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 ($> \sim 1$ 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.

Keywords

Magnesium alloys; Alloy design; Age-hardening; Precipitation; CALPHAD; ICME

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 $\text{Mg}_{41}\text{Sm}_5$, 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 (Mg-4Sm). The precipitation sequence was proposed to be: Super Saturated Solid Solution (S.S.S.S) $\rightarrow$ Guinier-Preston zone (G. P. zone) ($D0_{19}$, $a=0.642\text{nm}$, $c=0.521\text{nm}$) $\rightarrow$ β' (Mg_5Sm , orthorhombic, $a=0.642\text{nm}$, $b=3.334\text{nm}$, $c=0.521\text{nm}$) $\rightarrow$ β_1 (Mg_3Sm , FCC, $a=0.74\text{nm}$), 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 ($< \sim 1$ wt.%) of Zn promotes strength and creep resistance, while larger addition ($> \sim 1$ wt.%) of Zn 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. $\rightarrow$ solute clusters $\rightarrow$ γ'' (G. P. zone I, $a=0.556\text{ nm}$, $c=0.414\text{ nm}$) $\rightarrow$ γ' (G. P. zone II, $a=0.556\text{ nm}$, $c=0.414\text{ nm}$) ($\rightarrow$ stacking faults) $\rightarrow$ γ (FCC, $a=0.74\text{nm}$) [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.%), Mg-20Sm and Mg-30Zr master alloy ingots. The materials were melted in a graphite crucible coated with boron nitride. Cover gas CO₂-0.5vol.% SF₆ 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 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 hr).

Microhardness tests were conducted on a Wilson Tukon 1102/1202 microhardness tester with 20g 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 hr) and near-equilibrium (200 hr) samples. Samples were prepared with the wedge polish method followed by ion milling. 1000 μ m thick slices were cut from the samples and then ground down to $\sim$ 50 μ m 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/m³) 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-hardening response of the Mg-Sm-Zn-Zr alloy diminishes with the increase of Zn. Furthermore, the time to reach peak hardness increases (6-8-10-16 hr), suggesting a kinetic delay.

The true stress-strain curves of the peak-aged samples are shown in Fig.2a and the $YS_{0.2}$ (yield strength at 0.2% strain), UCS (ultimate compression stress), and strain to failure are listed in Table 2. Both strengths increase with Zn initially and then decreases, while the ductility stays almost unchanged. The optimum composition is identified as Mg-4Sm-(0.3-0.6)Zn-0.4Zr. The plastic deformation mechanism is phenomenologically determined from strain hardening rate, i.e., $d\sigma/d\epsilon$, as a function of strain as shown in Fig.2b. Only plastic regions within 0.025-0.2 strain are shown for better observation. The continuous drop of strain hardening rate has been attributed to dislocation slip as controlling mechanism [24, 25]. The suppression of twinning is believed to be related to formation of precipitates [5, 26-28].

Figs.3a and 3b reveal TEM bright field micrographs and diffraction patterns of Mg-4Sm-0.3Zn-0.4Zr alloy sample peak-aged at 200°C for 8 hr with B//[0001]_α and B//[2 $\bar{1}$ 10]_α, respectively. Plate-like precipitates of ~10-25 nm in length and ~1-5 nm in thickness lie on {2 $\bar{1}$ 10}_α prismatic planes and are composed of small solute bands perpendicular to the elongation direction.

Forming along three equivalent directions of the hexagonal Mg lattice, these precipitates correspond to star-shaped reflections at $\frac{1}{2}\{01\bar{1}0\}_\alpha$ and $\frac{1}{2}\{2\bar{1}\bar{1}0\}_\alpha$ in the diffraction pattern. From the $[2\bar{1}\bar{1}0]_\alpha$ view, the precipitates are parallel to each other and lie on $\{01\bar{1}0\}_\alpha$ planes, causing the diffraction spots at $\frac{1}{2}\{01\bar{1}0\}_\alpha$. These features are identical to those of β' in Mg-4Sm alloy [14], suggesting the same structure: orthorhombic, $a=2a_{\text{Mg}}=0.642$ nm, $b=6\sqrt{3}a_{\text{Mg}}=3.334$ nm, $c=c_{\text{Mg}}=0.521$ nm. In this work these precipitates are referred as β'_H . The composition is deduced from the crystal structure as $\text{Mg}_5(\text{Sm}, \text{Zn})$. β'_H dominates in the peak-aged sample, and is thus the key precipitate responsible for precipitation hardening in the low-Zn (0.3 wt.%) Mg-Sm-Zn-Zr alloy.

