Study of Microstructure and Modification Effect of Mg-Sr Master Alloy on AZ91D Magnesium Alloy

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The microstructure of Mg-Sr master alloy and its modification effect on the microstructure of AZ91D magnesium alloy were studied. Mg-Sr master alloy prepared by molten salt electrolysis was composed of α-Mg, $Mg_{17}Sr_2$, Mg_2Sr, $Mg_{23}Sr_6$ phases. With increasing Sr content, the morphology of the eutectic β-$Mg_{17}Al_{12}$ transformed from the continuous meshy distribution to a granular one. It was found that a small amount of Sr (0.01-0.03 %) added to the AZ91D magnesium alloy led to the β-$Mg_{17}Al_{12}$ grain size distinctly decreasing. The Sr addition was not only effective in modifying the eutectic β-$Mg_{17}Al_{12}$, but also had a lasting effect on maintaining a fine structure. The optimum Sr content and holding time to optimize the AZ91D magnesium alloy were 0.02 % and 150 min, respectively.

Keywords: Mg-Sr alloy, Modification, Sr content, Holding time.

INTRODUCTION

Magnesium alloys have become the focus of research and their application has been studied. The AZ91D magnesium alloys exhibits good casting and mechanical properties[1]. It easily forms microscopic shrinkage during solidification, especially in sand casting. In the case of a not sufficiently dense casting, the mechanical properties and casting performance diminish. However, an adequate design or micro-alloying process can eventually reduce and eliminate the microscopic shrinkage. Strontium can be used as a magnesium alloy modificator. Adding a small amount of Sr into the magnesium alloy enables it to refine the grain and improve its mechanical properties[2].

Some pronounced modifications were achieved by adding metal fluoride[3], several elements in the IA group (alkali metal)[4], IIA group (alkali earth metal)[5-7] and rare earth metals (Sc, Er and lanthanides)[8-10].

In various elements, Na, Sb and Sr have been commercially used. However, Na exhibits rapid fading that leads to the formation of micro-pores. Although the modification effect of Sb is lasting, it is inferior to that of Na or Sr. With the best overall performance, Sr exhibits a relatively good and long lasting modification effect and has therefore been extensively studied[11,12].

The modificator is generally added in the form of an Al-Sr master alloy. However, a Mg-Sr master alloy is superior to the Al-Sr master alloy. The Al-Sr alloy structure is mostly eutectic containing a substantial and thick high-temperature Al_4Sr phase. Its dissolved absorption is slow and Sr burns out rapidly. The melting point of the Mg-Sr alloy is lower than that of the Al-Sr alloy. In addition, there is no high-temperature phase in the Mg-Sr alloy that is, difficult to break down. The dissolved absorption of Sr is faster and Sr burns to a less extent[13]. Mg-Sr alloys and multi-component alloys have been studied by Argyropoulos *et al.*[14] and used in the modification of aluminum alloys.

There are two fundamental methods for the production of Mg-Sr alloys, which are a mixed method and a melt-immerse reduction. The mixed method can be used in the preparation of Mg-Sr alloys , but it needs the Mg and Sr to be prepared in advance, which is then remelted and doped into the alloys. This means that the process takes a long time and uses a large amount of energy. The melt-immersion reduction is achieved by adding Sr compounds to the Mg melt. Magnesium functions as a reducing agent, whereas the Sr concentration gradient of the reaction interface acts as the thermodynamic and kinetic driving force. Strontium precipitated from Sr compounds diffuses continuously into the Mg melt, forming the Mg-Sr alloy. However, due to the slow diffusion rate of the reduction, only a Mg-Sr alloy containing a small amount of Sr (generally not higher than 0.02 %) can be prepared[15].

This paper reports on the investigation of microstructure of Mg-Sr master alloy prepared by molten salt electrolysis and the effect of this Mg-Sr master alloy on the grain refinement of commercial AZ91D magnesium alloy.

EXPERIMENTAL

Commercial AZ91D magnesium alloy, where the normal compositions were 8.5-9.5 % Al, 0.45-0.90 % Zn, φ 0.05 % Si, ≤ 0.025 % Cu, ≤ 0.001 % Ni, ≤ 0.004 % Fe with the balance of Mg was used for the experiments.

The AZ91D magnesium alloy melted in a resistance furnace at 730 °C and then underwent a degassing treatment for 15 min. The molten alloy was stabilized by holding at 730 °C for 15 min and modified by adding different amounts of Sr to provide a final content ranging from 0.01 to 0.03 %. After various holding intervals, ranging from 30 to 180 min, the alloys were poured into pre-heated (to 200 °C) permanent molds, with the dimensions of $\Phi 60 \times 140$ mm. The Sr used in this study was in the form of Mg-Sr master alloy.

