HAADF-STEM images of precipitates

151°C, B//[2 $\bar{1}$ 10]_α 290°C, B//[2 $\bar{1}$ 10]_α 353°C, B//[2 $\bar{1}$ 10]_α

Precipitation Sequence and Kinetics in a Mg-4Sm-1Zn-0.4Zr (wt%) alloy

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Abstract

The present research presents a series of investigations into phase identification and precipitation sequence in Mg-4Sm-1Zn-0.4Zr¹ alloy, using differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). The precipitation sequence is: super saturated solid solution (S.S.S.S) $\rightarrow$ solute atom clusters $\rightarrow$ γ'' $\rightarrow$ γ' ($\rightarrow$ stacking faults) $\rightarrow$ γ . Structure of γ'' has been determined as an ordered hexagonal GP zone, $a=0.556\text{nm}$, $c=0.414\text{nm}$. γ' is composed of several γ'' layers. Kinetic studies show that quenched-in vacancies play an important role in the formation of solute clusters, while the growth of both precipitates are diffusion controlled. Analysis of microstructure evolution suggests that nucleation of γ' happens near existing γ'' precipitates.

Keywords: Mg-Sm-Zn-Zr alloys, precipitation, heat treatment, transmission electron microscopy, scanning transmission electron microscopy, kinetics

1. Introduction

Magnesium alloys have attracted considerable interest in transportation industries due to their low density, high specific stiffness, excellent castability, and other favorable attributes [1-4]. Addition of rare earth (RE) elements into Mg significantly improves strength and creep resistance through solid solution strengthening, precipitation hardening, and/or texture randomization [5, 6]. Studies on correlations between mechanical properties and microstructure evolution in several Mg-RE alloys, including yttrium (Y), cerium (Ce), neodymium (Nd), and gadolinium (Gd), have been reported [7-12]. Samarium (Sm) is considered as promising alloying

¹ All composition in wt.% except otherwise stated.

elements for Mg alloy optimization, due to its high solid solubility at high temperature ($\sim 530^{\circ}\text{C}$) and eutectic reaction near Mg side [13, 14]. Age-hardening response was reported in Mg-Sm-Zr alloys [15], in which ultimate tensile strength (UTS) improved dramatically from 172MPa to 286MPa, while elongation decreased only slightly, 9.2% to 8.4%. The dominant precipitate was reported as β'' (Mg_3Sm , D019, $a=0.642\text{ nm}$, $c=0.521\text{ nm}$), lying on $\{11\bar{2}0\}$ prismatic planes [15, 16]. Although contradictory reports can be found [17] stating the key precipitate is β' (Mg_7Sm , orthorhombic, $a=0.64\text{ nm}$, $b=3.334\text{ nm}$, $c=0.52\text{ nm}$), it can nevertheless be concluded that the prismatic β precipitates dominate the aging process [18] in Mg-Sm-Zr alloys.

Moderate ($<0.5\%$) addition of Zn enhances β -series formation, which is believed to increase creep resistance in Mg-RE alloys, while higher addition introduces γ -series precipitates that decrease aging response [18-22]. For example Yuan and Zheng [23, 24] investigated the effect of Zn on the aging behavior of Mg-xZn-3Sm-0.5Gd alloys ($x=0, 0.3, 0.6$), and found that with increase of Zn, the dominant strengthening precipitate changes from β'' to β' (orthorhombic, $a=0.64\text{ nm}$, $b=2.223\text{ nm}$, $c=0.52\text{ nm}$), and then to γ'' (HCP, $a=0.556\text{ nm}$). Similar aging response was reported in Mg-Sm-Zn-Zr [25], where the precipitation sequence was reported as super saturated solid solution (S.S.S.S) $\rightarrow$ solute atom clusters $\rightarrow \gamma''$ (Guinier Preston zone (GP zone), $a=0.556\text{ nm}$) $\rightarrow \gamma'$ (hexagonal, $a=0.556\text{ nm}$, $c=0.521\text{ nm}$) $\rightarrow \gamma$ (FCC, $a=0.73\text{ nm}$). The main strengthening precipitate is γ'' , which was identified as a single solute atom layer. It should be noted that for the structure of γ'' , while most researchers considered it as an ordered GP zone from diffraction pattern and assumed $c=c_{\text{Mg}}=0.521\text{ nm}$, Nie [26] identified $c=0.444\text{ nm}$, by direct observation through high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Such a discrepancy indicates that modification is necessary to determine the structure of γ'' .

