Microstructure evolution of semi-solid Mg–10Gd–3Y–0.5Zr alloy during isothermal heat treatment

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Abstract

In this study, the microstructure evolution of semi-solid Mg–10Gd–3Y–0.5Zr alloy during isothermal heat treatment has been investigated. The results show that primary particles coarsen continuously during the holding. Coarsening rate decreases with the increase of isothermal temperature. When isothermal temperature increases from 600 °C to 620 °C, the dominant mechanism for coarsening changes from particle coalescence to Ostwald ripening. Equiaxed as-cast microstructure is beneficial to the semi-solid microstructure after isothermal heat treatment, which brings about the refinement and spheroidization of primary particles, and shortening of holding time. Significant modification of second phases can also be achieved after isothermal heat treatment, due to its unique solidification process. The optimum processing parameters for Mg–10Gd–3Y–0.5Zr alloy in isothermal heat treatment are isothermal temperature of 610 °C–620 °C and holding time of 20–40 min.

Keywords: Mg–10Gd–3Y–0.5Zr; Semi-solid forming; Isothermal heat treatment; Microstructure

1. Introduction

In recent years, semi-solid metal (SSM) processing has been recognized as a potential process in light alloy forming, due to its unique advantages over conventional casting processes, such as near net shape forming, improved mechanical properties, low porosity and long die life. Generally, SSM processing can be divided into two routes, i.e. rheoforming and thixoforming. The distinct difference between rheoforming and thixoforming is that, semi-solid slurry used in rheoforming is partially solidified from the liquid state, while that used in thixoforming is partially melted from the solid state. For both rheoforming and thixoforming, the key requirement is the thixotropic slurry with non-dendritic primary particles uniformly distributed in the liquid matrix. It is well accepted that, the finer and rounder the primary particles, the better the rheology of semisolid slurry and the resulting mechanical properties [1–3].

Thixoforming involves the reheating of feedstock materials into semi-solid state [4]. In order to get non-dendritic microstructure via reheating, feedstock materials are always prepared by some special techniques, such as electromagnetic stirring [5,6], spray casting [7] and strain induced melt activation (SIMA) [8,9]. But these techniques will also introduce extra cost. Semi-solid isothermal heat treatment is a relatively simple method invented in the 1990s [10], which is able to produce non-dendritic slurries without any special procedures. So it is a promising technique for practical application of thixoforming.

Until now, magnesium alloys studied and used in SSM processing are limited to commercial Mg–Al alloys such as AZ91, AM60 and AM50 [11–13], the application is then restricted by
their inherent deficiencies, such as poor high temperature strength and creep resistance [14]. Rare earth metals (RE) have been demonstrated the most effective elements to improve the strength of Mg alloys especially at elevated temperature. It has been reported that the recently developed Mg-Gd-Y-Zr magnesium alloys showed considerable precipitation hardening, therefore exhibited higher specific strength at both room and elevated temperature and better creep resistance than conventional aluminium and magnesium alloys, including WE54 and QE22 [15-17]. The thixoformability of Mg-Gd-Y-Zr alloy has also been calculated quantitatively in previous work [18]. Recently, several works have focused on the SIMA route of Mg-Gd-Y-Zr alloy [19,20].

However, the amount of information available on the isothermal heat treatment of Mg-Gd-Y-Zr alloy remains quite scarce to date. Therefore, the present study was aimed at investigating the microstructure evolution of semi-solid Mg-10Gd-3Y-0.5Zr (wt. %) alloy during isothermal heat treatment. Particular emphasis was put on elucidating the effects of isothermal temperature and holding time on microstructure of semi-solid Mg-10Gd-3Y-0.5Zr alloy after isothermal heat treatment.

2. Experimental

Mg-10Gd-3Y-0.5Zr alloy used in this study was prepared with high purity Mg, Mg-90Gd (wt. %), Mg-30Y (wt. %) and Mg-30Zr (wt. %) master alloys by melting in an electric resistance furnace under the mixed atmosphere of CO2 and SF6 with the ratio of 100:1. The melt was cast into a permanent mould at pouring temperature of 730 °C and mould temperature of 200 °C. The real chemical composition was determined to be Mg-9.76Gd-2.65Y-0.48Zr (wt. %) by an inductively coupled plasma analyzer (Perkin Elmer, Plasma-400). Ø 16 mm × 10 mm samples were cut from ingots for isothermal heat treatment. The isothermal heat treatment was performed in an electric resistance furnace under the same protective atmosphere. When the furnace was heated to 600 °C, 610 °C and 620 °C, the samples were put into the furnace and held for 10, 20, 30, 40 and 50 min, respectively. After the isothermal heat treatment, the samples were taken out and quenched in cold water immediately.

