Effects of Cooling Rate and Component on the Microstructure and Mechanical Properties of Mg–Zn–Y Alloys

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Abstract The microstructure and mechanical properties of Mg–6Zn–1Y and Mg–6Zn–3Y (wt%) alloys under different cooling rates were investigated. The results show that the second dendrite arm spacing (SDAS) of Mg–6Zn–1Y and Mg–6Zn–3Y is reduced by 32 and 30% with increasing cooling rates (R_c) from 10.2 to 23 K/s, which can be predicted using an empirical model of $SDAS = 68R_c^{-0.45}$ and $SDAS = 73R_c^{-0.45}$, respectively. The compressive strength of both alloys increases with increasing the cooling rate, which is attributed to the increase of volume fraction (V_f) of secondary phases under high cooling rate. The interaction of the cooling rate and component with SDAS has been theoretically analyzed using interdependence theory.

KEY WORDS: Mg–Zn–Y alloys; Microstructural characterization; Compressive strength; Cooling rate; Interdependence theory

1 Introduction

During the latest two decades, Mg–Zn–RE (RE, rare earth elements) magnesium (Mg) alloys have attracted many attentions due to their high strength at both ambient temperature and elevated temperature [1–10]. The high strength of Mg–Zn–RE alloys is attributed to the formation of icosahedral quasicrystalline phase (I-phase), which forms in situ as a second phase in the α -Mg matrix during solidification [11]. As the reinforcement in Mg alloy, I-phase shows a high thermal stability and a strong interface bonding with the matrix, which could effectively pin grain boundaries and inhibit the movement of dislocations [12].

In the previous research, the chemical composition of I-phase in Mg–Zn–Y system has been confirmed as Mg_3Zn_6Y [13, 14]. It was reported that the yield strength of Mg–Zn–Y alloys with nanocrystalline structure has reached the value of 610 MPa [15]. Depending on the volume fraction (V_f) of I-phase, the yield strength of Mg–Zn–Y–Zr alloys varied from 150 to 450 MPa at room temperature [16]. Kim et al. [17] reported that I-phase appears in polygon shapes when they are formed directly from the melt. Zhang et al. [18] indicated that I-phase in Mg–Zn–Y is easy to nucleate in the slow cooling rate condition. With increasing Y content, the V_f of I-phase increased as well. For Mg–Zn–Gd system, the formation of I-phase could be accelerated by cooling rate increase [19], while the quantitative or semi-quantitative relationships between I-phase formation and cooling rate were rarely reported. Moreover, if both the content of Y and cooling rate is variable, their interaction on the microstructure of Mg–Zn–Y alloys is rarely studied, which may greatly influence the mechanical properties of Mg–Zn–Y alloys. In this paper, the effects of the cooling rate and the

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Fig. 1 **a** The dimension of the ingot; **b** the accurate position of section A, B, C; **c** the cooling curves and average cooling rates of section A, B, C

component on the microstructure and mechanical properties of Mg–6Zn–1Y and Mg–6Zn–3Y (wt%) alloy were studied. The interaction of the cooling rate and the component has been theoretically analyzed.

2 Experimental

Alloys with nominal components of Mg–6Zn–1Y and Mg–6Zn–3Y (wt%) were prepared. The raw materials were melted under the protection of 99% CO₂ and 1% SF₆. The ingots were cast into a wedge-shaped mold (ATS 1045 steel) and cooled in air. The dimensions of the cast were given in Fig. 1a, b. Since the solidification of the alloy varied with the section of the cast, three sections, marked

by A, B, and C were selected to represent the alloy under different cooling rates, as shown in Fig. 1b. The cooling rates during solidification were simulated by Anycasting software, as shown in Fig. 1c. The main parameters of simulation were listed as follows: pouring temperature was 993 K, preheating temperature of mold was 473 K, and pouring speed was 0.1 m/s. All the parameters were consistent with the ones in the actual process. The specimens for optical microscopy (OM) were etched in a solution of ethylic acid 2 mL and ethanol 98 mL. Phase analysis was performed by X-ray diffraction (XRD) with CuK_α radiation (Bruker AXS D8). Differential scanning calorimetry (DSC) (SDT Q600) was carried out with a heating rate of 0.17 K/s. The uniaxial compression test at room temperature was carried out on a universal test machine at a strain rate of

Fig. 2 XRD patterns of Mg-6Zn-1Y **a** and Mg-6Zn-3Y **b**

Fig. 3 DSC curves of Mg-6Zn-1Y and Mg-6Zn-3Y under different cooling rates

$10^{-3}/s$. The bars for compression test were cut by wire-electrode cutting from section A, B, and C with 5 mm in diameter and 9 mm in height. The micro-hardness (HV) was tested (HXS-1000Z) under a load of 200 g for 15 s.

