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Effects of Zr addition on the multi-scale second-phase particles and fracture behavior for Mg-3Gd-1Zn alloy

W. Fu [a], R.H. Wang [b], H. Xue [a], J. Kuang [a], J.Y. Zhang [a, *], G. Liu [a, **], J. Sun [a, ***]

[a] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, 710049, PR China
[b] School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, PR China

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ABSTRACT

Here we report the effects of Zr addition (0.1–0.3 at.%) on the multi-scale second-phase particles and fracture behavior for Mg-3Gd-1Zn (at.%) alloys. Microstructural features of the alloys in the as-cast, solutionized, and aged conditions have been investigated in detail. The results have revealed that the cast alloys are mainly composed of α-Mg matrix, eutectic phase $(Mg, Zn)_3Gd$, 14H long period stacking ordered (LPSO) structure and cuboid shaped GdH_2 phase. After solution heat treatment, the eutectic phase $(Mg, Zn)_3Gd$ has transformed to X phase with 14H-LPSO structure, which has different distributions and morphologies due to different Zr additions. When the Zr addition is 0.3 at.%, a large amount of microscale Mg(Gd, Zn, Zr) particles appear along the grain boundaries. After aging heat treatment, Mg-3Gd-1Zn alloy with basal precipitates γ'' exhibits poor age-strengthening response. In contrast, Zr addition to the Mg-3Gd-1Zn alloy gave rise to a strong age-strengthening response. The strength improved significantly due to dense distribution of nanoscale prismatic plate β' and β_1 precipitates, which are not observed in the Zr-free alloys. One key finding of this study is that Zr contributes to formation of the prismatic precipitates, and their amount increase with increase of Zr addition. The mechanical damage for these alloys is a sequence of microscale GdH_2 or Mg (Gd, Zn, Zr) particles cracking, followed by fracture of the surrounding particles, and finally the growth/coalescence of micron-voids in the α-Mg matrix. The fracture of microscale particles was quantitatively analyzed by a Weibull model.

1. Introduction

Magnesium (Mg) alloys containing rare earth (RE) metals have attracted increasing attention in the automotive, aerospace industries etc., owing to their high specific strength, good damping capacity/cast-ability/machinability/thermal stability/creep resistance and easy recyclability [1–7]. Among various Mg-RE alloys, Mg-Gd alloy is one of the most promising materials for the advantages of high strength through precipitate hardening [8]. For the Mg-Gd alloys containing less than 1.0 at.% (~6 wt%) Gd, there exhibits little or no precipitation hardening for the lack of appreciable volume fraction of precipitates [9]. When the Gd addition is above 1.67 at.% (~10 wt%), the formation of prismatic plate precipitate gives rise to a remarkable precipitation-hardening response [10–14]. In addition, adding Zn to the Mg-Gd alloys results in the formation of basal plates γ'' and γ' phases [15] and/or long period stacking ordered (LPSO) structure [16–19], which are very helpful to the improvement of strength and ductility.

Zirconium (Zr) is a potent grain refiner for Mg alloys. Qian et al. [20–22] have investigated the effects of Zr on Mg alloys, and found that Zr is beneficial to the grain refinement by promoting nucleation from heterogeneous zirconium-rich cores in the most grains. Zr is not only a grain refiner, but also has great influences on the multi-scale second-phase particles [23–28], including nanoscale precipitates, sub-micron-scale and microscale particles. For example, Honma et al. [23] have investigated the composition of precipitate β', β_1 and LPSO by three-dimensional atom probe (3DAP) in the Mg-2Gd-1.2Y-Zn-0.2Zr (at.%) alloy, and found each precipitate contains considerable Zr element, which is higher than the nominal composition 0.2 at.%. Also, Sitzmann et al. [24] have

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: jinyuzhang1002@mail.xjtu.edu.cn (J.Y. Zhang), lgsammer@mail.xjtu.edu.cn (G. Liu), junsun@mail.xjtu.edu.cn (J. Sun).

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investigated chemistry of β' precipitates in the Mg-Nd-Y-Zr alloy using atom probe tomography, and found unexpectedly high Zr concentration in the precipitates. Thermodynamic calculations and experimental observations indicate the sub-micron Zn_2Zr particles are formed during casting process, and were stable at the homogenization temperature in the commercial ZK60 alloy [25]. Furthermore, Fu et al. [26] have studied four kinds of sub-micron second-phase particles containing Zr, which is block-like ZrH_2, globular Zn_2Zr_3 and the other two Zr-containing particles in the NZ30K alloy. Adding Zr to Mg-Gd-Zn alloys could change the distribution and morphology of microscale LPSO phase [27], and introduce fine Mg (Zn, Zr) precipitates [28].

As mentioned above, Zr has great effects on the multi-scale second phase, which in turn influences on their strength and ductility, especially on the fracture behavior. Fracture is closely related to nucleation, growth/coalescence of voids [29–31]. The second-phase particles [32,33] or twins [34,35] usually serve as microcrack initiation and propagation sites. The competition between particles and twins is strongly dependent on the experimental conditions [36]. In addition, the nanoscale second-phase also affects the deformation and fracture of Mg alloys. Up to now, relatively few studies have concentrated on the role of multi-scale second phase particles in the fracture behavior of Mg alloys.

