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Precipitation evolution and hardening in Mg–Sm–Zn–Zr alloys

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ABSTRACT

Precipitation evolution and its correspondence to mechanical properties in Mg–4Sm–xZn–0.4Zr (x = 0, 0.3, 0.6, 1.3) (wt%) alloys are systematically investigated in this work. Precipitation sequences at 200 °C are identified using transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). A new precipitate β'_Z is found to present with the increase of Zn addition. With higher Zn content (>~1 wt%), basal γ-series precipitates dominate. The transition in precipitation sequence agrees well with the change of mechanical properties. The microstructure and property evolution in the optimum Mg–4Sm–0.3Zn–0.4Zr alloy is modeled based on obtained experimental data through a combination of classical nucleation and growth model and the CALPHAD (CALculation of PhAse Diagram) simulation. The obtained parameters are then used to predict the properties of other Mg–Sm–Zn–Zr alloys under other heat treatment conditions. Good agreements are found between the calculated and measured data, which validate the accuracy of the current database and suggest a powerful tool for future optimization of this promising alloy system.

1. Introduction

Magnesium (Mg) is the lightest structural metal and has been increasingly used in industries including aerospace, automotive and portable electronic devices where weight reduction is critical [1–4]. However, current commercial magnesium alloys provide limited mechanical properties which hinder its widespread applications [2–6]. Recently, a series of Mg-rare earth (RE) alloys, including Mg-Yttrium (Y), Mg-Cerium (Ce), Mg-Neodymium (Nd), and Mg-Gadolinium (Gd), have been developed [5,7–9] with improved mechanical properties. The main strengthening mechanism in Mg-RE based alloys is precipitation hardening of nano-scale Mg-RE precipitates in the α(Mg) matrix produced during aging treatment, and/or solid solution hardening [5]. Zirconium (Zr) is usually added in Mg-RE alloys as a grain refiner to provide additional strengthening effect by reducing the grain size [10].

Samarium (Sm) is one of the least expensive RE elements, about 20% the cost of Nd or Y [11]. The solid solubility of Sm in α(Mg) matrix decreases with temperature: 5.7% (540 °C) – 4.3% (500 °C) – 1.8% (400 °C) – 0.8% (300 °C) – 0.4% (200 °C) (wt%) [7], which makes it suitable for age hardening. The nearest intermetallic from the Mg side is $Mg_{41}Sm_5$, formed by a eutectic reaction similar to those in other Mg-RE systems [12]. Mg–Sm is thus considered as a promising, lower-cost alternative to other more expensive Mg-RE alloys and has great potential for future industrial applications. Significant age-hardening response of Mg–4Sm–0.5Zr (all composition in wt% except otherwise stated) alloy during 200 °C isothermal aging was reported by Zhang [13], i.e., about 66% increase in UTS (ultimate tensile strength) after peak-age treatment. Nishijima et. al. [14] investigated the precipitation evolution in Mg–0.99 at.% Sm (MgMACROBUTTON InsGlyph e4Sm). The precipitation sequence was proposed to be: Super Saturated Solid Solution (S.S.S.S) → Guinier-Preston zone (G. P. zone) ($D0_{19,}$ a = 0.642 nm, c = 0.521 nm) → β' (Mg_5Sm, orthorhombic, a = 0.642 nm, b = 3.334 nm, c = 0.521 nm) → β_1 (Mg_3Sm, FCC, a = 0.74 nm), and the main strengthening precipitates was identified as β'. In this article, all notations follow those of ref. [5] unless otherwise stated.

It has been reported that the strength of many age-hardened Mg-RE–Zr alloys can be further enhanced by controlled addition of zinc (Zn) [5,15]. Small addition (<~1 wt%) of Zn promotes strength and creep resistance, while larger addition (>~1 wt%) of Zn

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changes the prismatic ({11$\bar{2}$0}, or {10$\bar{1}$0}) β-series precipitates to basal ({0001}) γ-series, which are less effective in impeding basal dislocation motions [5]. The precipitation sequence of Mg–4Sm–1Zn–0.4Zr was investigated by the current authors as: S.S.S.S. → solute clusters → γ" (G. P. zone I, a = 0.556 nm, c = 0.414 nm) → γ' (G. P. zone II, a = 0.556 nm, c = 0.414 nm) (→ stacking faults) → γ (FCC, a = 0.74 nm) [16]. Yuan and Zheng [17,18] investigated the effect of Zn on the mechanical properties of Mg–xZn–3Sm–0.5Gd alloys (x = 0, 0.3, 0.6). It was reported that with the increase of Zn the strength of the peak-aged alloys increases first and then decreases. However, the lack of clear understanding of the structure-property relationship of Mg–Sm–Zn–Zr alloys restrains further development of this promising alloy system.

In the last few decades, CALPHAD (CALculation of PHAse Diagrams) modeling has been used to accelerate the design and development of new alloys [19]. More recently, the CALPHAD approach has been broadened to a holistic ICME (Integrated Computational Materials Engineering) framework in the design and development of new materials and products [19–23]. For precipitation-hardening alloys, precipitation kinetic parameters can be modeled based on thermodynamic description, atomic mobility and microstructure data of the alloys. Mechanical properties such as yield strength upon aging are predicted using these kinetic models. This approach has been successfully applied to simulate the precipitation evolution and strengthening effect in many alloy systems including Ni, Al and Mg [20–23]. The application of this approach in the development of novel alloys simplifies the composition design procedure and reduces the development cost [19].

