Abstract
The effects of 2 mass% Mg and 0.8 mass% RE additions on the microstructural evolution of a Zr modified zinc alloy ZA27 during isothermal holding at semi-solid temperature of 460 °C have been studied by optical microscope and scanning electron microscope. Results show that these two elements all decrease the coarsening rate of solid primary particles, and improve the uniformity of particle size. The addition of Mg greatly decreases the solid fraction, and then increases the distance between particles. However, the element of RE mainly concentrates at the liquid regions between particles, and hinders both the atom diffusion and the welding of contact particles. In addition, the behaviors of particle coarsening of these two alloys, together with that of the Zr modified ZA27 alloy without the other elements, obey the LSW law after the three semi-solid systems reach at their solid–liquid equilibrium states. The additions of these two elements have no visible effect on the shape factor of particles.

Keywords: ZA27 alloy; Semi-solid; Isothermal holding; Magnesium and rare earth additions; Microstructure

1. Introduction
Semi-solid forming (SSF) is a new technology to produce metal parts using alloys in the semi-solid state and offers numerous advantages over conventional technologies [1]. The key factor controlling both the flow of slurry and properties of formed products is the non-dendritic microstructure which behaves thixotropically. As a result, the major effort of all the semi-solid technologies is focused on the generation of small and globular morphologies [2]. The coarsening of solid primary particles during partial remelting of an alloy is one of important topics [3–5]. It has reported that semi-solid materials with coarse primary particles do not deform as easily as those with a fine primary particles [6]. Furthermore, it is well known that the mechanical properties of a product with fine grains are superior to those of a product with coarse grains. Therefore, to prevent or reduce the particle coarsening is of very important in practice.

From the microstructure-mechanical property relationship in SSF sample, Fan proposed that the SSF microstructure was similar to that of a metal toughened ceramic matrix composite [7]. In fact, as the constituents of SSF microstructure are all metals, it is more similar to a metal matrix composite. Whatever, there exists interface between the solid primary particles and the liquid phase in the semi-solid state. Kliauga investigated the influence of Sn additions on the microstructural evolution of A356 alloy during partial remelting and found that this element decreased the kinetics of solid particle growth [8]. He proposed that this behavior was attributed to a decreased solid–liquid interface energy brought by the presence of small globules of Sn at the Al–Si interface. However, the investigation on the influence of surface-active elements on the semi-solid microstructure is relatively less than the other studies in the SSF technology, and the study from this aspect on Zn–Al matrix materials is also scarce. Previous investigation showed that Mg was a surface-active element in SiC particles reinforced ZA27 composite and concentrated at the interfaces between SiC particles and metal matrix [9]. Furthermore, RE has been used as a modification agent to reduce the grain size of ZA27 alloy [10].
It has also been reported that RE segregates at solid–liquid interface to hinder the growth of the primary dendrites.

The aim of the present work is to evaluate the effects of Mg and RE additions on the semi-solid microstructure of ZA27 alloy and attempt to seek a method to reduce the coarsening rate of the solid primary particles.

2. Experimental

2.1. Materials

The nominal composition of ZA27 alloy used for this experiment is 26–28% Al, 1.7–0.2% Cu, 0.15–2% Zr, 0.02–0.04% Mg (in mass), with a balance of Zn. The role of Zr is to obtain an as-cast microstructure with small equiaxed grains, and then a semi-solid microstructure with globular solid primary particles during subsequent partial remelting [3]. When the ZA27 alloy ingot (about 800 g) was remelted in a resistant furnace, 2 mass% Mg was added into the melt at 670 °C, then poured at 550 °C into permanent mould with ambient temperature to form rods (named Mg sample in the following) with the dimensions of 120 mm long and 12 mm in diameter. Repeating the above process, some rods with 0.8 mass% RE were prepared (named RE samples). For the comparison with these two alloys, some rods with the original composition (named No element samples) were also prepared.

2.2. Isothermal holding process

Samples with the dimensions of 10 mm long and 12 mm in diameter were cut from the above mentioned three kinds of alloy rods and put into a chamber of a box-like resistant furnace at 460 °C, heated for different periods of time, then taken out quickly for water quenching. Temperature variation of the sample during the partial remelting was monitored by a thermocouples mounted at the center of sample. A typical temperature variation with heating time is presented in Fig. 1, showing that the temperature did not change after heating for about 27 min. To ensure the conditions of isothermal holding during semi-solid treatment at 460 °C, the sample water quenching was carried out after heating for 30 min. In this work, the beginning time of isothermal holding period was defined as the time when the samples were heated for 30 min.

