Microstructure, mechanical and corrosion properties of Mg–Dy–Gd–Zr alloys for medical applications ☆

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ABSTRACT

In previous investigations, a Mg–10Dy (wt.%) alloy with a good combination of corrosion resistance and cytocompatibility showed great potential for use as a biodegradable implant material. However, the mechanical properties of Mg–10Dy alloy are not satisfactory. In order to allow the tailoring of mechanical properties required for various medical applications, four Mg–10(Dy + Gd)–0.2Zr (wt.%) alloys were investigated with respect to microstructure, mechanical and corrosion properties. With the increase in Gd content, the number of second-phase particles increased in the as-cast alloys, and the age-hardening response increased at 200 °C. The yield strength increased, while the ductility reduced, especially for peak-aged alloys with the addition of Gd. Additionally, with increasing Gd content, the corrosion rate increased in the as-cast condition owing to the galvanic effect, but all the alloys had a similar corrosion rate (∼0.5 mm year^{-1}) in solution-treated and aged condition.

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1. Introduction

Mg alloys have attracted much attention for their potential use in medical applications owing to their low Young's modulus (40–45 GPa) compared with Ti alloys (Ti6Al4V, 114 GPa) and stainless steels (193 GPa), appropriate strength compared with bone, good biodegradability and bioresorbability [1–3]. Even though Mg and its alloys have been investigated as implants for almost two centuries, implants of Mg and its alloys are yet to be commercialized. One of the key issues preventing this is that Mg and its alloys would lose mechanical integrity before sufficient healing of body tissues could take place, which can be caused by low mechanical properties, high corrosion rate and localized corrosion [1]. One of the effective approaches to overcoming this is the use of alloying elements and heat treatments to enhance the mechanical properties and corrosion resistance, but eliminate localized corrosion behavior.

Many Mg-based alloy systems, such as Mg–Ca [4,5], Mg–Zn [6,7], Mg–Sr [8–10], Mg–Y [11], Mg–RE (RE = rare earth) [12–15] systems, are proposed for medical applications. Mg alloys containing RE elements, such as WE43 (Mg–4Y–3RE, wt.%) and AE42 (Mg–4Al–2RE, wt.%), have already shown a good combination of mechanical and corrosion properties in structural application. This has led to a continuous evaluation of RE-containing Mg alloys for

medical applications. In vivo studies on LAE442 (Mg–4Li–4Al–2RE, wt.%) alloy for orthopedics applications show that it has a low corrosion rate and an acceptable host response [16–18]. The more advanced applications are biodegradable cardiovascular stents made of Mg–RE alloys. Heublein et al. [19] reported on the degradation of AE21 (Mg–2Al–1RE, wt.%) in a coronary artery, and concluded that the vascular implants made of Mg alloys seemed to be a realistic alternative to permanent implants. Moreover, several clinical human trials have been conducted with biodegradable stents made of Mg–RE, and it was found that the Mg–RE stents had good biocompatibility, but the combination of mechanical and corrosion properties needs further improvement [20,21]. Mg–RE alloy was the only Mg alloy used in clinical trials reported to date [21]. These previous investigations indicate that some of the RE-containing Mg alloys are promising candidates for use as degradable biomaterials.

Previous work has shown that Mg–10Dy alloy has a low corrosion rate, uniform corrosion behavior and good cytocompatibility [22,23]. However, the mechanical properties of Mg–10Dy alloy are not satisfactory. Moreover, Mg–10Dy alloy shows no age-hardening response during ageing [24], which limits the potential for tailoring mechanical properties by heat treatment. Gd has similar chemical properties but better age-hardening response compared with Dy [25,26]. Based on earlier research [15,27], the use of Gd as alloying element seems to be suitable. Furthermore, Gd-based contrast agents are widely used as contrast media in magnetic resonance imaging, as the biocompatibility of Gd is acceptable [28–30]. Therefore, Mg–10(Dy + Gd)–0.2Zr alloys are developed in the present work to enhance the age-hardening response and to tailor

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the mechanical properties by replacing some of the Dy in Mg–10Dy alloy with Gd. The addition of Gd is expected potentially to improve the age-hardening response, while reducing the ductility. Meanwhile, the total amount of Dy and Gd is set at 10 wt.% to maintain the corrosion resistance. A small amount of Zr was added to the alloys as a grain refinement agent to obtain a homogeneous microstructure.

2. Experimental procedure

2.1. Material preparation

Mg–10(Dy + Gd)–0.2Zr alloys were designed, and their nominal chemical compositions are listed in Table 1. High-purity Mg (99.94%; Magnesium Elektron, UK) was molten in a mild steel crucible under a protective atmosphere (Ar + 2% SF_6). Pure Dy (99.5%; Grirem, Beijing), pure Gd (99.5%; Grirem, Beijing) and Mg–33 wt.% Zr master alloy (Magnesium Elektron, UK) were added to the melt at 720 °C in nominal amounts. The melt was stirred for 30 min at 200 rpm and then poured into a mold preheated to 500 °C. The filled mold was held at 670 °C for 30 min under the protective gas to let the heavy impurities settle to the bottom and let the light impurities float up to the top of the ingots. Then permanent mold direct chill casting [31] was used to prepare the alloys. The size of the ingots was Ø12 × 20 cm. After casting, both the bottoms and tops of the ingots were cut away, and the middle parts were used for further investigation. Solution treatment (T4) was carried out at 520 °C for 8 h, followed by water quenching. Ageing treatment (T6) was performed at 200 °C for various times followed by air cooling.