In this research, age-hardening response of a series of Mg–Sm–Zn–Zr alloys is investigated to optimize the alloy composition. Since the precipitation sequence of the Zn-free Mg–Sm–Zr has been reported, the focus of precipitation analysis in this work is on those in low (0.3 wt%), medium (0.6 wt%), high (1.3 wt%) Zn-content Mg–Sm–Zn–Zr alloys, which are investigated using transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). The types, structures, and orientation preferences of precipitates are identified along with the number density, size and volume fraction of the dominant precipitation responsible for hardening. The precipitation evolution and hardening effect in the optimized alloy are then modeled using the previously-mentioned integrated simulation approach according to the experimental data from this work and literature. Mechanical properties of other Mg–Sm–Zn–Zr alloys are predicted with the obtained parameters. The purpose of this study is to provide a systematical understanding of the microstructure evolution and structure-property relationship of Mg–Sm–Zn–Zr alloys, and to apply this understanding to build a simulation tool within the ICME framework for further optimization of this promising alloy system.

2. Experimental procedure

Four sample alloys with target compositions of Mg–4Sm–xZn–0.4Zr (x = 0, 0.3, 0.6, 1.3) were prepared using commercially pure Mg (>99.95 wt%), Zn (99.99 wt%), MgMACROBUTTON InsGlyph e20Sm and Mg–30Zr master alloy ingots. The materials were melted in a graphite crucible coated with boron nitride. Cover gas CO_2-0.5 vol% SF_6 was used to protect the melt from oxidation and burning. The liquid melt was stirred 3–5 times to ensure the homogeneity prior to cast into a steel permanent mold preheated at 200 °C. The chemical composition of each alloy was then analyzed by energy dispersive spectrometer (EDS) area scan and the results are listed in Table 1. As-cast samples were cut into rectangular

Table 1
Compositions of sample alloys.

Sample	Target composition (wt%)	Measured composition (wt%)
0Zn	Mg–4Sm–0.4Zr	Mg–4.3Sm–0.8Zr
0.3Zn	Mg–4Sm–0.3Zn–0.4Zr	Mg–4.4Sm–0.4Zn–0.6Zr
0.6Zn	Mg–4Sm–0.6Zn–0.4Zr	Mg–4.4Sm–1.1Zn–0.4Zr
1.3Zn	Mg–4Sm–1.3Zn–0.4Zr	Mg–4.3Sm–1.7Zn–0.7Zr

pieces approximately 10 mm × 5 mm × 5 mm and cleaned with ethanol. Wrapped with tantalum foil, samples were sealed in glass tubes back-filled with high-purity He atmosphere (>99.999%) to avoid oxidation, and then annealed at 520 °C for eight hours for solution treatment. Aging treatments were conducted in a horizontal tube furnace at 200 °C for various lengths of time (0.5, 1, 2, 4, 6, 8, 10, 16, 32, 64, 200 h).

Microhardness tests were conducted on a Wilson Tukon 1102/1202 microhardness tester with 20 g load. At least 8 indents per sample were analyzed to improve precision. The average value is reported as the hardness and the error bars are calculated based on standard error. For compression tests, samples are machined to cylinders of 6.67 mm diameter and 10 mm height following a length/diameter ratio of 3:2 to avoid buckling [24]. A dry film graphite lubricant was sprayed evenly on the surface of the cylinders to reduce frictions with the compression parts. The experiments were immediately stopped when fractures were observed.

TEM (Tecnai TF30, 300 kV) experiments were conducted to identify and quantify the precipitate types, morphology and diffraction patterns. HAADF-STEM analyses were performed by a TITAN microscope with Cs corrector and EDS to study the structure of precipitates with atomic weight contrast. The Cs corrector allows resolution of about 0.07 nm. The evolution of precipitates in 0.3, 0.6, 1.3Zn Mg–Sm–Zn–Zr alloys were determined through observations on peak-aged, over-aged (64 h) and near-equilibrium (200 h) samples. Samples were prepared with the wedge polish method followed by ion milling. 1000 μm thick slices were cut from the samples and then ground down to ~50 μm using an Allied Multiprep machine with diamond lapping films. The polished samples were then ion-milled with Fischione 1050, (3.0 kV ion gun energy and 5° milling angle). Afterwards 0.6 kV ion gun energy was used to clean up the sample surfaces.

The dimensions of the precipitates were directly measured from TEM bright field micrographs. Precipitates were counted and the size of the observed region was measured for each micrograph. The thicknesses of the samples were measured by electron energy loss spectroscopy (EELS) on regions where microstructure was analyzed. For each region three EELS runs were performed and the average thickness value was used. It is approximated that the precipitate distribution is uniform through the volume. The number density of the precipitates (counts/m^3) was calculated by dividing the number of counts by the volume (image size times the thickness) of the observed region. For each sample, at least three images were analyzed with approximately 100 counts on each image. The volume fraction of precipitates was estimated by multiplying the number density and the mean volume.

3. Experimental results

Age-hardening responses of the Mg–Sm–Zn–Zr alloy samples at 200 °C are shown in Fig. 1. All four samples exhibit significant hardening effect during aging treatment, indicating precipitation hardening. The decrease of hardness during over-age period corresponds to coarsening of precipitate particles. The maximum hardness increase of each sample (0Zn, 0.3Zn, 0.6Zn, 1.3Zn samples) is: 34 HV, 34 HV, 32 HV, 29 HV, respectively. Thus, the age-