The microstructures of the Mg-Sr alloy and AZ91D magnesium alloy were observed using an Optical Microscopy (OP, Nikon E600POL) and energy dispersive spectroscopy (EDS, TEAMApollo). The samples that were used in the microstructure analysis had etching performed on them using 4 % nitric acid alcohol solution. The grain size and aspect ratio of the β-$Mg_{17}Al_{12}$ were determined by image analysis (Image-Pro Plus).

The Mg-Sr alloy was etched with 4 % nitric acid and alcohol solution and was used for X-ray diffraction (XRD). Monochromatic CuK_{α} was used to obtain the XRD Spectra from the Mg-Sr alloy. Step scanning between $2\theta = 10$-$80°$ was conducted to accurately measure the peak shift caused by the change in the microstructure.

RESULTS AND DISCUSSION

Fig. 1(a) shows the microstructure of the Mg-Sr master alloy prepared by molten salt electrolysis. The Mg-Sr master alloy consisted of a magnesium matrix that had a spherical and granular morphology. The XRD results from Mg-Sr master alloy are shown in Fig. 1(b). It can be seen that the Mg-Sr alloy was composed of α-Mg, $Mg_{17}Sr_2$, Mg_2Sr and $Mg_{23}Sr_6$ phases.

Fig. 2 shows the SEM micrograph of the Mg-Sr master alloy and its EDS results. The white meshy distribution was the $Mg_{17}Sr_2$ phase; the Mg and Sr atom contents were 75.61 and 9.56 %, respectively, with the ratio close to 17:2. The white

granular distribution corresponds to the Mg_2Sr phase; Mg and Sr atom contents were 14.29 and 6.10 %, respectively, with the ratio close to 2:1. The black part corresponds to $Mg_{23}Sr_6$ phase; Mg and Sr atom contents were 37.42 and 8.19 %, respectively, with the ratio close to 23:6. Energy dispersive spectroscopic analysis revealed that each element was in the form of a solid solution in the Mg-Sr alloy. The study indicates that the presence of small amounts of C, O, Ca and other impurities aside from Mg and Sr elements.

Fig. 3 shows the micrographs of the AZ91D magnesium alloys with different Sr contents. The changes in the β-$Mg_{17}Al_{12}$ microstructure were clearly evident. The AZ91D magnesium alloy consisted of a primary white α-Mg solid solution and a continuous meshy distribution changed to eutectic β-$Mg_{17}Al_{12}$ phase at the grain boundaries.

The microstructure of the unmodified alloy was characterized by the continuous meshy distribution changed to eutectic β-$Mg_{17}Al_{12}$ phase [Fig. 3(a)]. The grain was relatively coarse which can be seen in Fig. 4 (a) and the grain size was about 230 μm. Fig. 3(b-f) shows the micrographs of the alloy with different Sr contents. After adding 0.005-0.01wt. % Sr, the grain size refinement was clearly evident and the size of the eutectic β-$Mg_{17}Al_{12}$ was about 40 μm when the amount of Sr reached 0.02 %, the eutectic β-$Mg_{17}Al_{12}$ became finer and the morphology changed to a granular type, which indicated the effect of the modifying element. The grain size was about 17 μm [Fig. 4(a)]. From the series of micrographs shown in Fig. 3 it can be observed that the addition of Sr greatly influenced the morphology of the eutectic β-$Mg_{17}Al_{12}$.