The dominance of γ -series precipitates, lying on (0001) basal planes, results in decrease in age hardening response as Zn content is increased, because the γ -series are less effective at impeding dislocations than the β -series precipitates are. Thus a clear understanding of the γ -series and the conditions under which they dominate is of essential importance for development of Mg-RE-Zn-Zr alloys. Although there have been some investigations on mechanical properties and microstructure evolution of Mg-Sm-Zn-Zr alloys, limited work is focused on precipitation kinetics of γ -series, and structures of them remain controversial. In this work, we present a systematical study on the nature and kinetics of γ precipitates, using transmission electron microscopy (TEM), HAADF-STEM, and differential scanning calorimetry (DSC), aiming to provide a comprehensive understanding of the microstructure evolution, properties of metastable precipitates, and kinetics of precipitation in relative high Zn content Mg-RE-Zn-Zr alloys, for further alloy design and processing optimization.

2. Experiment

Sample alloy with a target composition of Mg-4Sm-1Zn-0.4Zr were prepared using commercially pure Mg, Zn ($>99.9\%$), Mg-20Sm and Mg-30Zr master alloy ingots. The alloying ingredients were melted in a steel crucible, cast into a steel mold preheated to 230°C under protection of SF_6/CO_2 , and then degassed by bubbling pure Argon for about 20min at 740°C . The chemical composition of the as-cast sample alloy was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and determined as Mg-4.36Sm-1.27Zn-0.39Zr. For protection

against oxidation during heat treatment, all samples were wrapped with tantalum foil and sealed in quartz tubes back-filled with high-purity He atmosphere (>99.999%) before heating.

Solid solution treatment was conducted at 520°C for 8 hours, followed by quenching in room temperature (RT) water. The solid solutionized (S.S) samples were subsequently cut to small pieces of around 2x2x1 mm³ (~20mg), then cleaned with ethanol before DSC tests, which were performed on a DQ100 Differential Scanning Calorimeter from TA instruments. Standard aluminum pans were used as references as well as to encapsulate the samples. During the measurement, samples underwent cyclic thermal treatment from 40°C to 450°C, for three cycles, with 4 different heating rates of 5, 10, 15 and 20°C/min, respectively. The third cycle (over-aged condition) was used to establish a background, which was subtracted from the first cycle (S.S condition).

To identify precipitates formed in this process, S.S samples were heated at 10°C/min to temperatures where exothermic or endothermic peaks were measured in the 10°C/min DSC curve, held for 3 minutes, then quenched in RT water. These samples were subsequently analyzed by Transmission Electron Microscopy (TEM, FEG-Tecnai-TF30, 300kV) and Scanning Transmission Electron Microscopy (STEM, TITAN, 200kV) to identify the precipitation reactions that dominate at those peak temperatures. For sample preparation, 1000µm-thick slices were cut from these bulk samples and ground down to ~50µm, using Allied Multiprep machine with diamond lapping films (15, 6, 3, 1, then 0.1µm particle size). The polished samples were then ion milled with Fischione 1050, (3.0kV ion gun energy and 5° milling angle). Finally, 0.6kV ion gun energy was used to clean up surface.

3. Results and Discussion

Precipitation Sequence

Fig. 1 shows the DSC curve of S.S sample at heating rate of 10°C/min. Exothermal peaks are found at approximately 151, 290, and 353°C, representing three different precipitation reactions. Figs. 2a and b show HRTEM and corresponding Fast Fourier Transform (FFT) images of sample alloy heated to peak temperature 151°C, on zone axis [0001]_α and [2 $\bar{1}\bar{1}$ 0]_α, respectively. HRTEM image near [0001]_α show dark areas randomly distributed in the grain without specific diffraction features, tentatively identified as clusters of solute atoms. With zone axis near [2 $\bar{1}\bar{1}$ 0]_α, fig. 2b reveals that solute atoms cluster to form multiple atom layers with streaks in the corresponding FFT image.