2.3. Microstructure observation and morphology analysis

The above quenched samples were ground and polished to a 1/4 μm diamond finish and etched by 4% HNO₃ aqueous solution. Metallographic observations were carried out using Mef-3 optical microscope (OM). Before an image was analyzed to determine the solid fraction, the contrast between the former solid particles and the matrix solidified from the former liquid should be distinguished by adjusting the contrast threshold of the image analysis system equipped in the OM, such that the resulting solid primary particles and matrix were white and black, respectively. The ratio of the area A of the particles to the area B of the image was the solid fraction $f_s$.

$$f_s(\%) = 100 \times A/B$$

Subsequently, the particle size, size distribution and shape factor were determined. If the situation was not suitable for analysis due to some reasons, such as the entrapped liquid pools within the particles and the primary grains in the matrix from the liquid solidification during quenching, the manual covering and filling procedure were carried out. The area $A_i$ and perimeter $P_i$ of each particle were obtained and the average particle size $D$ was calculated from the following equation,

$$D = [\Sigma(A_i/\pi)^{1/2}]/N,$$

where $N$ was the total particle numbers in each image. The shape factor $F$ was calculated from the equation,

$$F = (\Sigma P_i^2/4 \pi A_i)/N,$$

If the particles are perfectly spherical, the shape factor is unity and it increases for less spherical particles [11]. Three images with magnification of 100 times were analyzed for each sample.

The size frequency distributions of primary particles are presented in histograms, in which the frequency is the ratio of number of particles with sizes from $D_i$ to $D_{i+1}$ to $N$ and $\rho$ is the ratio of $D_i$ to $D$. For the convenience to comparison in the following text, all of the histograms were smoothed by the least square fit by assuming Gauss distribution and some curves of frequency vs $\rho$ were obtained. An example is shown in Fig. 2.

It must be noted that if the welding distance between two contact particles is larger than the half of the total contact distance, these two contact particles are considered as one particle. Otherwise they are considered as two individual particles.

In order to verify the behaviors of Mg and RE in the ZA27 alloy and to clarify their effect mechanisms on
the semi-solid microstructures, the samples were also subject to observation by S-520 scanning electron microscope (SEM) and analyzed by energy dispersive spectroscopy (EDS) equipped in the SEM.

3. Results and discussion

3.1. Metallographic observations

Fig. 3 shows the as-cast microstructures of the three types of alloys. It is found that all of the alloys have small equiaxed dendrites but with small differences in grain size. The quantitative analysis shows that the grain size of the Mg sample is 16.79 μm, while the grain sizes of the No element and RE samples are 19.68 and 22.16 μm, respectively. No attempt was made to explain the effects of Mg and RE on the as-cast microstructures in this work. The previous investigation showed that the initial as-cast microstructure had significant influence on the semi-solid microstructure formed during the initial stage of partial remelting [12]. The finer initial grains result in the smaller and more spherical solid particles. However, this effect will diminish or disappear as the remelting process is prolonged due to coarsening of particles [1]. In addition, this work focuses on the structural evolution during the stage of isothermal holding and the differences in the initial grain size, 3–6 μm, are quite small. Therefore, we consider that these differences do not affect the resulting semi-solid microstructures in the present work.

Fig. 4 shows the typical semi-solid microstructures of the three types of alloys isothermally held for different periods of time. The followings should be noted: (1) The coarsening of the solid particles takes place with the holding time, while the coarsening degrees are different. The order of the coarsening degrees from large to small is the No element sample, RE sample and Mg sample. (2) The liquid fractions of these three alloys increase sharply when the holding time is increased from 0 to 30 min, and then tend to saturate.

(3) Because some of particles of the RE sample do not completely separate, its particle size is slightly larger than that of the No element sample at holding time of 0 min. Then, both of them decrease when held for 30 min. With the further increase of the holding time, the particle size of the No element sample gradually becomes larger than that of the RE sample. (4) The solid fraction of the RE sample is slightly higher than that of the No element sample at holding time of 0 min, and both of them become identical with the increase of the holding time. However, the faction of the Mg sample is always smaller than those of the former two. From these behaviors observed, it can be concluded that the additions of Mg and RE reduce the particle coarsening rate. The quantitative analysis and the interpretations about the effect mechanisms of these two elements will be discussed in the following section.
3.2. Quantitative analysis