The degree of modification was quantified by measuring the grain size and aspect ratio of the eutectic β-$Mg_{17}Al_{12}$. As shown in Fig. 4(a), the grain size of the eutectic β-$Mg_{17}Al_{12}$ decreased notably from 230 μm in the unmodified sample to 17 μm at a 0.02 % Sr content. In addition, as shown in Fig. 4(b), the aspect ratio of the eutectic β-$Mg_{17}Al_{12}$ was also measured to quantify the degree of modification. With increasing Sr content, the aspect ratio of the eutectic β-$Mg_{17}Al_{12}$ decreased greatly from 7.2 for the unmodified alloy to 1.54 when the alloy was modified with 0.02 % Sr.
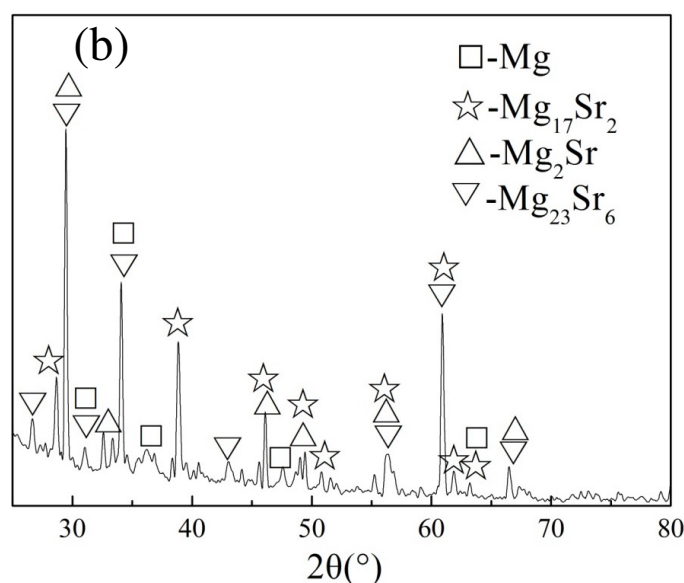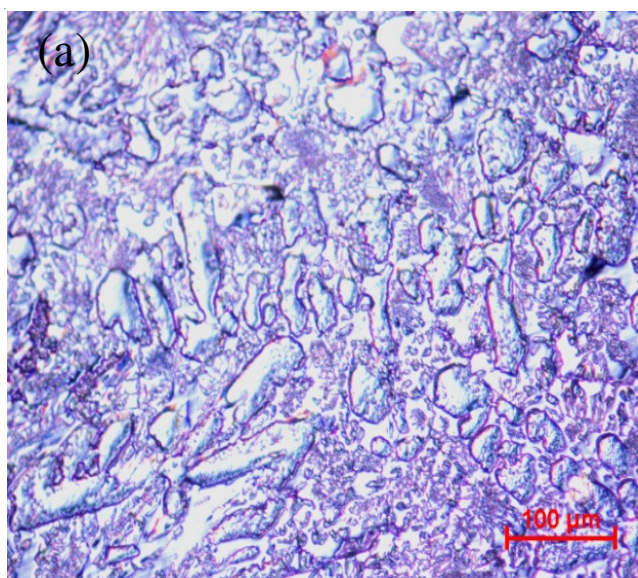

Fig. 1. Optical micrographs of the Mg-Sr master alloys using molten salt electrolysis method and its XRD pattern
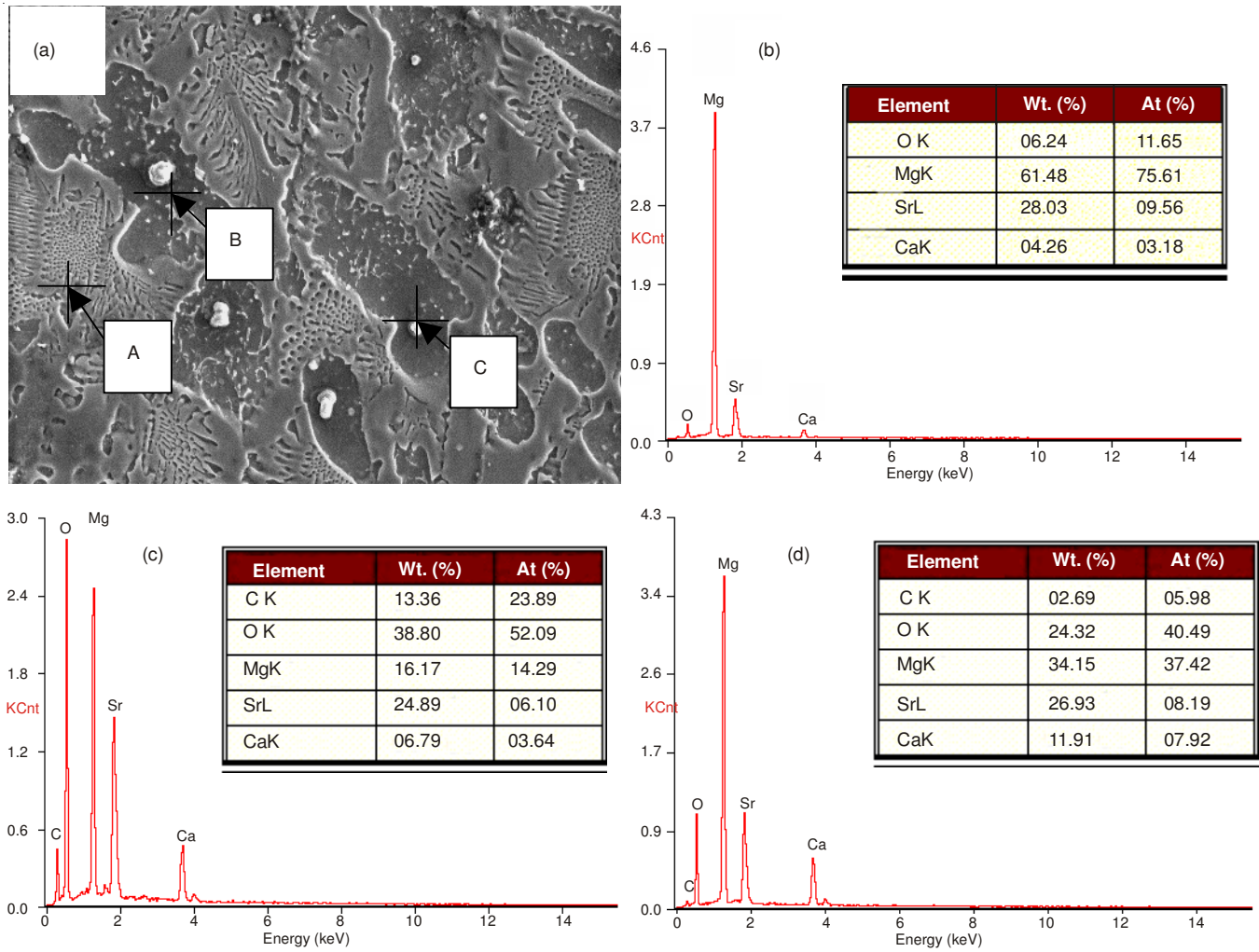
Element	Wt. (%)	At (%)
O K	06.24	11.65
MgK	61.48	75.61
SrL	28.03	09.56
CaK	04.26	03.18