Microstructures and corresponding diffraction patterns of the sample alloy annealed at 290°C are shown in figs. 3a-b, taken near zone axis [0001]_α and [2 $\bar{1}\bar{1}$ 0]_α, respectively. From fig. 3a, no obvious features can be observed in TEM bright field image. In corresponding diffraction pattern extra spots are found at 1/3 and 2/3 {2 $\bar{1}\bar{1}$ 0}_α, representing a phase with hexagonal structure and a=0.556nm. Fig.3b reveals 5-20nm long and 1-2nm thick needle-like precipitates, lying on (0001)_α basal planes. Strong streaks are present along {0001}_α in the corresponding diffraction pattern, indicating a GP zone structure. Atomic structure of this needle-like precipitate is shown by HAADF-STEM image in Fig.3c. The contrast of HAADF-STEM image is proportional to square of the atomic number of the element. Thus the light spots represent Sm or Zn atom columns. Apparently, instead of a single solute atom layer as reported in [25], two Sm/Zn layers

lie on the Mg matrix, with one Zn/Mg layer in between. Compared with Mg atoms (0.137nm), smaller Zn atoms (0.120nm) release the strain from the large Sm atoms (0.181nm). Such a structure, together with diffraction patterns, resembles γ'' in Mg-Gd-Zn alloys, and could be determined as ordered hexagonal, $a=0.556\text{nm}$. It is named as γ'' in this work. The orientation relationship with Mg matrix is such that $[10\bar{1}0]_{\gamma''} // [2\bar{1}\bar{1}0]_{\alpha}$. Taking c constant of Mg as 0.521nm [27], the distance between Sm layers could be measured directly as $c=0.414(\pm 9)\text{nm}$, which is close to that reported for γ'' in Mg-Gd-Zn system (0.444nm). The chemical composition is derived from the crystal structure as $(\text{Mg,Zn})_5\text{Sm}$, though a full crystal structure is not observed since γ'' has a GP zone structure.

Diffraction patterns of phase product of transition reaction at 353°C are shown in figs.4a and b, with beam parallel to $[0001]_{\alpha}$ and $[2\bar{1}\bar{1}0]_{\alpha}$, respectively. Similar extra spots at $1/3$ and $2/3\{2\bar{1}\bar{1}0\}_{\alpha}$ are present when $B//[0001]_{\alpha}$, and similar streaks can be found along $\{0001\}_{\alpha}$ when $B//[2\bar{1}\bar{1}0]_{\alpha}$. Such diffraction features suggest presence of a phase with a structure similar to γ'' . Microstructure observations reveal laminate structures of 15-80nm in length, as shown in fig.4c and d. Fig.4e and f show that each laminate structure is composed of two or more layers of solute atoms, which have the same structure as γ'' , making them GP II zones. In this work they are named as γ' . Apparently formation of γ' might involve nucleation and growth of a new layer of γ'' next to the existing γ'' . In this structure, the adjacent γ'' layers are separated by 3 or 4 layers of Mg atoms, thus the distance between are $2c_{\text{Mg}}$ or $2.5c_{\text{Mg}}$.

It was pointed out in [25] that the equilibrium precipitate in γ series is γ (FCC, $a=0.74\text{nm}$), but in this work there is no sign of γ , except on the grain boundaries, as seen in fig.5a taken from the 353°C sample. From the FFT image (fig.5b) the beam is parallel to $[001]_{\gamma}$, and the FCC structure could thus be determined. Besides, the precipitate free zone (PFZ) with $\sim 200\text{nm}$ thickness could be found near the grain boundary, which is attributed to depletion of vacancies and solute atoms near grain boundaries during heat treatment. Overall, the DSC signal increases steadily after 330°C (fig.1), which is probably related to formation of γ .