3 Results

3.1 Microstructure

The XRD patterns of Mg-6Zn-1Y and Mg-6Zn-3Y were given in Fig. 2. Mg-6Zn-1Y alloy only contains two phases of α -Mg and I-phase, as shown in Fig. 2a. However, besides of α -Mg and I-phase, W-phase ($Mg_3Y_2Zn_3$) was also identified in Mg-6Zn-3Y alloy, as shown in Fig. 2b. In the previous research [20], it suggested that the

formation of I-phase and W-phase is closely related with the Zn/Y ratio (in atomic) of alloy in Mg-Zn-Y system. When the Zn/Y ratio is higher than the value of 4.38, there forms only I-phase. When the Zn/Y ratio is between in 1.10 and 4.38, both I-phase and W-phase could be simultaneously formed. The Zn/Y ratio of Mg-6Zn-1Y and Mg-6Zn-3Y is 8.24 and 2.75 in atomic, respectively. Therefore, Mg-6Zn-1Y only contains I-phase as a secondary phase, while Mg-6Zn-3Y contains both I-phase and W-phase. Figure 3 depicts the DSC curves of Mg-6Zn-1Y and Mg-6Zn-3Y under different cooling rates. The curves of Mg-6Zn-1Y only contain an endothermic peak at 720 K, which corresponds to the transformation temperature of I-phase. The curves of Mg-6Zn-3Y contain another endothermic peak at 780 K, which represents the transformation temperature of W-phase.

The microstructures of the as-cast Mg-6Zn-1Y and Mg-6Zn-3Y alloy under different cooling rates are given in Fig. 4. Under the cooling rate of 10.2 K/s, the Mg-6Zn-1Y alloy exhibits a coarse dendritic microstructure with a second dendrite arm spacing (SDAS) of 25.1 μm , as shown in Fig. 4a. The primary α -Mg appears as the dendrites, while the I-phase located in the inter-dendritic regions. When the cooling rate increases to 15.7 K/s, as shown in Fig. 4b, the microstructure of Mg-6Zn-1Y alloy was refined and exhibited the SDAS with the value of 21 μm , since a higher cooling rate leads to a higher undercooling. When increasing the cooling rate to 23 K/s, as shown in Fig. 4c, the SDAS of Mg-6Zn-1Y is further reduced to the value of 17 μm . The microstructure evolution of Mg-6Zn-3Y shows a similar trend with the one of Mg-6Zn-1Y when the cooling rate increases from 10.2 to 23 K/s, as shown in Fig. 4d-f. Under the same cooling rate, the microstructure of Mg-6Zn-3Y is finer than the one of Mg-6Zn-1Y, as shown in Table 1, which is attributed to the difference of components and it will be analyzed in the

Fig. 4 Microstructures of Mg-6Zn-1Y **a–c** and Mg-6Zn-3Y **d–f** under different cooling rates: **a, d** 10.2 K/s, **b, f** 15.7 K/s, **c, e** 23 K/s

Sect. 4.2. In addition, the V_f of the secondary phases increases as well with the increase of cooling rate, as shown in Table 1. According to the studies of Shechtman *et al.* [21] and Sastry [22], there exists a critical cooling rate to form quasicrystals at a certain alloy composition. The solidification of the quasicrystals must be slow enough to prevent the formation of the amorphous phase, and rapid enough to prevent crystallization. The formation of the I-phase would be accelerated with increasing cooling rate when it is lower than the critical value. In the present work,

Table 1 The value of second dendrite arm spacing (SDAS) and volume fraction of secondary phase (V_f) of Mg-6Zn-1Y and Mg-6Zn-3Y alloys under different cooling rate