Element	Wt. (%)	At (%)
C K	13.36	23.89
O K	38.80	52.09
MgK	16.17	14.29
SrL	24.89	06.10
CaK	06.79	03.64

Element	Wt. (%)	At (%)
C K	02.69	05.98
O K	24.32	40.49
MgK	34.15	37.42
SrL	26.93	08.19
CaK	11.91	07.92

Fig. 2. SEM Micrograph of the Mg-Sr master alloy and its EDS results: (a) SEM Micrograph, (b) EDS of $Mg_{17}Sr_2$, (c) EDS of Mg_2Sr, (d) EDS of $Mg_{23}Sr_6$
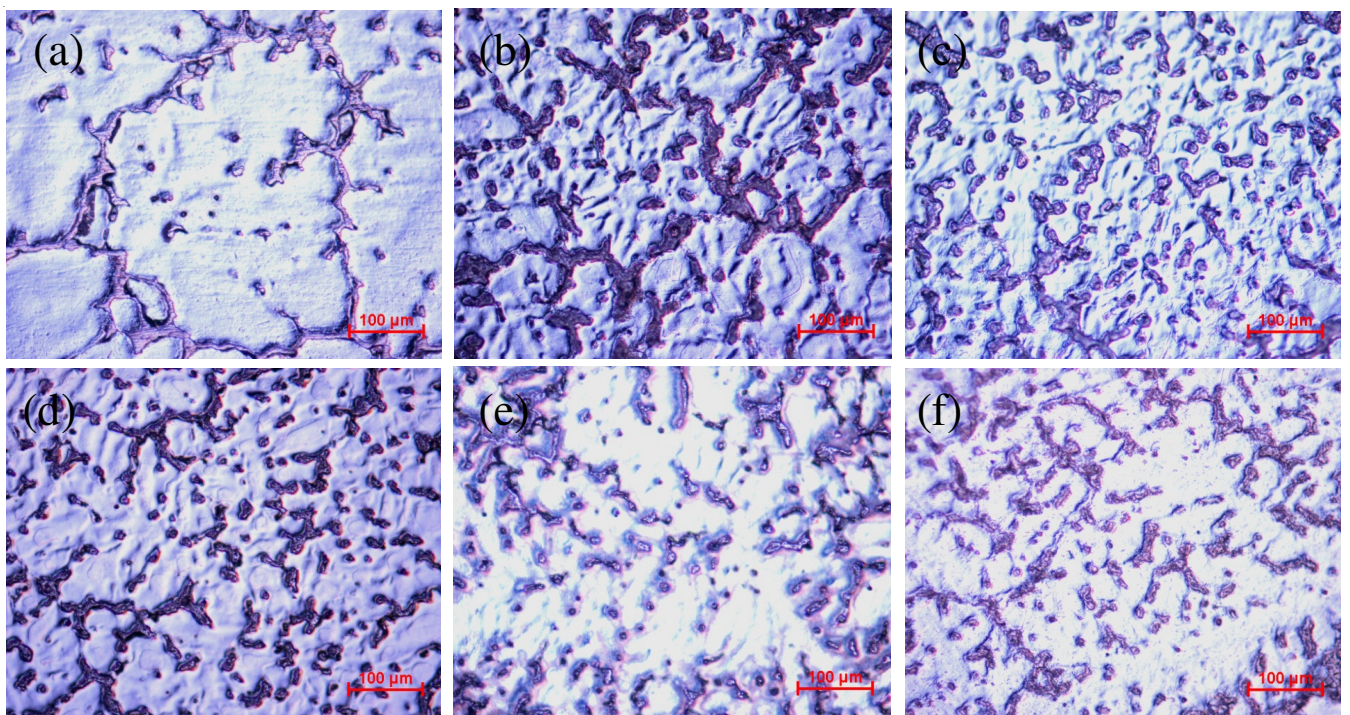