The samples were prepared with standard metallographic procedures. Phase composition was characterized by X-ray diffraction (XRD) using Ni-filtered Cu-Kα radiation. Microstructure characterization was carried out with optical microscopy (OM). Detailed morphological characterization was conducted using scanning electron microscopy (SEM). Quantitative metallographic analysis carried out by a quantitative image analysis software was used to evaluate the quality of semi-solid slurry, including solid fraction, average size and shape factor of primary particles. Shape factor is defined as \( SF = \frac{4\pi A}{P^2} \), where \( A \) and \( P \) represent the area and the perimeter of primary particles. Shape factor varies between 0 and 1 and \( SF = 1 \) indicates ideally circular.

3. Results and discussion

3.1. Microstructure of as-cast Mg-10Gd-3Y-0.5Zr alloy

The XRD pattern of as-cast Mg-10Gd-3Y-0.5Zr alloy is shown in Fig. 1. The XRD peaks evidently indicate that the alloy consists of \( \alpha \)-Mg and \(\text{Mg}_{24}(\text{Gd,Y})_5 \) phases. According to
previous work [21], this alloy also contains Mg5(Gd,Y) phase, but no peaks of Mg5(Gd,Y) phase can be seen in the XRD pattern, this may be because the content of Mg5(Gd,Y) phase is too low.

Fig. 2 shows the microstructure of as-cast Mg10Gd3Y0.5Zr alloy observed by OM and SEM. As seen from Fig. 2a, the microstructure of Mg10Gd3Y0.5Zr alloy consists of near-equiaxed primary α-Mg and eutectic. The average grain size of primary α-Mg is about 52.1 μm. As shown in Fig. 2b, the eutectic mainly consists of α-Mg and Mg24(Gd,Y)5. Cube-shaped Mg5(Gd,Y) phase can also be seen occasionally in the SEM image as bright ones [17].

3.2. Microstructure of semi-solid Mg10Gd3Y0.5Zr alloy after isothermal heat treatment

Fig. 3 shows the solid fraction versus temperature curve of Mg10Gd3Y0.5Zr alloy, which was calculated based on Scheil equation, with a commercial thermodynamic database software package called Pandat. According to the calculation result, the liquidus and solidus of Mg10Gd3Y0.5Zr alloy are about 631 °C and 566 °C, and the theoretical solid fraction of Mg10Gd3Y0.5Zr alloy at 600 °C, 610 °C and 620 °C are 0.63, 0.52 and 0.34, respectively.

Fig. 4 shows the microstructures of semi-solid Mg10Gd3Y0.5Zr alloy after isothermal heat treatment for 30 min at 600 °C, 610 °C and 620 °C, respectively. As seen from Fig. 4, the microstructures of semi-solid Mg10Gd3Y0.5Zr alloy consist of liquid matrix and primary α-Mg particles. The liquid matrix formed during the heating and then solidified during the quenching. Small liquid droplets can be observed within the primary particles, indicating the partial melting inside of primary particles. It is evident that solid fraction decreases significantly with the increase of isothermal temperature.

Fig. 5 shows the microstructures of semi-solid Mg10Gd3Y0.5Zr alloy after isothermal heat treatment at 610 °C for 10, 20, 30, 40 and 50 min, respectively. As shown in Fig. 5, the solid fraction decreases gradually and approaches the equilibrium during the holding. With the prolongation of holding time, size of primary particles increases continuously and size difference of primary particles is more and more significant.
The quantitative result of effects of isothermal temperature and holding time on solid fraction of semi-solid Mg–10Gd–3Y–0.5Zr alloy after isothermal heat treatment is illustrated in Fig. 6. It should be noted that, all solid fractions are higher than the theoretical results calculated above, more or less, resulting from the secondary solidification during quenching [22,23]. The result of quantitative metallographic analysis supports the observation mentioned above. Higher isothermal temperature corresponds to less solid fraction. Although solid fraction varies with isothermal temperature, the general trend is the same. During isothermal heat treatment, solid fraction first decreases then changes little, indicating the approach of equilibrium solid fraction. High temperature shortens the time for approaching the equilibrium solid fraction, e.g. for 600 °C, it takes about 30 min, but only about 20 min for 610 °C and 620 °C.

Fig. 7 presents the quantitative result of effects of isothermal temperature and holding time on average size of

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Fig. 5. Optical microstructures of semi-solid Mg–10Gd–3Y–0.5Zr alloy after isothermal heat treatment at 610 °C for different holding times: (a) 10 min; (b) 20 min; (c) 30 min; (d) 40 min and (e) 50 min.

