from localized corrosion.

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