

## Comparison about efficiency of Al–10Sr and Mg–10Sr master alloys to grain refinement of AZ31 magnesium alloy

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Received: 5 March 2007 / Accepted: 20 July 2007 / Published online: 6 September 2007  
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**Abstract** In the article, the effects of Al–10Sr and Mg–10Sr master alloys on the grain refinement of AZ31 magnesium alloy, are compared and analyzed. The results indicate that adding Al–10Sr or Mg–10Sr master alloys to AZ31 magnesium alloy could effectively reduce its grain size, but the refinement efficiency of Mg–10Sr master alloys is higher than that of the Al–10Sr master alloys. In addition, for a given melt holding time, the refinement efficiency of the two master alloys respectively increase with Sr adding amount increasing from 0 to 0.1 wt%, and the increasing laws are similar. For a given Sr adding amount, the refinement efficiency of Al–10Sr mater alloy gradually increases with the melt holding time increasing from 20 to 80 min, but its changing is not obvious for the Mg–10Sr mater alloy. The difference of refinement efficiency for the Al–10Sr and Mg–10Sr master alloys might be related to the dissolution modes and rates of  $\text{Al}_4\text{Sr}$  and  $\text{Mg}_{17}\text{Sr}_2$  phases in the melt of AZ31 magnesium alloy.

### Introduction

At present, the AZ series magnesium alloys have been widely applied in industrial production, but their mechanical properties and processing performances still could not meet the needs of some important parts in vehicles and

other application fields. Therefore, a lot of ways are being investigated in the world in order to improve further the mechanical properties and processing performances of the AZ series magnesium alloys [1–4]. It is known that the grain refinement is an important method of elevating property and improving formability for magnesium alloys. Recent results indicated that Sr additions such as Al–Sr master alloys which have been widely used in industrial practice especially for the modification of Al–Si alloys, were thought as to be potential effective additions of grain refinement for Mg–Al series alloys [5–11]. For example, Srinivasan and Nam et al. [12, 13] reported that adding Al–10Sr master alloy to a Si-containing AZ91–Mg alloy appeared to refine the microstructure by promoting a finer grain size, and similar results were also obtained in AM50–Mg alloy and AZ91–Mg alloy by Zhao and Hirai et al. [14, 15]. In addition, Zeng and Chen et al. [16, 17] respectively reported that adding pure Sr and Al–10Sr alloy to AZ31–Mg alloy effectively reduced its grain size, and similar results were reported by other researchers [5, 6]. At present, the types of Sr additions added to magnesium alloys, mainly focus on the pure Sr and Al–Sr master alloy. The investigation about effects of other Sr additions on the grain refinement of magnesium alloys are very limited. In recent studies, we found that Mg–Sr master alloy is also an effective refiner in magnesium alloys. But up to now, the comparison about the efficiency of Al–Sr and Mg–Sr master alloys to grain refinement of magnesium alloys has not been reported. In order to provide an optimum choosing for the grain refinement of AZ31 magnesium alloy by adding Sr-containing master alloys, the effects of Al–10Sr and Mg–10Sr master alloys on the grain refinement of AZ31 magnesium alloy, especially the refinement efficiency of the two master alloys, are compared and analyzed in this article.

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### Experimental

The rods of commercial Al–10Sr master alloy which were prepared by traditional casting and subsequent extrusion at Changzhou Metal Materials Company Limited in China, was used to compare with Mg–Sr master alloy. The Mg–Sr master alloy was prepared from commercial pure Mg and Sr. The pure Mg was melted in a crucible resistance furnace and protected by a flux addition. When the melt temperature approximately reached 993 K, the pure Sr was rapidly added to the melt. After held at 1,023 K for 60 min, the melt was poured into a permanent moulds whose mould cavities are  $\Phi 20 \times 90$  mm. The chemical compositions of Mg–Sr master alloy obtained was listed in Table 1 As a reference, the chemical compositions of commercial Al–10Sr master alloy was also given in Table 1

The Al–10Sr and Mg–10Sr master alloys were used to refine the as-cast microstructure of AZ31 magnesium alloy respectively. The refinement treatment was carried out in an electrical resistance furnace using a graphite crucible and protected by a flux addition. When the melt temperature approximately reached 1,013 K, the Al–10Sr or Mg–10Sr master alloys whose weight were calculated according to the Sr adding amount, 0.01, 0.05, and 0.1 wt%, were respectively added to the melt. After respectively held at 1,013 K for 20, 40, 60, or 80 min, the melt was poured into a permanent mould whose mould cavity is  $\Phi 20 \times 90$  mm. Table 2 showed the chemical compositions of parts of the experimental alloys treated by Al–10Sr and Mg–10Sr master alloys.