Fig. 5 shows the variation of particle size of the three alloys with the holding time. It clearly shows that the particle size of all the alloys increases with the holding time except that the particle size of the No element and RE samples decreases during the initial holding period (0–30 min). The previous investigation showed that the microstructure of ZA27 alloy or matrix composite experienced four stages during partial remelting, the initial rapid coarsening, structural separation, spheroidization and the final coarsening [3]. The stages of the structural separation and spheroidization were always accompanied by the increase of liquid fraction resulting from the melting of interdendritic eutectics and edge of primary grains. From Fig. 4(a) and (c), it can be found that the structural separation of the No element at holding time of 0 min have completed because its microstructures have separated into independent particles, and for the RE sample, there were still some interconnected particles in it. During the subsequent holding, for the RE sample, the structural separation continues, and then the spheroidization initiates. In contrast, for the No element sample, it directly enters to the stage of the spheroidization. In order to achieve the equilibrium state between solid and liquid phases, the edge of the particles melts through the transformations of $\beta \rightarrow L + \alpha'$ and $\alpha' \rightarrow L$ during this stage (0–30 min) [4], resulting in the rapid increase of the liquid fraction (Fig. 6), which corresponds to the decrease in the particle size of these two alloys observed in Fig. 5. But for the Mg sample, its particle size continuously increases during

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**Fig. 4.** OM micorgaphs of the used three alloys isothermally held at 460 °C for different periods of time. (a), (d), (g) and (j) for the No element sample held for 0 min (a), 30 min (d), 690 min (g) and 2850 min (j). (b), (e), (h) and (k) for the RE sample held for 0 min (b), 30 min (e), 690 min (h) and 2850 min (k). (c), (f), (i) and (l) for the Mg sample held for 0 min (c), 30 min (f), 690 min (i) and 2850 min (l).

**Fig. 5.** Variation of particle size of the used three alloys during isothermal holding at 460 °C.
the initial holding period (0–30 min) while the solid fraction also decreases. In fact, particle coarsening and particle reducing from the melting of part of particles simultaneously occur in a competitive condition before the solid–liquid equilibrium is attained. The particle coarsening is superior to the particle reducing during the initial stage of partial remelting due to the high solid fraction [13], and vice versa during the subsequent stage. Fig. 6 also shows that the solid fraction of the RE sample at the holding time of 0 min is slightly higher than that of the No element sample, which further demonstrates that the addition of RE lowers the microstructural evolution.

From Fig. 6, it can be seen that both the No element sample and RE sample reach at the solid–liquid equilibrium state after holding for about 90 min and the Mg sample after for 30 min. Together with the variation of particle size with the holding time, it can be concluded that the order of the microstructural evolution rate from fast to slow is the Mg sample, No element sample and RE sample. This standpoint is also supported by the variation of particle shape factor with the holding time shown in Fig. 7. The time for the shape factor of the Mg sample reaching at a constant value (completion of spheroidization) is shorter than those of the other two. Fig. 6 shows that the liquid fraction of the Mg sample is always higher than the others. It can be proposed that the addition of Mg reduces the solidus temperature of ZA27 alloy. This is equivalent to an increase in the holding temperature in comparing with the other two alloys.

It can be found that the particle coarsening is the most dominant phenomenon during the isothermal holding, which is driven by the motive force of reduction of the interfacial energy between the particles and liquid phase [13]. Two types of contributions include coalescence and Ostwald ripening. The coalescence is usually defined as the nearly instantaneous formation of two or more particles in contact with each other and the Ostwald ripening is the growth of large particles by the exhaustion of small particles, governed by the Gibbs–Thompson effect which alters the chemical potential of solutes at the particle–liquid interface, depending on the curvature of the interface [14]. During the initial stage of the holding period, the particle coarsening of all the three alloys is very intense mainly due to the coalescence, resulting from the high solid fraction (Fig. 6). With the increase of the holding time, the solid fraction decreases and the average distance between particles increases. Then, the coalescence becomes less active. Therefore, the changes of the coarsening rates with the holding time are almost completely consistent with the changes of the solid fractions (comparing Fig. 5 with Fig. 6).

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\[ D^3(t) - D^3(0) = Kt = K_{LSW} f(\Phi)t, \]

where \( D(0) \) is the average particle size (diameter) at time \( t, D(0) \) is the initial particles size, \( K \) and \( K_{LSW} \) is the coarsening rate constant for a system with the particle volume fraction of \( \Phi \) and Ostwald ripening, respectively, and \( f(\Phi) \) is a coefficient depending on the particle volume fraction \( \Phi \) and its value is higher than unity in most practical cases. The experimental result in the present work is shown in Fig. 8, where \( D(0) \) was the particle size at 90 min. It can be found that this result well obeys the formula. Again, it clearly shows that the additions of Mg and RE decrease the particle coarsening rate and the coarsening rate of the RE sample is higher than that of the Mg sample.