Fig. 3.   Microstructures of the AZ91D alloy with different Sr contents: (a) AZ91D (b) AZ91D-0.005 Sr (c) AZ91D-0.01Sr (d) AZ91D-0.015 Sr (e) AZ91D-0.02 Sr (f) AZ91D-0.03 Sr
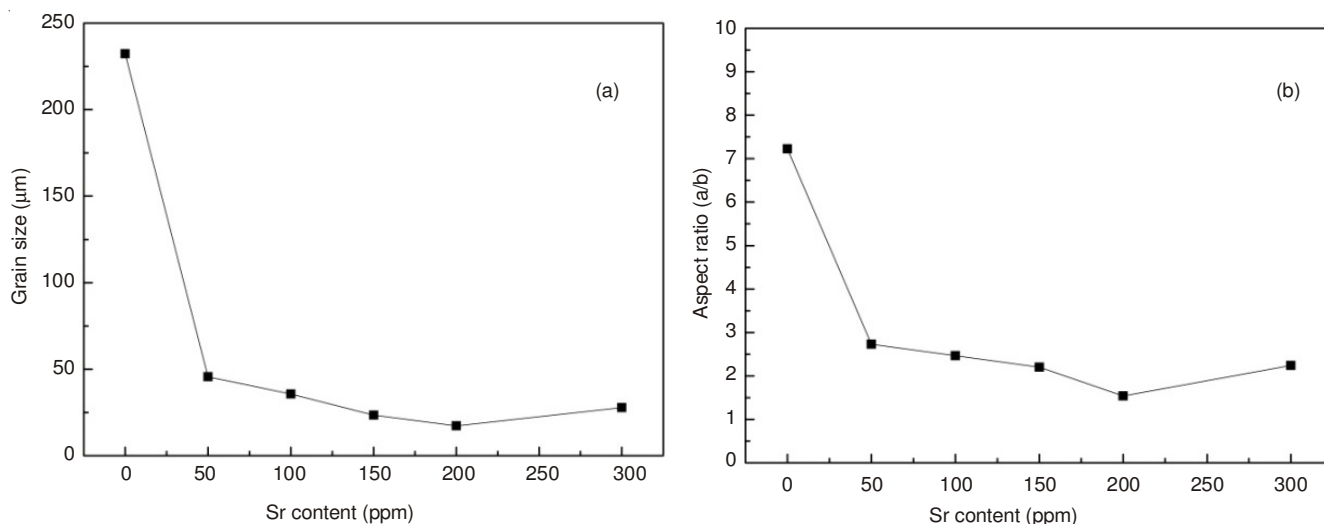
Fig. 4. Variations of (a) the grain size and (b) the aspect ratio of the β-Mg$_{17}$Al$_{12}$ in the AZ91D alloy treated with different Sr contents

Fig.5 shows the micrographs of the AZ91D magnesium alloys with different holding time. It can be seen that the Mg-Sr modificator had a beneficial long-term nature. Holding time ranging between 30-90 min and resulted in significantly refined eutectic β-Mg$_{17}$Al$_{12}$ grains, as shown in Fig. 5(a-c). According to Fig. 5(d-e), when the melt was maintained for 120-150 min, the grain size reached the minimum and had a homogeneous distribution. The presence of the fine eutectic β-Mg$_{17}$Al$_{12}$ indicates that the Sr addition not only was effective in modifying the eutectic β-Mg$_{17}$Al$_{12}$, but it also had a lasting effect in maintaining a fine structure.