The crystal structure of β'_H is verified by Z-contrast HAADF-STEM technique as shown in Fig. 3c, in which the contrast is proportional to the square of the atomic number of the element. $Z(\text{Sm})=62$, $Z(\text{Zn})=30$, $Z(\text{Mg})=12$, $Z(\text{Zr})=40$, which make the Sm, Zn, Zr columns brighter than those of Mg atoms. Zr only exists as particles of Zr-Zn solid solution in Mg-RE-Zn-Zr alloys [29]. Thus the bright spots in HAADF-STEM observations are Sm or Zn columns. As seen, the bright solute columns consist of “hexagonal ring” layers, which are seen as short bands in the bright field observations of Fig. 3a. In addition, individual “hexagonal ring” and “zigzag chain” are present, as labeled with white circles. Direct observation of the solute columns allows us to determine their structure as HCP, $a=0.642$ nm, $c=0.521$ nm, though the full crystal structure is absent. The composition is $\text{Mg}_3(\text{Sm}, \text{Zn})$, assuming a complete unit cell. While the “hexagonal rings” have been observed in Zn-free Mg-Sm-Zn alloys during early stage of aging treatment [14], the “zigzag chains” have never been reported for the current alloy system. The difference between them is the array of the basic “zigzag” solute atom arrangements shown by atomic

models in Figs.4a and 4b. In this work the “hexagon ring” and “zigzag chain” are named as G. P. zones I and II, respectively. Both G. P. zones are coherent with the $\alpha(\text{Mg})$ matrix.

Microstructures and diffraction patterns of over-aged (64 hr) and near-equilibrium (200 hr) 0.3Zn samples are shown respectively in Figs.5a and 5b, with $B//[0001]_{\alpha}$. The morphology and reflection spots of precipitates in the over-aged sample are identical to those of the peak-aged sample (Fig.3a), suggesting that β'_H dominates in the over-aged sample. Compared to Fig.3a, the dimensions of particles grow to $\sim 25\text{-}55$ nm, while the thicknesses stay almost unchanged $\sim 1\text{-}6$ nm. After 200 hr of aging, the precipitates change to $\sim 60\text{-}600$ nm in length and $\sim 10\text{-}20$ nm in thickness, and lie on $\{01\bar{1}0\}_{\alpha}$ prismatic plane. The morphology and diffraction pattern suggest it is β_1 having a FCC structure, $a=0.74$ nm. $\{110\}_{\beta_1} // \{0001\}_{\alpha}$. The complex reflection patterns are due to the fact that β_1 lie on three equivalent directions of Mg lattice.

It can be concluded that the precipitation sequence in low-Zn (0.3 wt.%) sample is the same as that in 0Zn Mg-Sm-Zr alloys. The results of quantitative measurements are listed in Table 3. Only the peak-aged and the over-aged samples are analyzed so the measured values are those of β'_H . The morphology of the particle is elliptical disc with the short (L1) and long (L2) diameter measured separately from the $[0001]_{\alpha}$ and $[2\bar{1}\bar{1}0]_{\alpha}$ views. While the growth along the short diameter is obvious, those in the other two directions are rare. The reason is believed to be the anisotropy of interfacial energy [30, 31]. As aging proceeds, the number density of particles decreases and the size increases, corresponding to the growth and coarsening stages in classical nucleation and growth theory. The volume fraction stays almost unchanged after the peak-age condition, indicating that equilibrium has been reached with a volume fraction of $\sim 3.3\%$. Similar phenomenon has been observed in NZ30K alloy (Mg-3Nd-0.2Zn-0.4Zr) [22]. Due to the similarities between these two alloy systems, the precipitation evolution of β'_H can as well be

described with the classical nucleation and growth model.

