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Magnesium alloys as implant materials – Principles of property design for Mg–RE alloys ☆

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ABSTRACT

Magnesium alloys have attracted increasing interest in the past years due to their potential as implant materials. This interest is based on the fact that magnesium and its alloys are degradable during their time of service in the human body. Moreover magnesium alloys offer a property profile that is very close or even similar to that of human bone. The chemical composition triggers the resulting microstructure and features of degradation. In addition, the entire manufacturing route has an influence on the morphology of the microstructure after processing. Therefore the composition and the manufacturing route have to be chosen carefully with regard to the requirements of an application. This paper discusses the influence of composition and heat treatments on the microstructure, mechanical properties and corrosion behaviour of cast Mg–Gd alloys. Recommendations are given for the design of future degradable magnesium based implant materials.

1. Introduction

The great interest in magnesium and its alloys as degradable material for implants has led to numerous publications in this field [1–22]. Alloys like AZ91, AM50, LAE442 and WE43 have been under investigation. Standard tests were applied and their mechanical properties and corrosion behaviour evaluated under standard conditions and in simulated body fluids. From these tests, the conclusion has been drawn that these alloys are good potential implant materials. This conclusion seems to be questionable to some extent because, in most cases, the studies did not consider the interactions of all the alloying elements and common impurities with cells.

In most cases, standard commercial alloys contain more components than their designation shows [23–29]. Almost any aluminium-containing commercial magnesium alloy also contains manganese in the range of 0.4–0.6 wt.%. Even silicon is allowed in an amount up to 0.3 wt.%. In general, impurities may sum up to a total content of 0.3 wt.%, and very often these impurities are not listed in detail or even analysed. Moreover, the composition is even more complicated when it comes to magnesium alloys that contain rare earth elements. The E in the designation of a number of magnesium alloys represents rare earth elements (REE) in general (yttrium has its own designation letter, W). In the standard practice of alloying Mg with REE, so-called hardeners are widely used. These are basically master alloys which contain a major REE, like cerium or neodymium, and almost any other REE in different amounts up to 25 wt.% [29]. When the compositions of REE-containing magnesium alloys in particular are carefully contemplated, it is obvious that the influence of the entire group of REE is not thoroughly considered. In general, in the case of standard alloys of the AZ, AM, WE and LAE series, the impression is given that these materials have been selected simply because they are readily available.

For standard magnesium alloys the different alloying elements have been introduced for specific reasons. Due to the use of magnesium alloys as constructional materials, quite often the mechanical properties are of primary consideration. For example, in the case of Al as the alloying element it can be used both for solid solution strengthening and for precipitation hardening, both of which are useful when the yield stress needs to be improved [24–30]. However, almost any strengthening also has a detrimental influence on the ductility. With regard to the Mg–Al phase diagram, it is also obvious that Al lowers the melting and casting temperatures [31]. Therefore the use of Al also has an influence on the processing route. In consequence, both the alloying elements and the processing parameters influence the formation of the microstructure,

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which is responsible for the properties relevant to an application. Similar considerations can be made for other alloying elements.

Strength is often regarded as a critical property, especially for a mechanical engineer. However, it is not the only property that has to be considered [19,28,30]. Ductility, elastic moduli, corrosion behaviour under service conditions, rate of degradation (if applicable) and toxicology, amongst others, are also part of the property profile, which is basically influenced by the alloy composition and by the different processing steps applied before a component is ready, e.g. as a functional implant. The different properties that are required for an implant also require a vast number of different methods to determine them. This needs a highly interdisciplinary approach and interaction of specialists from different fields of research [19].

A number of cast Mg alloys containing gadolinium and additional REE have been investigated recently [32–52]. These investigations have shown that Gd can be used to adjust mechanical properties with a wide range of alloy compositions and heat treatments due to its large solubility of 23.49 wt.% at the eutectic temperature and the formation of intermetallic phases like Mg_5Gd (Fig. 1) [31]. As a single alloying element, Gd is present in solid solution, and can be used in a concentration-dependent manner to contribute to precipitation strengthening. Although many authors state that gadolinium is highly toxic, the acute toxicity is only moderate. The intraperitoneal LD_{50} dose of $GdCl_3$ was 550 mg kg^{-1} in mice, while $GdNO_3$ induced acute toxicity ar a concentration of 300 mg kg^{-1} in mice and 230 mg kg^{-1} in rats, respectively [53,54]. Tests regarding the cytotoxicity of Gd in osteoblast-like cells showed that it could be a suitable element with which to design Mg–Gd-based implant materials for medical applications [55]. Additionally, there is increasing evidence that many REE exhibit anticarcinogenic properties, which could lead to multifunctionailty of the designated alloys [56–59]. On the other hand, Gd-based contrast agents are widely used as the contrast medium in magnetic resonance imaging [60–62]. However, there are indications that Gd ions released by transmetallation can induce nephrogenic systemic fibrosis in patients with renal failure, though not in healthy patients [63]. Although this would be a noteworthy problem in, for example, vascular applications, Gd has also been observed to have a certain retention rate in bone prior to redistribution to spleen and liver [64]. Bearing in mind this retention, and the ability to control the corrosion rate by careful alloy design, it can be envisaged that the release of Gd ions could be controlled such that it would not evoke systemic effects. In this paper binary Mg–Gd alloys are investigated to determine the influence of different amounts of Gd and of subsequent heat treatments on microstructure and properties.