In order to show the crystal grains of AZ31 magnesium alloys clearly, the solid solution treatment of the obtaining castings were carried out at 688 K for 12 h and followed by water quenching. Furthermore, optical microscope samples of experimental AZ31 magnesium alloys were etched with a solution of 1.5 g picric, 25 mL ethanol, 5 mL acetic acid and 10 mL distilled water and then were examined using a Olympus optical microscope and JOEL JSM-6460LV type scanning electron microscope (SEM)

**Table 1** Chemical compositions of the master alloys, wt%

Nominal alloy	Sr	Ca	Ba	Fe	Si	Al	Mg
Al–Sr master alloy	10.0	0.016	0.02	0.29	0.20	Bal.	–
Mg–Sr master alloy	10.1	–	–	0.17	0.15	–	Bal.

**Table 2** Chemical compositions of parts of the experimental alloys, wt%

Nominal alloy	Melt holding time/min	Types of master alloy	Al	Zn	Mn	Sr	Mg
AZ31	60	Untreatment	2.85	0.76	0.17	–	Bal.
AZ31 + 0.1 wt% Sr	60	Al–10Sr alloy	2.88	0.77	0.16	0.087	Bal.
AZ31 + 0.1 wt% Sr	60	Mg–10Sr alloy	2.87	0.75	0.16	0.088	Bal.

equipped with Oxford energy dispersive X-ray spectrometer (EDS). The grain size was analyzed by the standard linear intercept method using a Olympus stereomicroscope. The phases in the experimental alloys were analyzed by D/Max-1200X type analyzer operated at 40 kV and 30 mA.

### Results and discussion

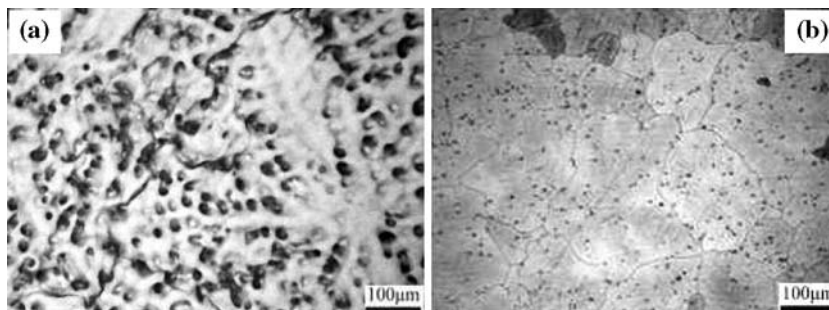
#### Microstructure of AZ31 magnesium alloy

Figure 1 shows the as-cast and solutionized microstructures of AZ31 magnesium alloy untreated. At the same time, under the condition of Sr adding amount being 0.1% and melt holding time being 60 min, the optical microstructures of as-cast AZ31 magnesium alloy treated by the Al–10Sr and Mg–10Sr master alloys, are also showed in Fig. 2. In Fig. 1, it is found that the dendritic arm spacing and grain size of AZ31 magnesium alloy untreated, are big. However, after treated by the Sr-containing master alloys, the dendritic arm spacings and grain sizes decrease (seeing Fig. 2). Then it is believed that the Al–10Sr and Mg–10Sr master alloys could effectively refine the microstructures of AZ31 magnesium alloy. In addition, it is found from the Fig. 2 that the refinement efficiency of Mg–10Sr master alloy is higher than that of the Al–10Sr master alloy.

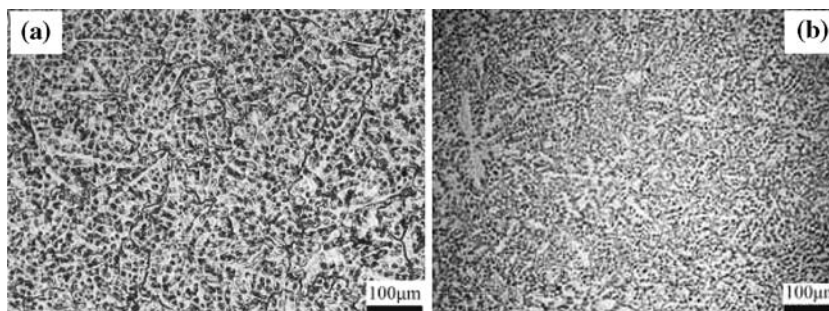
Under the condition of Sr adding amount being 0.1% and melt holding time being 60 min, the SEM microstructures of as-cast AZ31 magnesium alloys treated by the Al–10Sr and Mg–10Sr master alloys, are showed in Fig. 3. These views show some insular particles (arrow A) and acicular particles (arrow B). According to the EDS analyses listed in Table 3, the insular and nubbly particles contain Al, Zn, and Mg. Obviously, the insular and nubbly particles are  $Mg_{17}Al_{12}$  phases that are commonly observed in AZ31 magnesium alloy. The Mg–Al–Mn, Al–Mn and  $Mg_{20}Al_{20}Mn_5Sr$  phases reported by Zeng et al. [16], are not found in the investigation of this article. Considering that the  $Mg_{17}Al_{12}$  phases do not cause the formation of any new phases containing Sr, the effects of these phases on the grain refinement are neglected in this article.