Holding time is another important parameter determining the size of the eutectic β-Mg$_{17}$Al$_{12}$. The grain size and aspect ratio of the eutectic β-Mg$_{17}$Al$_{12}$ were measured to quantify the degree of modification. As shown in Fig. 6 (a), the grain size of the eutectic β-Mg$_{17}$Al$_{12}$ in the alloy greatly reduced from 18 μm during the first 0.5 min to 10 μm at a holding time of 150 min. The degree of modification was also quantified by measuring the aspect ratio of the eutectic β-Mg$_{17}$Al$_{12}$, the results are shown in Fig. 6(b). An increase in the holding time beyond 0.5 h did not alter the aspect ratio of the eutectic β-Mg$_{17}$Al$_{12}$.

Based on Kurfman theory[16], as the coarse-grain was formed in the magnesium alloy melt, undercooling appeared on the cooling curve [Fig. 7(a)], while, there was no undercooling during fine grain formation [Fig. 7(c)]. In other words, if there was no magnesium heterogeneous nucleation during the melt solidification, the cooled melt had to undercool a sufficient nucleation undercooling. Once nucleation was produced, the
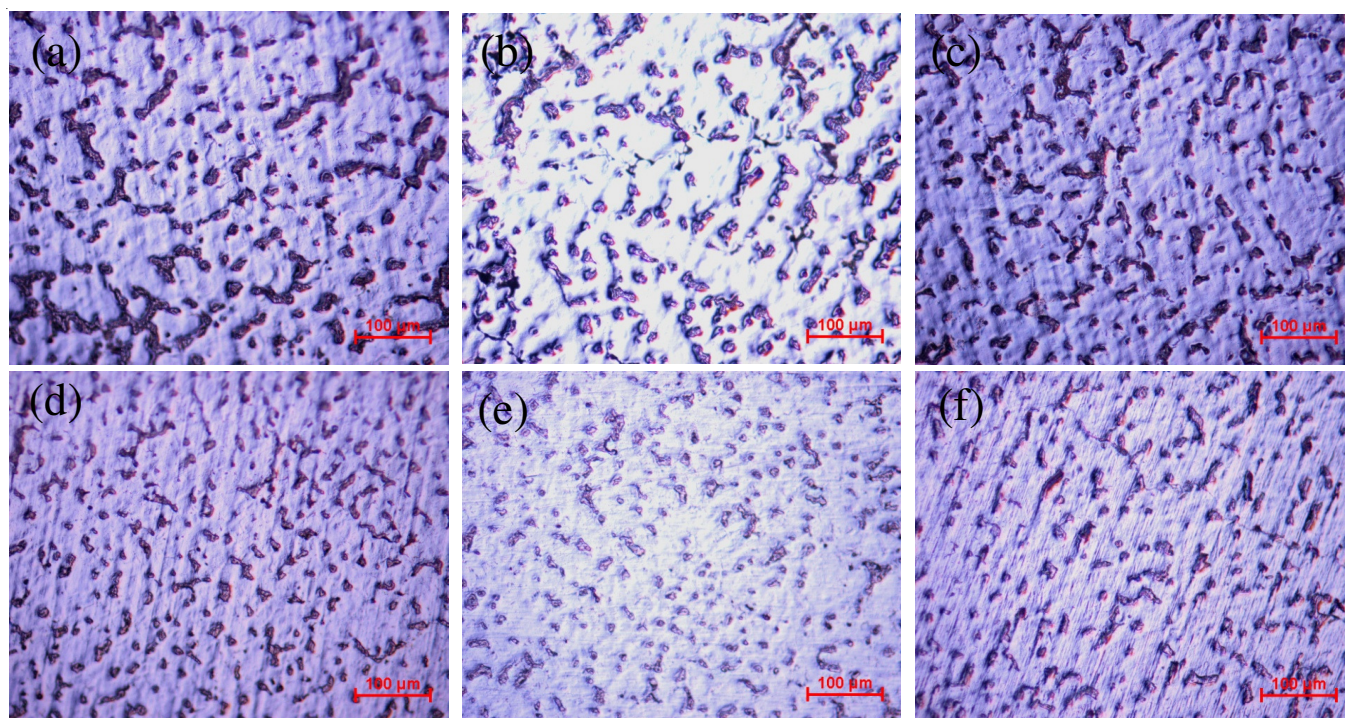