Precipitation Kinetics

The DSC curves of S.S samples at four heating rates are presented in fig. 6. Peak temperatures increase with increasing heating rates, indicating these precipitation reactions are kinetically controlled. Kinetic properties of these precipitates can thus be calculated based on John-Mehl-Avrami-Kilmogoroc (JMAK) relation [28-32], in which volume fraction of precipitate phases is related to kinetic laws of growth. For non-isothermal processes, several methods have been developed based on this relation [33-37] for calculation of kinetic parameter. Among them, the Kissinger method [35], which takes into account the shift of peak positions under different heating rates, has been most commonly used. Here, the relation between peak temperature T_p and heating rate ϕ is

$$\ln \frac{T_p^2}{\phi} = \frac{Q}{RT_p} + C \quad (1)$$

Where R is gas constant, C is a constant, Q is activation energy and $Q = \frac{Q_N + nQ_G}{n+1}$ [38], in which Q_N is nucleation activation energy and Q_G is growth activation energy. n is time exponent.

According to Farjas [38], the general equation for calculation of the fraction of transformed phases for non-isothermal processes can be written as:

$$X = 1 - \exp\left\{-k_0 C \frac{Q}{R\phi} p\left(\frac{Q}{RT}\right)\right\}^{n+1} \quad (2)$$

Here X is the fraction of transformed phase, $p(x) = \int_x^\infty \frac{\exp(-\mu)}{\mu^2} d\mu$. With a first-order approximation,

$$p(x) \approx \frac{\exp(-x)}{x^2} \quad (3)$$

In DSC analysis, $X_i(t)$, the fraction of transformed phase at peak i (phase transition reaction i) as a function of temperature, can be defined by using the following equation

$$X_i(t) = \frac{A_i(T)}{A_i} \quad (4)$$

A_i represents total area of the peak i , and $A_i(T)$ is the area of the peak i at temperature T . The fraction of transform phase can thus be represented as a function of temperature.

Rearranging Eq(2) and substitute p with Eq(3) gives [38]

$$\ln[-\ln(1 - X)] = (n + 1) \ln \left[\frac{\exp\left(-\frac{Q}{RT}\right)}{\left(\frac{Q}{RT}\right)^2} \right] + (n + 1) \ln(k_0 C \frac{Q}{R\phi}) \quad (5)$$

Since $(n + 1) \ln(k_0 C \frac{Q}{R\phi})$ is constant under the same heating rate for the same phase transition reaction, one can plot $\ln[-\ln(1 - X)]$ vs $\ln \left[\frac{\exp\left(-\frac{Q}{RT}\right)}{\left(\frac{Q}{RT}\right)^2} \right]$ and the slope gives $n + 1$.

Calculation results are listed in Table.1, along with precipitates' morphologies and structures. For the 151°C peak, phase product is solute atom clusters, and the corresponding activation energy is 75kJ/mol. Such a value is much lower than the activation energy reported for self-diffusion (134kJ/mol [39]) of Mg, and higher than that for vacancy migration (48kJ/mol [40]). Therefore the migration of quenched in vacancies plays an important role in the formation of these clusters. This conclusion is supported by the calculated time exponent, i.e., 0.21. This value suggests that the nucleation happens instantaneously [41], which is expected because of its coherent nature, and growth happens with the help of defects or vacancies [41].

The activation energies of γ'' is calculated as 132kJ/mol, indicating it is diffusion-controlled growth and quenched-in vacancies are no longer effective. Growth of γ'' is shown in Fig. 7a-d for alloys annealed at 340°C for 3min, 353°C for 1min, 3min, 6min, respectively, all on zone axis

$[2\bar{1}\bar{1}0]_{\alpha}$. Comparing fig.7a with fig.3b, the length of γ'' increases from 5-20nm to 10-50nm, while the thickness remains unchanged, indicating diffusional growth in one dimension and agreeing to the activation energy. The time exponent of γ'' is 1.56, close to that reported for γ'' in Mg-Nd-Zn system (1.5) [20], and corresponding to growth from small particles [42]. This is to be expected since pre-existing solute atom clusters work as nuclei for γ'' . The length of γ' grows from 15-80nm to 20-100nm with increasing annealing time as shown in fig.7b-d., corresponding to diffusional growth indicated by the calculated activation energy of γ' , i.e. 140 kJ/mol. It is difficult to assess the time exponent using the Avrami analysis because the peak is too small compared to the background.