Fig.6a reveals typical microstructure and diffraction pattern of over-aged Mg-4Sm-0.6Zn-0.4Zr alloys, with beam parallel to $[0001]_{\alpha}$. While the reflection spots are similar to those of β'_H , broader features of ~ 6 nm in thickness and ~ 4 nm in length are present. The morphology is clearly different from that of β'_H while their amounts are comparable, as seen in HRTEM and HAADF-STEM micrographs in Figs.6b and 6c. A closer look at the broad feature gives better understanding of its structures, as exhibited by HAADF-STEM image in Fig.6d. Having a structure identical to those of β' precipitate in Mg-Gd and Mg-Y systems [32] (orthorhombic, $a=0.642$ nm, $b=2.224$ nm, $c=0.521$ nm), it is named as β'_Z in this work and its structure is modeled and shown in Fig.7. The composition is deduced from the crystal structure as $Mg_7(Sm, Zn)$. Compared to the observation in over-aged 0.3Zn sample (Fig.5a), the amount of β'_Z is obviously increased in the 0.6Zn sample after the same aging procedure. It is thus reasonable to suggest that the formation of β'_Z is favored by increase of Zn. The reason might be the dissolution of Zn in the precipitates, which increases the Gibbs energy of β'_H and decreases that of β'_Z . Similarities between G. P. zone I and β'_H as well as G. P. zone II and β'_Z are obvious, suggesting that the two G. P. zones lead to the formation of β'_H and β'_Z , respectively. As the final stage of precipitation within studied time range, both β'_H and β'_Z transition to β_1 . The precipitation sequence in low- and mid-Zn SZK alloy system is thus determined as S. S. S. S. $\rightarrow$ G. P. zones I, II $\rightarrow \beta'_H, \beta'_Z \rightarrow \beta_1$, as schematically shown in Fig.7.

Both β'_Z and β'_H are in contact with β_1 , indicating that both of them are involved in the formation of β_1 following a similar transition mechanism. This contact is commonly seen in Mg-RE-based alloys, while the transition mechanism remains controversial. Nie and Muddle [33] proposed that β_1 is generated from the $\alpha(Mg)$ lattice with a shear of ~ 0.22 on the $\{01\bar{1}0\}_{\alpha}$ plane, in which

case the contact with β' is to relieve the shear stress. Apps [34] suggested that both β' and β_1 form by nucleation and growth of β'' (Mg_3Sm , D0_{19} , $a=0.642\text{ nm}$, $c=0.521\text{ nm}$) that generates during earlier stage of precipitation. According to this physical picture, the center of β'' remains solute-rich and works as nucleus for β_1 . By growing from the residual β'' , the central β_1 remains in contact with β' at two ends. Although this theory explains the contacts between β' and β_1 , its overall validity is questionable since more recent studies [14, 15, 32] do not support the presence of β'' that has a full crystal structure of D0_{19} and a higher solute concentration Mg_3RE . In contrary, G. P. zones that are mostly dilute solute atom clusters dominate prior to β' . Fig.8a shows β_1 in contact with β'_H in 0.6Zn over-aged sample, $B//[0001]_\alpha$. β'_H is composed of “hexagon ring” layers as labeled with parallel lines in Fig.8b. The same kind of layer is clearly seen at the tip of β_1 . From these observations, it is proposed that a solute-rich region within β' , rather than β'' , acts as the nucleus for the formation of β_1 . This region is generated by long-range diffusion of solute atoms into the Mg lattice between the “hexagon ring” layers. In other words, the nuclei of β_1 form within β' after β' has formed. Growing from this region, the newly-formed β_1 is in contact with β' in two ends. Fig.8 suggests that β_1 grows as atomic planes fill in with (Sm,Zn) between the “hexagon ring” layers, labeled with red lines in Fig. 8b.

High additions of Zn into Mg-Sm-Zr system have been reported to introduce γ -series precipitates [16]. This is also observed in the current investigation. Figs.9a and 9b respectively show TEM bright field images and diffraction patterns of over-aged (64h) 0.6Zn and 1.3Zn samples, $B//[2\bar{1}\bar{1}0]_\alpha$. Needle-like precipitates of $\sim 10\text{-}30\text{ nm}$ long and $\sim 1\text{ nm}$ thick lie on $\{0001\}_\alpha$ basal planes. The density of these precipitates increases with the increase of Zn. The continuous streak in diffraction pattern along $\{0001\}_\alpha$ suggests it has a G. P. zone structure. These characteristics

indicate these needle-like precipitates are γ'' (G. P. zone I structure, HCP, $a=0.556$ nm, $c=0.414$ nm) [16]. γ'' is thus the key strengthening precipitates in the 1.3Zn sample.