Fig. 5. Microstructure of as-cast alloys with different holding time [w(Sr) = 0.02 %]: (a) 30 min (b) 60 min (c) 90 min (d) 120 min (e)150 min (f)180 min
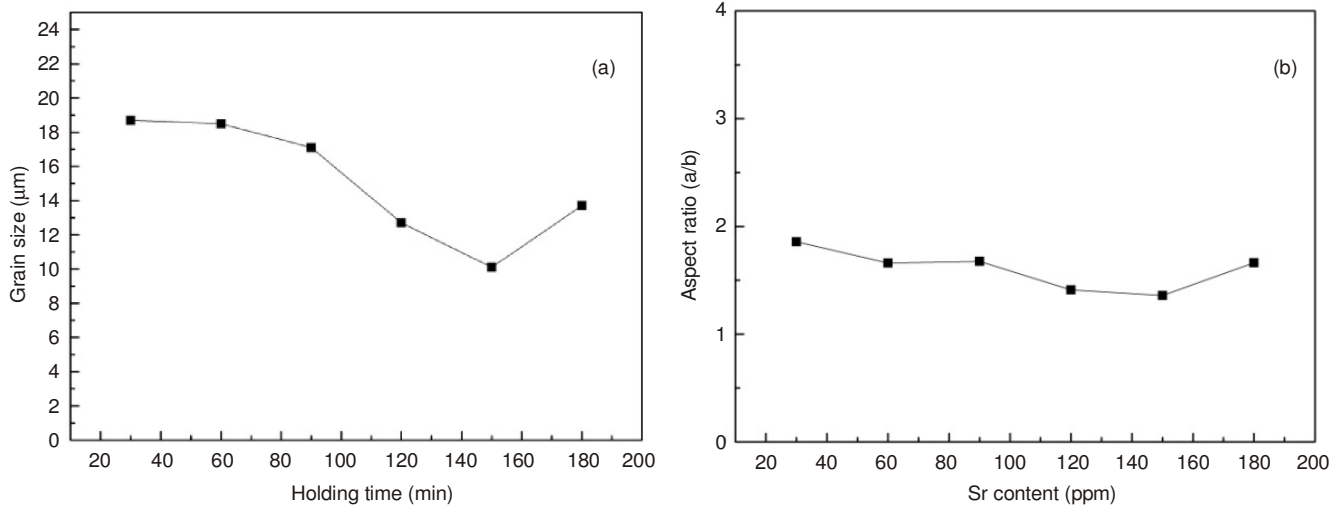
Fig. 6. Variations of (a) the grain size and (b) the aspect ratio of the β-Mg$_{17}$Al$_{12}$ in AZ91D alloy treated with different holding time

melt temperature increased and consequently, crystal growth occurred in the normal equilibrium temperature. The melt nucleation rate and the nucleation number increased when grain refining agents or nucleating agents were utilized. Additionally, the melt obtain a fine grain structure without any undercooling or under a small undercooling condition.
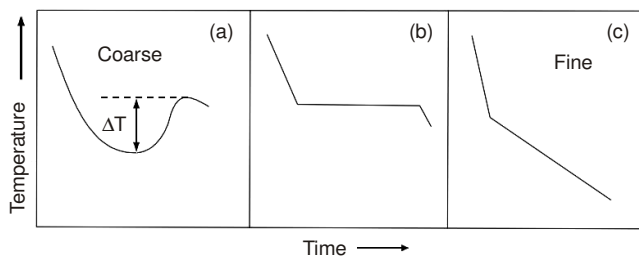

Fig. 7. Relationship between cooling curve liquidus-arrests and grain size

The liquidus and solidus temperature of the AZ91, AZ91-0.02 Sr alloy were measured by differential thermal analysis (DTA) (Fig. 8). It can be seen that adding the Sr element to the matrix alloy reduced the liquidus and solidus temperature, with the reduced values being -4.57 and -3.47 °C, respectively. The

results showed that, the addition of the Sr element to the AZ91D alloy decreased the undercooling in the same cooling conditions. Based on Kurfman theory, the decrease in the undercooling meant microstructure refinement.