Fig. 6. Effects of isothermal temperature and holding time on solid fraction of semi-solid Mg–10Gd–3Y–0.5Zr alloy after isothermal heat treatment.
primary particles. As shown in Fig. 7, for all three isothermal temperatures, average particle sizes increase continuously during isothermal holding, indicating continuous coarsening of primary particles. Difference of average particle size between 610 °C and 620 °C is not distinct, but average particle size of 600 °C increases obviously, showing that coarsening at 600 °C is faster than 610 °C and 620 °C. Fig. 8 shows the quantitative result of effects of isothermal temperature and holding time on shape of primary particles. It can be seen that, for 610 °C and 620 °C, the average shape factor keeps in a relatively high level between 0.7 and 0.8, but for 600 °C, average shape factor decreases with the prolongation of holding time for more than 30 min. The evolution mechanism of semi-solid microstructure will be discussed in detail later.

For thixoforming, the expected slurry is of a solid fraction of 0.4–0.6 with fine and round primary particles. In this study, considering solid fraction, average size and shape factor of primary particles comprehensively, the suitable processing parameters for Mg–10Gd–3Y–0.5Zr alloy in isothermal heat treatment are isothermal temperature of 610 °C–620 °C and holding time of 20–40 min.

3.3. Microstructure evolution mechanism during isothermal heat treatment

Evolution mechanism of semi-solid microstructure during isothermal heat treatment has been discussed in previous works. Four processes are operating in the semi-solid state, i.e. remelting of phases with a low melting temperature, partial remelting of primary particles, coarsening of primary particles and spheroidization of primary particles [24]. These four processes are not independent. Conversely, they coexist for most of the time. It is also concluded that, for a certain alloy, the final semi-solid microstructure after isothermal heat treatment is mainly affected by its as-cast microstructure and processing parameters of isothermal heat treatment [25].

Unlike other semi-solid processes, isothermal heat treatment does no pre-treating on feedstock materials (neither stirring nor pre-deformation). Therefore, the as-cast microstructure has great effect on semi-solid microstructure prepared by isothermal heat treatment. It has been proven that equiaxed as-cast microstructure is desired to subsequent treatment. Chen et al. [26] found that, when as-cast microstructure of AZ91D alloy gradually changed from well developed dendrites to equiaxed dendrites, the primary particles became small and round. In this study, due to the strong refinement efficiency of Zr, very equiaxed microstructure of Mg–10Gd–3Y–0.5Zr alloy can be produced by conventional casting [27]. The advantages of this kind of microstructure for semi-solid slurry are summarized in three aspects:

(1) Refinement of primary particles.

For dendritic as-cast microstructure, primary particles are developed from coarse dendrites and their fragment, so size of primary particles has been always large. But for equiaxed as-cast microstructure, primary particles are directly developed from equiaxed grains, therefore, size of primary particles is much smaller because of the well refined as-cast microstructure.

(2) Spheroidization of primary particles.

Different from dendritic as-cast microstructure, it is very easy to become spherical for primary particles from equiaxed as-cast microstructure. During the whole treatment, the average shape factor of primary particles fluctuates on a small range in a relatively high level.

(3) Shortening of holding time.

Long holding time is usually needed in isothermal heat treatment, for spheroidization of primary particles [28]. But for alloys with equiaxed as-cast microstructure, the holding
time can be shortened obviously, because their primary particles are almost spherical at the beginning. Meanwhile, shortening of holding time will also restrict the coarsening of primary particles.

The driving force for the change of primary particles is to reduce the total area of solid/liquid interface [29]. In this study, for primary particles are almost spherical from the beginning, change mainly presents in their coarsening. Two theories are often used to explain the coarsening kinetics of primary particles in the semi-solid state, i.e. particle coalescence and Ostwald ripening. Tzimas and Zavaliangos [30] studied the evolution of near-equiaxed microstructures in the semi-solid state and proposed that, particle coalescence and Ostwald ripening operated simultaneously and independently as soon as liquid was formed. At a high solid fraction, coarsening is driven by the migration of grain boundary liquid films and the dominant mechanism for coarsening is coalescence of adjacent particles. While at low solid fractions, coarsening is driven by the dissolution of small particles and Ostwald ripening makes a major contribution to the coarsening. In this study, it can be assumed that solid fractions of 600 °C, 610 °C and 620 °C correspond to high, medium and low solid fraction respectively. So the dominant mechanism for coarsening at each temperature is different. The unexpected worsening of roundness during the isothermal holding at 600 °C (see Fig. 8) can be due to the excessive coarsening of primary particles caused by coalescence. Even after holding at 620 °C for 50 min (see Fig. 9), which possesses typical characteristics of Ostwald ripening, coalescence of adjacent particles can still be observed, proving the coexistence of Ostwald ripening and coalescence.