Microstructures of grain boundaries are exhibited in Fig.10a of HAADF-STEM image and 10b of HRTEM observation. The FFT (fast Fourier transform) of the HRTEM image is also shown as small figure. The composition of the bright contrast grain boundary is measured with EDS: Mg-23.5Sm-2.5Zn-0.5Zr (at.%), i.e. Mg_3Sm . From the FFT, the beam is parallel to $[0001]_a$, as labeled with white squares, and $[011]_{Mg_3Sm}$, as labeled with white circles. Thus the FCC structure of Mg_3Sm is confirmed. In addition, a precipitate free zone (PFZ) with ~ 200 nm thickness is found near the grain boundary, which is attributed to depletion of vacancies and solute atoms near grain boundaries during heat treatment.

While the distribution of β_1 is mostly uniform, relatively fewer but larger β_1 particles segregate, as shown in Fig.10c. The composition of the particles is measured with EDS: Mg-28.0Sm-1.3Zn-0.7Zr (at.%), i.e., Mg_3Sm . The sizes of individual particles are ~ 10 -80 nm long and ~ 5 nm thick, while together they form a PFZ of ~ 500 nm $\times$ 20 nm area. Similar phenomenon was reported in ref. [15] and the segregation of these particles was believed to occur at early stages of precipitation. The resulted inhomogeneity is harmful for mechanical properties.

Zr solid solution particles are commonly seen as cuboid particles in Mg-RE-Zn-Zr alloys [12, 29, 35]. Similar particles are observed in the current work, as shown in Fig.11. The HAADF-STEM image reveals cuboid-like particle with brightest contrast and shadows with intermediate contrast near the two ends of the particle. EDS analysis gives composition of the particle as Mg-2.2Sm-27.3Zn-40.3Zr (at.%), i.e., Zr-Zn solid solution, and that of the shadows: Mg-22.5Sm-1.1Zn-0.2Zr (wt.%), i.e., Mg-20Sm. The Mg-20Sm is probably residual master alloy that did not completely melt during casting due to incomplete stir.

4. Discussion

The hardness values of peak-aged Mg-Sm-Zn-Zr alloys show a non-monotonic trend as a function of Zn concentration, first increasing and then decreasing as Zn is increased. The cause for this behavior can be explained by the precipitation evolution of the alloys shown in Table 4. The precipitation sequence in low-Zn ($< \sim 1$ wt.%) Mg-Sm-Zn-Zr alloys is S.S.S.S. $\rightarrow$ G. P. zones I, II $\rightarrow \beta'_H, \beta'_Z \rightarrow \beta_1$, while for higher Zn content ($> \sim 1$ wt.%) the dominant precipitate is basal γ -series. The Zn addition favors the formation of β'_Z , and introduces the γ -series precipitates. While the solubility of Zn in β -series is limited ($\sim 4\%$ in Mg-Nd-Zn-Zr alloys [15], $< 1\%$ in Mg-Gd-Y-Zn-Zr alloys [36]), it is much higher in γ -series [37]. It is reasonable to speculate that β -series are binary Mg-RE compounds with small solubility of Zn, while γ -series are Mg-RE-Zn ternary compounds. Dilute addition of Zn dissolves into the β -series precipitates and enhances precipitation by altering free energies or interfacial energies of β -series precipitates leading to increased volume fraction. With higher addition of Zn, the γ -series are thermodynamically favored and the amount of the β -series diminishes. Lying on $\{0001\}_\alpha$ basal planes, the γ -series precipitates are less effective at impeding basal dislocation glide, which is the main deformation mechanism of peak-aged Mg-Sm-Zn-Zr alloys at room temperature, assuming the same volume fraction as β -series [5]. In high-Zn alloys, the presence of γ -series is not able to compensate for the loss of β -series precipitates, resulting in decreased strength. Moreover, an increased high density of γ -series precipitates might decrease ductility. According to our measurements, the optimum Zn composition falls within 0.3-0.6 wt.%.