Conclusion

It is possible to draw several conclusions from the experimental result as follows. The Mg-Sr master alloy prepared by molten salt electrolysis was composed of α-Mg, Mg$_{17}$Sr$_2$, Mg$_2$Sr and Mg$_{23}$Sr$_6$ phases. The addition of Sr to provide a content of 0.02-0.03 wt. % in the AZ91D magnesium alloy transformed the morphology of the eutectic β-Mg$_{17}$Al$_{12}$ from a continuous meshy distribution to a granular one. The Sr addition was not only effective in modifying the eutectic β-Mg$_{17}$Al$_{12}$, but also had a lasting effect in maintaining a fine structure. The grain size of the β-Mg$_{17}$Al$_{12}$ decreased notably from 230 μm in the unmodified sample to 17 μm at a Sr content of 0.02 %. This refinement was attributed to the reduction of the liquidus and solidus temperature and the decrease in undercooling. The optimum Sr content and holding time to optimize the AZ91D magnesium alloy were 0.02 % Sr and 150 min, respectively
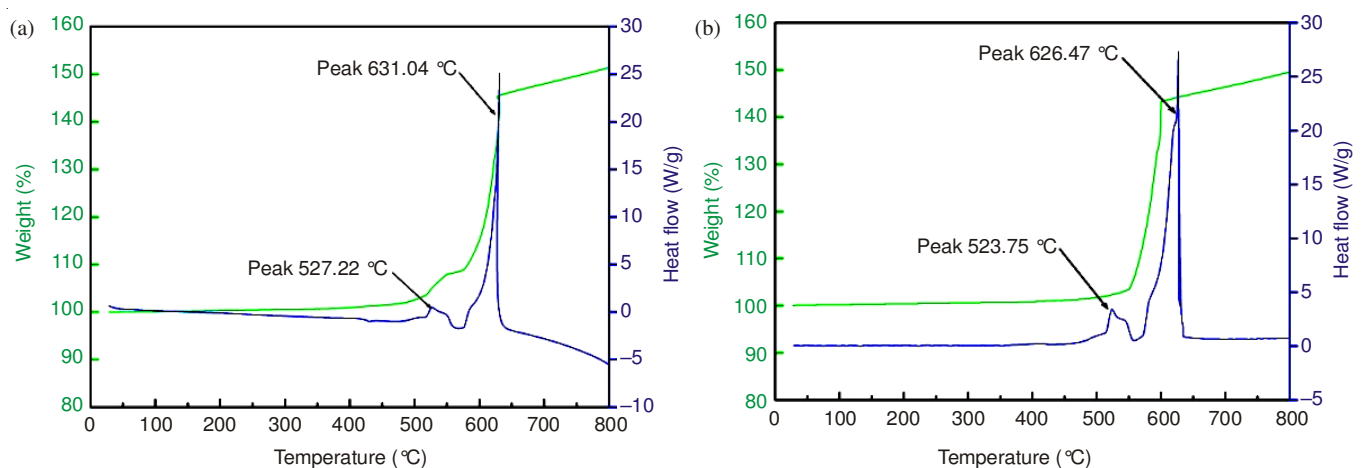

Fig. 8. Liquidus and solidus temperature of the alloys: (a) AZ91D, (b) AZ91D-0.03 Sr

REFERENCES

1. B.L. Mordike and T. Ebert, *Mater. Sci. Eng. A*, **302**, 37 (2001).
2. W.H. Cui, G.H. Min and J.C. Liu, *Rare Met. Mater. Des.*, **39**, 273 (2010).
3. R.M. Pillai, Proceedings of the 2nd AFS International Conference on Molten Aluminum Processing, November (1989).
4. A. Pacz, US Patent 1, 387, 900 (1921).
5. A.K. Dahle, K. Nogita, S.D. McDonald, C. Dinnis and L. Lu, *Mater. Sci. Eng. A*, **413-414**, 243 (2005).
6. S.S. Sreeja Kumari, R.M. Pillai and B.C. Pai, *J. Light Met.*, **460**, 472 (2008).
7. K. Suresh, K.P. Rao, Y.V.R.K. Prasad, N. Hort and K.U. Kainer, *Mater. Sci. Eng. A*, **588**, 272 (2013).
8. W. Prukkanon, N. Srisukhumbowornchai and C. Limmaneevichitr, *J. Alloys Comp.*, **477**, 454 (2009).
9. Q.L. Li, T.D. Xia, Y.F. Lan, P.F. Li and L. Fan, *Mater. Sci. Eng. A*, **588**, 97 (2013).
10. L.P. Wang, E.J. Guo and B.X. Ma, *J. Rare Earths*, **26**, 105 (2008).
11. S.D. McDonald, K. Nogita and A.K. Dahle, *Acta Mater.*, **52**, 4273 (2004).
12. S. Hegde and K.N. Prabhu, *J. Mater. Sci.*, **43**, 3009 (2008).
13. S.-S. Shin, E.-S. Kim, G.-Y. Yeom and J.-C. Lee, *Mater. Sci. Eng. A*, **532**, 151 (2012).
14. S.A. Argyropoulos and L.S. Chow, *J. Light Met.*, **2**, 253 (2002).
15. H.-M. Liao, S.-Y. Long, C.-B. Guo and Z.-B. Zhu, *Trans. Nonferr. Metals Soc. China*, **18 (Suppl. 1)**, s44 (2008).
16. C.A. Aliravci, J.E. Gruzleski and F.C. Dimaylga, *AFS Trans.*, **115**, 353 (1992).