A classical LSW analysis results in a relationship of the following form:

$$\overline{d} - \overline{d}_0 = Kt$$  

(1)

$$K = \frac{3D(C_L(\infty) - C_S)}{2RT}$$  

(2)

Where $\overline{d}$ is the average particle size at time $t$, $\overline{d}_0$ is the average particle size at time $t = 0$, $K$ is the coarsening rate constant, $D$ is the diffusion coefficient of solute in the liquid, $\sigma$ is the solid/liquid interfacial energy, $V_m$ is the molar volume, $R$ is the universal gas constant, $T$ is the absolute temperature, $C_L(\infty)$ is the molar composition of the liquid in equilibrium with solid particles of infinite radius and $C_S$ is the composition of the solid. Although the LSW theory is only suitable for coarsening of a low solid fraction, the form of the equation is valid for most of the solid fraction range, which has been confirmed by a number of theoretical and experimental results [31,32]. Fig. 10 shows the effects of isothermal temperature and holding time on a cube of average particle size. Coarsening rate constant $K$ is calculated by linear regression based on Equation (1). According to Equation (2), $K$ will decrease with the increase of temperature $T$, indicating a lower coarsening rate at high temperature. In this study, the values of $K$ are 340 $\mu m^3 s^{-1}$ ($R^2 = 0.8967$) at 600 °C, 237 $\mu m^3 s^{-1}$ ($R^2 = 0.9155$) at 610 °C and 203 $\mu m^3 s^{-1}$ ($R^2 = 0.9685$) at 620 °C, which is consistent with the theoretical prediction given above.

In previous works on SSM, the major focus is on the evolution of primary particles during processing. Recently, it has been reported that effective modification of second phases was achieved by SSM [33,34]. In this study, as seen in Fig. 11, size, morphology and distribution of second phases are significantly modified after isothermal heat treatment, compared with the as-cast state. The modification of second phases after isothermal heat treatment is a result of the unique solidification process of semi-solid isothermal heat treatment. As mentioned above, semi-solid slurry during isothermal holding is a mixture of primary particles and liquid matrix. With a relatively high isothermal temperature and long holding time, the solute diffusion is sufficient and a homogeneous chemical composition field is formed finally. During the following quenching process, with the cooperative effect of homogeneous composition field and high cooling rate, formation of coarse second phases is suppressed and uniform microstructure with fine and dispersed second phases is formed in the liquid matrix [35]. The application of Mg–RE

![Fig. 9. Optical microstructures of semi-solid Mg–10Gd–3Y–0.5Zr alloy after isothermal heat treatment at 620 °C for 50 min.](image)

![Fig. 10. Effects of isothermal temperature and holding time on cube of average particle size and the results of linear regression.](image)
alloys is now restricted by their poor elongation, which is partially caused by coarse second phases. This kind of microstructure after isothermal heat treatment is assuredly beneficial to the final mechanical properties especially the elongation. In practical applications of SSM, such high cooling rate can also be achieved by die casting or squeeze casting. So it reveals a promising way to further improve the mechanical performance of Mg–RE alloys via semi-solid isothermal heat treatment.

4. Conclusions

The microstructure evolution of the semi-solid Mg–10Gd–3Y–0.5Zr alloy during isothermal heat treatment was investigated. The following conclusions can be drawn:

(1) Semi-solid Mg–10Gd–3Y–0.5Zr alloy with non-dendritic microstructure is prepared successfully via isothermal heat treatment in this study. The suitable processing parameters for Mg–10Gd–3Y–0.5Zr alloy in isothermal heat treatment are an isothermal temperature of 610 °C–620 °C and holding time of 20–40 min.

(2) The primary particles coarsen continuously during the holding. Coarsening rate decreases with the increase of isothermal temperature. When isothermal temperature increases from 600 °C to 620 °C, the dominant mechanism for coarsening changes from particle coalescence to Ostwald ripening.

(3) Equiaxed as-cast microstructure is beneficial to the semi-solid microstructure after isothermal heat treatment, which brings about the refinement and spheroidization of primary particles, and shortening of holding time.

(4) Significant modification of second phases can also be achieved after isothermal heat treatment due to its unique solidification process.

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References