2. Materials and methods

For the present investigation, Mg–2 wt.% Gd, Mg–5 wt.% Gd, Mg–10 wt.% Gd and Mg–15 wt.% Gd were used. High-purity magnesium was melted in mild steel crucibles under a protective atmosphere (Ar + 2% SF_6). Gd was added as a pure element at a melt temperature of 750 °C. The melt then was stirred for 30 min at 200 rpm to prevent the Gd from settling prior to casting. The melt was poured into preheated mild steel moulds (550 °C) to produce plates (300 mm × 210 mm × 30 mm) for further investigations. The mould was made up from two mirror-inverted halves, including the gating system. Fig. 2 shows the schematic sketch of one half of the mould. A filter (Foseco SIVEX FC) was used to assure the cleanliness of the cast ingots.

All materials were investigated in the as-cast condition (F) and after solutionizing (T4) and artificial ageing (T6) heat treatments [65]. For the T4 treatment, a temperature of 525 °C was chosen and the specimens were annealed for 24 h. A water quench of the specimens followed immediately after the heat treatment. Ageing at 250 °C for 6 h was done for the T6 treatment on specimens that had also been solutionized for the T4 conditions.

To investigate the microstructure all materials were grinded, polished and etched according to Kree et al. [66]. Microstructures were investigated using a Zeiss Ultra 55 (Carl Zeiss GmbH, Oberkochen, Germany) scanning electron microscope (SEM) including energy-dispersive X-ray analysis (EDX) to determine the local chemical compositions. Transmission electron microscopy (TEM) investigations were employed on thin foil samples of the different

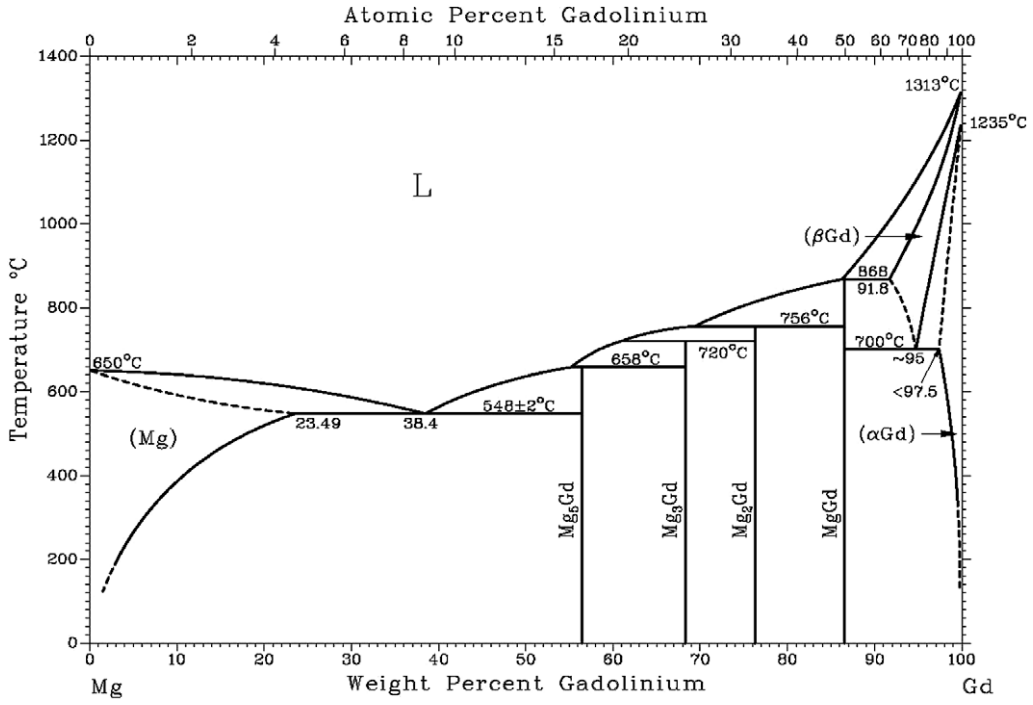

Fig. 1. Mg–Gd phase diagram.