The chemical composition of the alloys and impurities were analyzed using an X-ray fluorescence (XRF) analyzer (Bruker AXS S4 Explorer, Germany) for Dy, Gd, Zr and Ni, and using spark optical emission spectroscopy (Spectrolab M9 Kleve, Germany) for Fe and Cu. The Ni content could not be determined by spark optical emission spectroscopy, owing to interference from strong Dy peaks. Therefore, the Ni content was determined from the XRF results. The content of Zr at the bottom of the ingots (the cut away part) was also measured using XRF.

2.2. Microstructure analysis

Specimens were ground using silicon carbide emery paper up to 2500 grit, and mechanically polished. The optical microstructure was characterized using a light microscope (Reichert-Jung MeF3, Germany) with a polarization system. Grain sizes were determined using the line intercept method [32]. For scanning electron microscopy (SEM), specimens were electropolished using an electrolytic apparatus (LectroPol-5, Struers Inc). A Zeiss Ultra 55 (Carl Zeiss GmbH, Oberkochen, Germany) SEM instrument, operating at 15 kV, equipped with energy dispersive X-ray spectroscopy (EDX) was used to observe the microstructure.

Transmission electron microscopy (TEM) specimens were ground mechanically to ~120 µm and then thinned by twin jet electropolishing in a solution of 2.5% $HClO_4$ and 97.5% ethanol at ~−45 °C and a voltage of 40 V. The TEM examinations were carried out on a Philips CM 200 instrument operating at 200 kV.

For the phase analysis, X-ray diffraction (XRD) measurements were performed using a diffractometer (Siemens D5000, Germany) with Cu $K_{\alpha 1}$ radiation (wavelength λ = 0.15406 nm) and a secondary monochromator. The step size was 0.02°, and the time at each step was 3 s. CaRIne crystallography software (version 3.1) was used to simulate the diffraction peak of β′ phase based on its crystal structure (orthorhombic, a = 0.64, b = 0.22, c = 0.52) [33,34].

2.3. Mechanical tests

Hardness measurements were carried out using a Vickers hardness test machine (Karl Frank GMBH, Germany) with a load of 5 kg and a dwelling time of 10 s. Ten points were averaged for each test condition. Tension and compression tests were performed at room temperature using a Zwick 050 testing machine (Zwick GmbH & Co., KG, Ulm, Germany) according to DIN EN 10002 [35] and DIN 50106 [36]. Tensile specimens with gauge length 30 mm, diameter 6 mm and threaded heads of 10 mm were used. The compression specimens were cylinders with a height of 16.5 mm and a diameter of 11 mm. Both tension and compression tests were done at a strain rate of 1×10^{-3} s^{-1}. A minimum of three specimens were tested for each condition.

2.4. Corrosion

Weight loss tests were performed in a cell culture medium (CCM) under cell culture conditions (37 °C, 21% O_2, 5% CO_2, 95% rH). The CCM consisted of Dulbecco's modified Eagle medium (DMEM; Life Technologies, Darmstadt, Germany) and 10% fetal bovine serum (PAA Laboratories, Linz, Austria). The composition of the DMEM can be found elsewhere [23]. Compared with simulated body fluid and Hanks' solution, the composition of CCM is closer to real body fluid. The cell culture conditions are more similar to an in vivo environment. The specimens size $10 \times 10 \times 10$ mm^3 were prepared by grinding each side with 2400 grid emery paper and degreasing the surfaces with ethanol prior to corrosion tests. For the corrosion tests in CCM, the specimens were sterilized in 70% ethanol for 15 min before the tests, and all subsequent procedures were carried out under sterile conditions. The specimens were immersed in CCM with a ratio of 1.5 ml cm^{-2} for 14 days. Corrosion products were removed by immersing the specimens in chromic acid (180 g l^{-1}) for 20 min at room temperature. The average corrosion rate was calculated in millimeters per year (mm y^{-1}) using the following equation [37]:

$$CR = \frac{8.76 \times 10^4 \times \Delta g}{A \cdot t \cdot \rho}$$

where Δg is weight change in grams, A is the surface area in square centimeters, t is the immersion time in hours, and ρ is the density of the alloy in grams per cubic centimeter. At least three specimens were tested for each condition. In order to understand the corrosion mechanism, the corrosion morphology was examined.

3. Results

3.1. Chemical compositions

Table 2 shows the experimentally measured compositions of Mg–Dy–Gd–Zr alloys. The loss of alloying elements was ~10–20% for Gd and Dy, but was much higher for Zr (~85%). Only ~0.03 wt.% Zr was detected in the middle part of the ingots. However, the content of Zr at the bottom of the ingots (the part cut away) was ~1 wt.%, which is much higher than its nominal content (0.2 wt.%). No Ni content was detected using XRF. Since the detec-

Table 1
Nominal chemical composition of experimental alloys (wt.%).

Alloys	Code	Dy	Gd	Zr	Mg
Mg–10Dy–0.2Zr	D10k	10		0.2	Balance
Mg–8Dy–2Gd–0.2Zr	DG82K	8	2	0.2	Balance
Mg–5Dy–5Gd–0.2Zr	DG55K	5	5	0.2	Balance
Mg–2Dy–8Gd–0.2Zr	DG28K	2	8	0.2	Balance