5. Simulation

The precipitation evolution and hardening of the optimum sample Mg-4Sm-0.3Zn-0.4Zr are modeled using a classical nucleation and growth model [39-42] integrated with the CALPHAD simulation [43]. Parameters are generated by fitting the model to the quantitative measurements of precipitates in this work. The model is then extrapolated to simulate age hardening of other Mg-Sm-Zn-Zr alloys reported elsewhere [13, 35]. Focus of analysis is set on the key precipitate β'_H . The G. P. zone I is pre- β'_H cluster and is assumed to be the nucleus for β'_H . Thus the precipitation hardening effect until over-age condition (64 hr) is dependent on nucleation, growth and coarsening of β'_H . The simulation flowchart is schematically shown in Fig.12. Thermodynamic description provides thermodynamic driving force for nucleation of β' particles and is obtained using CALPHAD method. Atomic mobility of solutes species describes the diffusion of solute atoms in $\alpha(\text{Mg})$ matrix, through which particles grow and coarsen, and is obtained with a CALPHAD-like approach [44]. Through integration with precipitation kinetic parameters, the microstructure evolutions are simulated. The simulation results are then compared with experimental measurements both from this work and from literature to validate their accuracy. All calculations are performed in the built-in models in the PanPrecipitation module of PandatTM [20]. This method is recently applied to development of Mg-Nd-Zn-Zr alloys by the current authors [23]. Due to the lack of information on the newly-developed Mg-Sm-Zn-Zr system, the simulation results of Mg-Nd-Zn-Zr system are adopted with minor modifications, providing a good example of extension of this integrated simulation approach.

Several assumptions are made to simplify the precipitation simulation. The small Zn solubility in β'_H is neglected so the chemical formula of β'_H is Mg_5Sm . Since deformation is dominated by dislocation motion, the effect of twinning is neglected. Moreover, the morphology of β'_H is converted from elliptical disc to sphere assuming that the latter has the same volume as the former. The purpose is to avoid the complex strengthening models based on plate-like precipitates [21, 38], and for future integration with other alloy systems. It should be noted that the anisotropic interfacial energy is not considered in this assumption. We therefore refer to it as effective interfacial energy. An additive rule is assumed for the different strengthening contributions coming from intrinsic, solid solution, and precipitation hardening.

The thermodynamic description of Mg-Sm-Zn system has been developed in a previous publication [12]. The formation energy of β'_H is obtained according to its equilibrium volume fraction in matrix: $-6200 + 1 \times T$ (J/mole), where T is temperature. Critical parameters used in this work are listed in Table 5. Figs. 13a-c reveal simulated microstructure evolution (precipitate's volume fraction, size and number density) of Mg-4Sm-0.3Zn-0.4Zr during isothermal age treatment at 200°C comparing with experimental measurements in this work. Good agreements are found between the calculated and measured values in all comparisons, which validate the accuracy of current precipitation simulation.

Age-hardening responses of Mg-4Sm-0.3Zn-0.4Zr, Mg-6Sm-0.3Zn-0.4Zr, Mg-8Sm-0.3Zn-0.4Zr alloys at 175°C, 200°C, 225°C are calculated and shown in Fig. 14a-c to compare with experimental data [35]. This comparison shows the ability of this model to accurately extrapolate the effects of chemical compositions and aging temperatures on the properties of Mg-Sm-Zn-Zr alloys. As seen separately in Figs. 14a, b, and c, hardness increases with increasing Sm content due to increase of volume fraction of the solute-rich precipitates. The kinetics, or the aging time

to reach peak hardness, exhibit negligible change under different Sm concentrations, but are significantly delayed at lower age temperature if one compares Figs.14a, b and c. These trends are successfully modeled by the current simulation. Major discrepancies are observed in the absolute hardness values especially in the 225°C comparison of Fig.14c. It should be pointed out that the parameters in this work are adopted from those of Mg-Nd-Zn-Zr alloys without specific assessment, making the discrepancies within expectations. The successful modeling of the trends suggests that the extension of precipitation simulation is valuable for novel Mg-RE-Zn-Zr alloy design and development.