From Fig. 7 it can be seen that the additions of Mg and RE have no obvious effect on the particle shape factor except for the initial stage of isothermal holding (0–90 min). Besides the size and shape factor, size distribution is also an important parameter to characterize particles in semi-solid microstructure. The results of the size distribution of the present work show that the distribution curves of the used three alloys show similar tendency in the variation with the holding time; the peak (maximum frequency) decreased and the width broadened.
The result of the No element sample is shown in Fig. 9 as an example. This implies that the particle size becomes more inhomogeneous with the holding time. In other words, the large particles become larger and the small particles become smaller, as can be seen in Fig. 4. The size distribution curve satisfies the relation,

\[ \Sigma \rho(x)dx = 1, \]  

where \( \rho(x) \) is the frequency, and \( x = D/D_s \) [17]. Since the decrease of the peak should be always accompanied by the broadening of the curve, the change of the peak can completely reflect the change of the size distribution. The result of the present work is given in Fig. 10, which shows that the uniformity of the particle size decreases in the order of the Mg sample, RE sample and No element sample. During the initial stage of the holding time, the coalescence is intense due to the relatively high solid fraction, which results in the rapid decrease of the peaks. It was reported that even a small contribution of the coalescence broadened the size distribution curve significantly [18]. With the increase of the holding time, as the particle coarsening decreased, especially the coalescence became less active, the decrease of the peaks became slow (Fig. 10).

From the slope of the curves at the long holding time we also can conclude that the Mg sample has the highest resistance to the particle coarsening, compared with the No element and RE samples. This is completely consistent with the particle coarsening behaviors shown in Fig. 8. In addition, due to the slow structural evolution of the RE sample at the initial stage of the holding, its particle size is less uniform than that of the No element sample (Fig. 7).

### 3.3. Effect mechanisms of Mg and RE on semi-solid microstructures

The SEM image shows that there are some small particulates existed in the inter-dendrites of the as-cast RE sample as shown in Fig. 11. The results of EDS indicates that these particulates are a Ce-rich compound or solid solution; the content of Ce is up to 25.56% while the content is only 1.27% in the primary dendrites (Table 1). The previous investigation reported that the atomic radius of Ce was 27% and 46% larger than that of Zn and Al, respectively, and Ce always enriched at the solid–liquid interface [10], and finally segregated in the interdendritic...
eutectics. It is expected that the large Ce atoms have a hindering action to the diffusion of the small Zn and Al atoms, and then lower the phase transformation rate. Thereby the microstructural evolution of the RE sample is relatively slower than that of the No element sample during the initial stage of the holding period. From Table 1, it can be found that Ce still mainly concentrates in the liquid phase although its content decreases due to the increase of the liquid fraction with the holding time. This is also consistent with the results of the reference [10]; Ce enriched at the solid–liquid interfaces, and then hindered the atom diffusion, resulting in the slow Ostwald ripening. Furthermore, when two particles have just impinged, they are always separated by a thin liquid layer [6]. It was reported that these two particles did not weld together until the interfacial energy $\gamma_{ls}$ between the two particles and $\gamma_{il}$ between the particles and the liquid layer satisfied the condition, $\gamma_{ls} < 2 \gamma_{il}$ [19]. It is easily expected that RE atoms with large radius might increase $\gamma_{ls}$, lead this condition to be difficult to be matched, and thus the coalescence be hindered. Due to these two contributions, the lower particle coarsening and more uniform particle size than the No element sample are obtained.

In contrast to the RE sample, the result of the Mg sample shows that Mg is concentrated preferentially in the primary particles (Table 1), which is consistent with the result from Durman [20]. As the addition of Mg increases the liquid fraction, leading to the increase in the distance between the particles, the Ostwald ripening controlled by diffusion lowers and the coalescence controlled by the frequency of particle impingement becomes less active. Therefore, the particle coarsening rate of the alloy greatly decreased and the resistance to particle coarsening are enhanced.

### 4. Conclusions

1. The additions of Mg and RE into the Zr modified ZA27 alloy decrease the coarsening rate of solid primary particles during isothermal holding at 460 °C. The addition of Mg decreases the solid fraction, and then increases the distance between particles, resulting in the low Ostwald ripening rate and less active coalescence. However, RE concentrates in the liquid regions between particles and then hinders the atom diffusion and obstructs the welding of contact particles, also resulting the low Ostwald ripening rate and less active coalescence.

2. After the semi-solid systems reaching at the solid–liquid equilibrium state, the particle coarsening of all of the materials used in this work obeys the LSW law, showing that the coarsening rate increases in the order of the Mg sample, RE sample and No element sample.