It is interesting to notice that in addition to γ' , a long (>100nm), thin (~1-5nm) linear feature could be observed after annealing at 353°C for 6min, as labeled with red arrow in fig.7d. Being similar to stacking faults reported in Mg-Gd-Zn system [44], this feature is tentatively determined as stacking fault. Lack of observation of this feature during age hardening [25] indicates that it has a very low number density and little effect on age hardening in Mg-Sm-Zn-Zr alloys.

4. Conclusion

1. Precipitation sequence in a high-Zn Mg-Sm-Zn-Zr alloy has been identified as: S.S.S.S $\rightarrow$ solute atom clusters $\rightarrow \gamma'' \rightarrow \gamma'$ ($\rightarrow$ stacking faults) $\rightarrow \gamma$. Structure of γ'' has been determined as an ordered hexagonal GP zone, $a=0.556\text{nm}$ and the c constant has been measured directly with HAADF-STEM observation: $c=0.414\text{nm}$. γ' has a GP II structure and is composed of several γ'' layers.
2. Kinetic studies show that quenched-in vacancies play an important role in the formation of solute clusters, while the growth of γ'' and γ' are diffusion controlled under equilibrium vacancy concentrations. Analysis of microstructure evolution suggests that nucleation of γ' happens near existing γ'' precipitates.

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Table.1. Characteristics and kinetic parameters of metastable phases in Mg-4Sm-1Zn-0.4Zr

Phase	Structure	Morphology	Activation energy (kJ/mol)	Time exponent
Solute atom clusters	-	-	75	0.21
γ''	Ordered hexagonal (GP I) a=0.556nm c=0.414nm	Needle-like 5-20nm long 1-2nm thick	132	1.56
γ'	Ordered hexagonal (GP II) a=0.556nm c=0.414nm	Plate 20-80nm long 5-15nm thick	140	-

Figure captions

Fig.1. DSC curve of S.S sample alloy at 10°C/min

Fig.2. TEM Bright Field images and corresponding Fast Fourier Transform images of sample alloy annealed 151°C (a): B//[0001]_α; (b): B//[2 $\bar{1}$ $\bar{1}$ 0]_α

Fig.3. TEM Bright Field image and corresponding Diffraction Patterns of sample alloy annealed 290°C at 10°C/min (a): B//[0001]_α; (b): B//[2 $\bar{1}$ $\bar{1}$ 0]_α; (c): HAADF-STEM image of the same sample, B//[2 $\bar{1}$ $\bar{1}$ 0]_α

Fig.4. Diffraction Patterns of sample alloy annealed 353°C at 10°C/min (a): B//[0001]_α; (b): B//[2 $\bar{1}$ $\bar{1}$ 0]_α; (c): TEM Bright Field image of the same sample, B//[2 $\bar{1}$ $\bar{1}$ 0]_α; (d-f): HAADF-STEM image of the same sample, B//[2 $\bar{1}$ $\bar{1}$ 0]_α

Fig.5. TEM Bright Field image of the 353°C sample alloy (a): grain boundary, B//[2 $\bar{1}$ $\bar{1}$ 0]_α; (b): HRTEM of the grain boundary and corresponding Fast Fourier Transform (FFT) image

Fig.6. DSC curves of S.S sample alloys at 5, 10, 15, 20°C/min

Fig.7. TEM Bright Field image of the sample alloys annealed at (a): 340°C for 1min; (b): 353°C for 1min; (c): 353°C for 3min; (d): 353°C for 6min, B//[2 $\bar{1}$ 10]_α

Fig.1

(a)

(b)

Fig.2

(a)

(b)

(c)

Fig.3

(a)

(b)

(c)

(d)

(e)

(f)

Fig.4

Fig.5

Fig.6

(a)

(b)

(c)

(d)

Fig.7

Precipitation sequence in a high-zinc magnesium-samarium-zinc-zirconium alloy has been identified;

Structures of metastable precipitates are modified directly with HAADF-STEM;

Kinetic calculations were performed to understand nucleation/growth mechanisms of these precipitates