6. Conclusion

This article presents an experimental investigation on precipitation hardening and evolution in a newly-developed Mg-Sm-Zn-Zr alloys, a promising low-cost alternative to commercial Mg-RE based alloys. Based on the experimental measurements a precipitation database is developed within the framework of CALPHAD approach. Major outcomes include:

- Age-hardening behavior and compression properties of Mg-4Sm-xZn-0.4Zr (x=0, 0.3, 0.6, 1.3) alloys are systematically investigated. All samples exhibit significant precipitation hardening effect. The optimum composition is determined as Mg-4Sm-(0.3-0.6)Zn-0.4Zr;
- The precipitation evolution and strengthening in the Mg-Sm-Zn-Zr system are illustrated for the first time. A new precipitate β'_Z is identified whose formation is favored with increase of Zn addition;
- The precipitation evolution and its correspondence to property in Mg-4Sm-0.3Zn-0.4Zr alloy are modeled by an integrated computational simulation method combining

CALPHAD and classical nucleation and growth model. Good agreement between simulation results and experimental measurements suggest accuracy of the current model, which will be a powerful tool for future optimization of this promising alloy system.

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Precipitation Evolution and Hardening in Mg-Sm-Zn-Zr alloys: a Combinatory Study of Experimental Investigation and Computational Simulation

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

Table 2. Compression properties of peak-aged Mg-4Sm-xZn-0.4Zr (x=0, 0.3, 0.6, 1.3) alloys

Sample	Condition	YS(MPa)	UCS(MPa)	Strain to failure
0Zn	200°C 6 hr	132	363	0.18
0.3Zn	200°C 8 hr	146	377	0.19
0.6Zn	200°C 10 hr	173	406	0.18
1.3Zn	200°C 16 hr	161	382	0.17

Table 3. Quantitative measurements of Mg-4Sm-0.3Zn-0.4Zr alloys (errors calculated by standard error)

Condition	Length1 (nm) (B//[0001] _a)	Length2 (nm) (B//[2 $\bar{1}$ 10] _a)	Thickness (nm)	Number density (10 ²² /m ³)	Volume fraction (%)
Peak-aged (8 hr)	12.1±0.6	33.8±0.9	2.6±0.1	3.86	3.28
Over-aged (64 hr)	28.4±1.5	34.0±1.8	3.7±0.2	1.21	3.36

Table 4. Summary of precipitates identified in this work

Phase	Structure	Composition	Morphology	Orientation Preference
G. P. zone I	HCP a=0.642 nm, c=0.521 nm	Mg ₃ (Sm, Zn)	“Hexagon rings” of solute atoms	-
G. P. zone II	HCP a=0.642 nm,	Mg ₃ (Sm, Zn)	“Zigzag chains” of solute atoms	-

	c=0.521 nm			
β'_H	orthorhombic, a=0.642 nm, b=3.334 nm, c=0.521 nm	Mg ₅ (Sm, Zn)	Elliptical plate-like, L1 ~10-30 nm, L2 ~20-50 nm, thickness ~1-4nm	$\{100\}_{\beta'_H} // \{0001\}_\alpha$, $[001]_{\beta'_H} // [0001]_\alpha$
β'_Z	orthorhombic, a=0.642 nm, b=2.228 nm, c=0.521 nm	Mg ₇ (Sm, Zn)	Elliptical plate-like, L1~2- 5 nm, L2 ~20-50 nm, thickness ~4-10 nm	$\{100\}_{\beta'_Z} // \{0001\}_\alpha$, $[001]_{\beta'_Z} // [0001]_\alpha$
β_1/γ	FCC, a=0.74 nm	Mg ₃ (Sm, Zn)	Plate-like, length ~60-600nm, thickness ~10-20nm	$[112]_{\beta_1} // [\bar{2}110]_\alpha$ $\}_{\beta_1} //$ α
γ''	Ordered hexagonal (GP I) a=0.556 nm c=0.414 nm [16]	Mg ₅ (Sm, Zn)	Needle-like, length ~5-20nm, thickness ~1-2nm	$[01\ 0]_{\gamma''} // [\bar{2}110]_\alpha$, $(0001)_{\gamma''} // (0001)_\alpha$