3. The uniformity of particle size is significantly affected by particle coalescence. The particle size uniformity decreases in the order of the Mg sample, RE sample and No element sample.

4. The addition of Mg accelerates the microstructural evolution during the initial stage of the holding period while the RE decelerates.

5. The additions of these two elements have no affect on the particle shape factor.

## Acknowledgements

The authors would like to thank the financial support of the Gansu Province Key Program and Natural Science Foundation (GS992-A52-024 and ZS011-A25-048-C). One of the authors, T. J. Chen is also grateful for the support of the Development Program for Outstanding Young Teachers in Lanzhou university of Technology.

## References

[1] M.C. Flemings, Behavior of metal alloy in the semi-solid state, Metall. Trans. 22A (1991) 957–981.

[2] F. Czerwinski, On the generation of thixotropic structures during melting of Mg–9%Al–1%Zn, Acta Mater. 50 (2002) 3265–3281.
[3] T.J. Chen, Y. Ma, Y. Hao, S. Lu, G.J. Xu, J. Sun, Structural evolution of ZA27 alloy during semi-solid isothermal heat treatment, Trans. Nonferrous Met. Soc. China 11 (2001) 98–102.

[4] T.J. Chen, Y. Hao, J. Sun, Microstructural evolution of previously deformed ZA27 alloy during partial remelting, Mater. Sci. Engng A337 (2002) 73–81.

[5] W.R. Loue, M. Suery, Microstructural evolution during partial remelting of Al–Si7Mg alloys, Mater. Sci. Engng A203 (1995) 1–13.

[6] E.D. Manson-Whitton, I.C. Stone, J.R. Jones, P.S. Grant, B. Cantor, Isothermal grain coarsening of spray formed alloys in the semi-solid state, Acta Mater. 50 (2002) 2517–2535.

[7] Z. Fan, Semisolid metal processing, Int. Mater. Rev. 47 (2002) 49–82.

[8] A.M. Kliauga, M. Ferrante, The effect of Sn additions on the semisolid microstructure of an Al–7Si–0.3Mg alloy, Mater. Sci. Engng A337 (2002) 67–72.

[9] Z.Q. Li, S.Y. Zhang, B.Y. W, Solidification and microstructure of ZA27/5SiCp composite fabricated by mechanical–electromagnetic combination stirring process, Mater. Sci. Technol. 17 (2001) 465–471.

[10] Y.Y. Tan, H.F. Yan, Effect of RE on constituent phases of ZA27 alloy, Chinese J. Nonferrous Metals (in Chinese) 11 (2001) 72–74.

[11] E. Tzimas, A. Zavaliangos, A comparative characterization of near-equiaxed microstructures as produced by spray casting, magnetohydrodynamic casting and the stress induced, melt activated process, Mater. Sci. Engng A289 (2000) 217–227.

[12] E.J. Zoqui, M.H. Robert, Contribution to the study of mechanisms involved in the formation of rheocast structure, J. Mater. Proc. Technol. 109 (2001) 215–219.

[13] V.A. Snyder, J. Alkemper, W. Voorhees, The development of spatial correlations during Ostwald ripening: a test of theory, Acta Mater. 48 (2000) 2689–2701.

[14] F. Czerwinski, Size evolution of the unmelted phase during injection molding of semi-solid magnesium alloys, Scripta Mater. 48 (2003) 327–331.

[15] I. Seyhan, L. Ratke, W. Bender, P.W. Voorhees, Ostwald ripening of solid–liquid Pb–Sn dispersions, Metall. Mater. Trans. 27A (1996) 2470–2478.

[16] V.A. Snyder, J. Alkemper, P.W. Voorhees, Transient Ostwald ripening and the disagreement between steady state coarsening theory and experiment, Acta Mater. 49 (2001) 699–709.

[17] D. Fan, S.P. Chen, L.Q. Chen, P.W. Voorhees, Phase-field simulation of 2-D Ostwald ripening in the high volume fraction regime, Acta Mater. 50 (2002) 1895–1907.

[18] S. Takajo, W.A. Kaysser, G. Petzow, Analysis of particle growth by coalescence during liquid phase sintering, Acta Metall. 32 (1984) 107–113.

[19] L. Arnberg, A. Bardal, H. Sund, Agglomeration in two semisolid type 6082 aluminum alloys, Mater. Sci. Engng A262 (1999) 300–303.

[20] M. Durman, S. Murphy, An electron metallographic study of pressure die-cast commercial zinc–aluminum-based alloy ZA27, J. Mater. Sci. 32 (1997) 1603–1611.