Mg-Gd-Zn-Zr alloy with second-phase including nanoscale precipitates and microscale LPSO structure is promising in developing high strength/toughness Mg alloys. Understanding the effects of Zr addition on the multi-scale second-phase particles and fracture behavior in the Mg-Gd-Zn alloy is crucial for the design of alloys with enhanced strength and ductility. Here we prepared Mg-3Gd-1Zn alloys with different Zr additions, and investigated their mechanical properties based on the microstructural observations by using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The alloying mechanisms of Zr addition on the multi-scale second-phase and fracture behavior for the Mg-Gd-Zn alloys were discussed in detail.

2. Experimental procedures

2.1. Material preparation and heat treatments

The nominal composition of Mg alloys were Mg-3Gd-1Zn (at.%), Mg-3Gd-1Zn-0.1Zr (at.%), Mg-3Gd-1Zn-0.2Zr (at.%), and Mg-3Gd-1Zn-0.3Zr (at.%), which are named as GZ31, GZ31-0.1Zr, GZ31-0.2Zr and GZ31-0.3Zr, respectively. The chemical composition of these alloys was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), as listed in Table 1. One can see that the actual composition is quite close to the nominal one. These alloys were prepared from high pure Mg (≥99.99 wt%), Zn (≥99.99 wt%), and master alloys of Mg-6.19 at. % Gd and Mg-10.25 at. % Zr. They were induction melted in a graphite crucible under a protected argon atmosphere at approximate 740 °C, and then poured into a steel mold preheated at 200 °C. To avoid texture effect and clearly reveal the second-phase effects, the cast alloys were studied. All the samples covered by MgO powders were subjected to the same heat treatment, i.e., solution treated at 500 °C for 12 h, followed by quenched into hot water of approximate 80 °C and subsequently aged at 200 °C for a series of time. The maximum error of all the temperature measurements in the experiments was ±1 °C.

Table 1
Actual chemical composition (at. %) of the four alloys, as obtained by ICP-AES.

Materials	Nominal composition	Gd	Zn	Zr	Mg
GZ31	Mg-3Gd-1Zn	2.87	0.97	–	Bal.
GZ31-0.1Zr	Mg-3Gd-1Zn-0.1Zr	2.83	0.94	0.09	Bal.
GZ31-0.2Zr	Mg-3Gd-1Zn-0.2Zr	2.84	0.94	0.18	Bal.
GZ31-0.3Zr	Mg-3Gd-1Zn-0.3Zr	2.89	0.95	0.27	Bal.

2.2. Microstructural characterizations

Microstructures of these Mg alloys were examined using optical microscopy (OM). Metallographic specimens were treated in standard surface preparation procedures, which were etched using an acetic-picric solution (10 ml acetic acid, 6 g picric acid and 8 ml H_2O in 70 ml ethanol). The volume fraction of primary intermetallic particles was measured using point counting with a grid containing 900 points [37,38]. Ten random views on each of the three specimens per alloys were examined. Scanning electron microscopy (SEM) with energy dispersive spectroscope (EDS) was employed to determine size of the primary intermetallic particles [37]. At least 200 particles were measured for average. Transmission electron microscopy (TEM), equipped with an Oxford INCA energy-dispersive X-ray (EDX) spectrometer was employed to determine the compositions of the cuboid-shaped particles.

Precipitates in the aged alloys were characterized by TEM/HRTEM. All the TEM foils were twin-jet electro-polished by using a solution of 5.3 g lithium chloride and 11.2 g magnesium perchlorate mixed in 500 ml methanol and 100 ml 2-butoxy-ethanol at −55 °C and 0.1 A. Quantitative measures of the number density and size of the precipitates were reported as average value of more than 300 measurements. For the plate-shaped precipitates, the volume fraction was determined by employing a corrected projection method [39,40], in which the foil thickness of each captured region was obtained through convergent beam electron diffraction patterns [41]. Using the raw radius data of particles and the foil thickness in each area, the radius distributions were calculated after correction for the truncation effects based on a method by Crompton et al. [42]. Details about the measurements of plate-shaped precipitates can be found in our previous publications [38,39,43,44].

2.3. Measurements of mechanical properties

Tensile test was performed on an Instron-type tester to measure yield strength and ductility (elongation to failure) of the alloys before and after aging treatment. Specimens with the dimension of 17 mm × 3 mm × 2 mm were tensile tested at a constant strain rate of $5 \times 10^{-4}\ s^{-1}$ at ambient temperature. Stress-strain curves were recorded and the yield strength was determined as the 0.2% offset.

3. Results

3.1. Microstructures of the as-cast, solutionized and aged alloys

Microstructures of the as-cast GZ31 alloys with different Zr additions are shown in Fig. 1. In the GZ31 and GZ31-0.1Zr alloys, coarse dendrite α-Mg grains were observed (Fig. 1(a and b)). With increasing Zr addition in GZ31-0.2Zr and GZ31-0.3Zr alloys, the grain size of the α-Mg decreases (Fig. 1(c and d)). Fig. 1(e and f) show SEM micrographs of the as-cast alloys. They all have similar microstructures, consisting of α-Mg matrix, $(Mg, Zn)_3Gd$ phase, LPSO and GdH_2 particles. The eutectic phase of block $(Mg, Zn)_3Gd$ particles are distributed along the eutectic boundaries, as marked by yellow arrows in Fig. 1, consistent with the previous results [16,17,19]. The amount of $(Mg, Zn)_3Gd$ particles increases greatly with increasing Zr contents. The lamellar LPSO structure within the α-Mg grain is also observed, as marked by blue arrows in Fig. 1. In addition, some cuboid shaped GdH_2 phase can be observed near the