Cooling rate (K/s)	Mg-6Zn-1Y		Mg-6Zn-3Y	
	V_f (%)	SDAS (μm)	V_f (%)	SDAS (μm)
10.2	8.6	25.1 ± 2	8.9	21.8 ± 2
15.7	15.5	21 ± 2	17.1	18.5 ± 2
23	20.7	17 ± 2	25.7	15.2 ± 2

Fig. 5 Compression properties of alloys Mg–6Zn–1Y **a**, Mg–6Zn–3Y **b**, and their micro-hardness variation with the cooling rates **c**

the relationship between the cooling rate and V_f shows a same trend with that of Mg–Zn–Gd system [19], which means that the cooling rate is lower than the critical ones. Therefore, increasing cooling rate from 10.2 to 23 K/s would accelerate the formation of I-phase in Mg–Zn–Y alloy.

3.2 Mechanical Properties

The uniaxial compressive properties of two alloys under different cooling rates are given in Fig. 5. When the cooling rate increases from 10.2 to 23 K/s, the ultimate compressive strengths (UCS) of Mg–6Zn–1Y and Mg–6Zn–3Y are increased with an improvement of 24.9% and 25.8%, respectively. In addition, the hardness of the alloys are also enhanced with increasing the cooling rate, as shown in Fig. 5c. According to Hall–Petch equation, the improvements of the strength and hardness could be attributed to the refinement of the microstructure under high cooling rate. Meanwhile, under the same cooling rate, the strength and hardness of Mg–6Zn–3Y are higher than

those of Mg–6Zn–1Y due to higher V_f of secondary phase, as shown in Fig. 5a, b.

4 Discussion

4.1 Individual Effect of Cooling Rate and Component

In general, the cooling rate reflects the heat transfer conditions of the solidification. Traditional solidification theory indicates that a higher cooling rate (R_c) leads to a greater undercooling, which could promote the nucleation process and results in a finer microstructure. Theoretically, The SDAS is derived for the velocity of the dendrite tip (A) and the thermal gradient at the solid–liquid interface (G) [23]:

$$\text{SDAS} = A \cdot (\text{GR})^\beta, \quad (1)$$

where β is the parameter for different alloys. In industrial practice, the R_c is respected as (GR) in Eq. (1), thus Eq. (1) can be deduced as [24]

Fig. 6 SDASs of Mg alloys as a function of cooling rate

$$\text{SDAS} = A \cdot R_c^\beta. \quad (2)$$

Figure 6 gives the SDAS of Mg alloys as a function of cooling rate, which fits well with the earlier works [25, 26]. The values of α and β calculated by power approximation are shown in Table 2.

Meanwhile, the SDAS is also dependent on the component of the alloys even under the same cooling rate. This phenomenon could be explained in terms of the growth restriction factor (Q) mechanism. Q is a parameter decided by the component of the alloy, which is defined as following [27, 28]:

$$Q = \sum_{i=1}^n m_i (k_i - 1) C_{0i}, \quad (3)$$

where m_i is the slope of the liquidus line, C_{0i} is the initial concentration of element, and i and k_i is the partition coefficient. The value of Q represents the difficulty for dendrite to grow up. According to the phase diagrams [29, 30], the value of Q of Mg–6Zn–3Y is 32.1, while that of Mg–6Zn–1Y is 28.7. Thus, the value of SDAS of Mg–6Zn–3Y is smaller than that of Mg–6Zn–1Y under the same cooling condition.

4.2 Interaction of Cooling Rate and Component

Theoretical SDAS can be obtained using Eq. (1) and Eq. (2) when cooling rate and Q appear as single variables. For the both two equations, the nucleation and growth of a grain are regarded as two separate events. However, the formation of grains and their morphology are controlled by both nucleation and growth concerning with the environment dictated by the alloy chemistry. In other words, if both the cooling rate and Q varies, such as the case in our present work, it is difficult to clarify the respective contribution of Q and the cooling rate to the SDAS. In order to evaluate the