Table 5. Critical parameters used in the current simulation

Parameter	Value	Unit	description
		m ³ /mol	Molar volume of α (Mg) matrix
		m ³ /mol	Molar volume of β'_H precipitates
	23	J/m ²	Effective interfacial energy
		-	Nucleation site parameter

Fig.1. Age-hardening response of Mg-4Sm-xZn-0.4Zr (x=0, 0.3, 0.6, 1.3) alloys

(a)

(b)

Fig.2. (a): True stress-strain curves of peak-aged Mg-4Sm-xZn-0.4Zr ($x=0, 0.3, 0.6, 1.3$) alloys; (b): Strain hardening rate of peak-aged Mg-4Sm-xZn-0.4Zr ($x=0, 0.3, 0.6, 1.3$) alloys. (The curves are separated vertically (arrow) to allow comparison.)

(a)

(b)

(c)

Fig.3. (a): TEM bright field micrograph and diffraction pattern of peak-aged Mg-4Sm-0.3Zn-0.4Zr alloy, $B// [0001]_a$; (b): TEM bright field micrograph and diffraction pattern of peak-aged Mg-4Sm-0.3Zn-0.4Zr alloy, $B// [2\bar{1}\bar{1}0]_a$; (c): HAADF-STEM micrograph of peak-aged Mg-4Sm-0.3Zn-0.4Zr alloy, $B// [0001]_a$

- Mg, $z=0$
- Mg, $z=1/2$
- Sm/Zn, $z=0$
- Sm/Zn, $z=1/2$

(a)

(b)

(c)

Fig.4. Schematic atomic models of (a): G. P. zone I (“hexagonal ring”); (b): G. P. zone II (“zigzag chain”); (c): β'_H , from $[0001]_\alpha$ view, (visualized using VESTA [45])

(a)

(b)

Fig.5. (a): TEM bright field micrograph and diffraction pattern of over-aged (64 hr) Mg-4Sm-0.3Zn-0.4Zr alloy, B// $[0001]_{\alpha}$; (b): TEM bright field micrograph and diffraction pattern of near-equilibrium (200 hr) Mg-4Sm-0.3Zn-0.4Zr alloy, B// $[0001]_{\alpha}$

(a)

(b)

(c)

(d)

Fig.6. (a): TEM bright field micrograph and diffraction pattern (b): HRTEM micrograph; (c): HAADF-STEM micrograph; (d): magnified HAADF-STEM micrograph of over-aged (64 hr) Mg-4Sm-0.6Zn-0.4Zr alloy, B// $[0001]_\alpha$;

Fig.7. Dominant precipitation sequence in low-Zn (<~1 wt.%) Mg-Sm-Zn-Zr alloys, from $[0001]_{\alpha}$ view, (visualized using VESTA [45])

(a)

(b)

Fig.8. HAADF-STEM micrograph of β'_H in contact with β_1

(a)

(b)

Fig.9. TEM bright field micrograph and diffraction of over-aged (64 hr) (a): Mg-4Sm-0.6Zn-0.4Zr alloy; (b): Mg-4Sm-1.3Zn-0.4Zr alloy, B// $[2\bar{1}\bar{1}0]_a$

(a)

(b)

(c)

Fig.10. (a): HAADF-STEM image of grain boundary in Mg-4Sm-0.6Zn-0.4Zr; (b): HRTEM and corresponding FFT of grain boundary in Mg-4Sm-0.6Zn-0.4Zr; (c): HAADF-STEM image of segregation of large β_1 particles

Fig.11. HAADF-STEM observation of Zr particles in Mg-Sm-Zn-Zr alloys

Fig.12. Schematic strategy of computational simulation method used in this study

Fig.13(a)

Fig.13(b)

Fig.13(c)

Fig.13. Calculated (a): volume fraction; (b): size; (c): number density of β'_H precipitates in Mg-4Sm-0.3Zn-0.4Zr alloy aged at 200°C, in comparison with experimental measurements from this work

Fig.14(a)

Fig.14(b)

Fig.14(c)

Fig.14. Calculated age-hardening response of Mg-4Sm-0.3Zn-0.4Zr, Mg-6Sm-0.3Zn-0.4Zr, Mg-8Sm-0.3Zn-0.4Zr alloys at (a): 175°C; (b): 200°C; (c): 250°C, in comparison with experimental data from ref. [35]