Table 2 The fitting parameters of different Mg alloys

Material	α	n
Mg–6Zn–1Y	68	–0.45
Mg–6Zn–3Y	73	–0.45
AZ91D [25]	49	–0.42
Mg–1Zn–2Y [26]	37.1	–0.33

interaction of the cooling rate and Q with SDAS, the interdependence theory is introduced [31]. The interdependence theory links grain formation and nucleation selection to improve the ability to reveal the mechanisms of the grain refinement. This theory divides the final SDAS into three parts:

$$\text{SDAS} = X_{cs} + X_{dl} + X_{sd}, \quad (4)$$

where X_{cs} is the distance that a grain needs to grow creating sufficient constitutional supercooling (CS) for its nucleation. X_{dl} is the distance from the solid–liquid interface to the point where CS is sufficient to nucleate a grain. X_{sd} is the distance between the length of the nucleation-free zone and the next most potent particle in the melt. In the present work, X_{sd} can be seen as zero because no particles addition in the melt. X_{cs} is a parameter related with both Q and the cooling rate [31]:

$$X_{cs} = \frac{D \Delta T}{v Q}, \quad (5)$$

where ΔT is the undercooling, D is the diffusion coefficient, and v is the growth velocity. If the cooling rate is given, ΔT and v could be estimated by the following equations [32, 33]:

$$\ln R_c = 8.3 + 3.93 \ln \Delta T, \quad (6)$$

$$v = \frac{\Delta T^2 D}{2\pi^2 \Gamma m_L (k - 1) C_0}, \quad (7)$$

where Γ is the Gibbs–Thompson parameter.

X_{dl} is given by [31]

$$X_{dl} = \frac{4.6D}{v} \left(\frac{C_1^* - C_0}{C_1^* (1 - k)} \right), \quad (8)$$

where C_1^* is the composition of the liquid at the solid–liquid interface, which could be equal to C_0/k approximately. The main parameters used in the calculation are given in Table 3.

The theoretical SDAS of Mg–6Zn–1Y and Mg–6Zn–3Y under different cooling rates are given in Fig. 7. The result shows that the theoretical values of SDAS are consistent with the experimental result substantially. However, the values of the experimental SDAS are lower than the one of theoretical SDAS. It should be indicated that in the theoretical calculation of v , only Mg–Zn system is taken into

Table 3 The parameters used in the calculation of interdependence theory

Parameter	Value
D	$1 \times 10^{-12} \text{ m}^2/\text{s}$ [34]
Γ	$1.52 \times 10^{-7} \text{ km}$ [33]
m_{Zn}	4.9 K/wt%
k_{Zn}	0.94
m_{Y} (Mg–6Zn–1Y)	1.35 K/wt%
k_{Y} (Mg–6Zn–1Y)	0.78
m_{Y} (Mg–6Zn–3Y)	1.44 K/wt%
k_{Y} (Mg–6Zn–3Y)	0.76

Fig. 7 Experimental and theoretical SDASs of Mg–6Zn–1Y and Mg–6Zn–3Y alloy

consideration, since the atomic percentage of Y element is too low. Moreover, Ma et al. [35] have studied the effect of Y addition on the phase transformation of Mg–Zn alloy, and the results of which indicated that Y could change solution degree of Zn in the Mg matrix and shorten the time for nucleation. Thus, the Y element would also induce the discrepancy between the experimental and theoretical values of SDAS.

5 Conclusions

- (1) The second dendrite arm spacing of Mg–6Zn–1Y and Mg–6Zn–3Y are reduced with increasing cooling rates from 10.2 to 23 K/s, which can be predicted using an empirical model of $\text{SDAS} = 68R_c^{-0.45}$ and $\text{SDAS} = 73R_c^{-0.45}$, respectively.
- (2) The ultimate compression strengths of Mg–6Zn–1Y and Mg–6Zn–3Y are improved by 24.9 and 25.8% with increasing cooling rates from 10.2 to 23 K/s, respectively. The Mg–6Zn–3Y exhibits higher value

of the ultimate compression strength than Mg–6Zn–1Y due to the higher V_f of secondary phase.

- (3) The interaction of the cooling rates and the component was analyzed using the interdependence model. The theoretical values of SDAS of both Mg–6Zn–1Y and Mg–6Zn–3Y alloys agree well with the experimental results.

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