For a given melt holding time or Sr adding amount, the effects of Sr adding amount and melt holding time on the macrostructures and average grain sizes of AZ31 magnesium alloys treated by Al–10Sr and Mg–10Sr master alloys

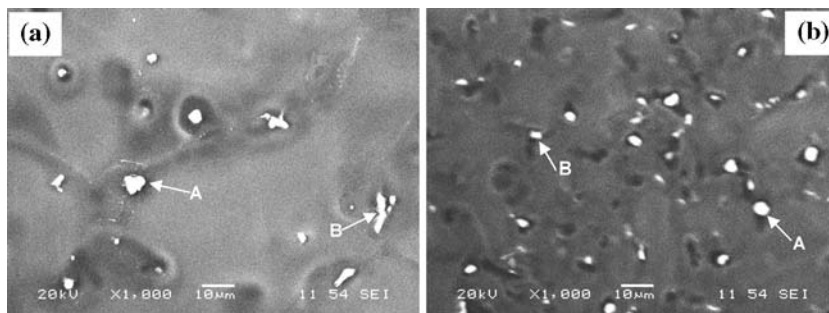
**Fig. 1** As-cast and solutionized microstructures of AZ31 magnesium alloys untreated: (a) as-cast, and (b) solutionized



**Fig. 2** As-cast microstructures of AZ31 magnesium alloys treated by the Al–10Sr and Mg–10Sr master alloys: (a) Al–10Sr alloy, and (b) Mg–10Sr alloy



**Fig. 3** SEM images of as-cast AZ31 magnesium alloys treated by the Al–10Sr and Mg–10Sr master alloys: (a) Al–10Sr alloy, and (b) Mg–10Sr alloy



**Table 3** EDS results of the different positions in Fig. 3

Positions	Mg	Al	Zn	Total, Atomic%
“A” in Fig. 3a	69.05	24.41	6.54	100
“B” in Fig. 3a	68.97	26.21	4.82	100
“A” in Fig. 3b	64.22	27.21	8.57	100
“B” in Fig. 3b	65.71	24.36	9.93	100

are showed in Figs. 4–6. According to the Figs. 4–6, the experimental results obtained from the Figs. 1 and 2 could be further confirmed quantitatively. In addition, it is also found from the Fig. 6 that with the Sr adding amount increasing from 0 to 0.1%, the refinement efficiency of Al–10Sr and Mg–10Sr master alloys respectively increase, and the increasing laws are approximately similar. However, with the melt holding time increasing from 20 to 80 min, the different changing laws for refinement efficiency of Al–10Sr and Mg–10Sr master alloys are observed. The refinement efficiency of Al–10Sr mater alloy increases

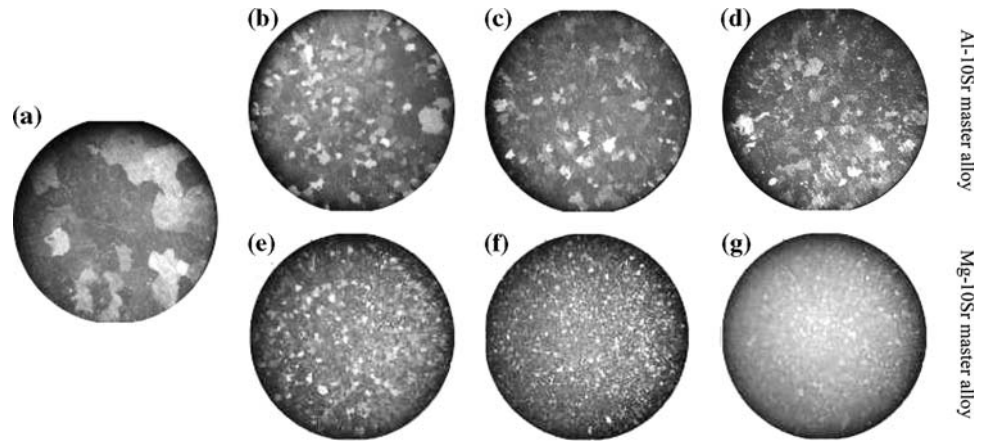
gradually. Oppositely, the changing of refinement efficiency for Mg–10Sr mater alloy is not obvious.

To clearly reveal the grain boundaries in the AZ31magnesium alloy treated by Al–10Sr and Mg–10Sr master alloys, a solution heat treatment was applied, and the solutionized microstructures are shown in Fig. 7. In Fig. 7, many second phase particles are clearly observed. Obviously, these second phase particles are the remnant  $Mg_{17}Al_{12}$  phases. In addition, to confirm whether grain growth occurs during the solid solution treatment, the grain size of the solutionized alloys are measured and compared to Fig. 6, only slightly larger than that of the as-cast alloys, indicating that the solid solution treatment caused little grain growth.

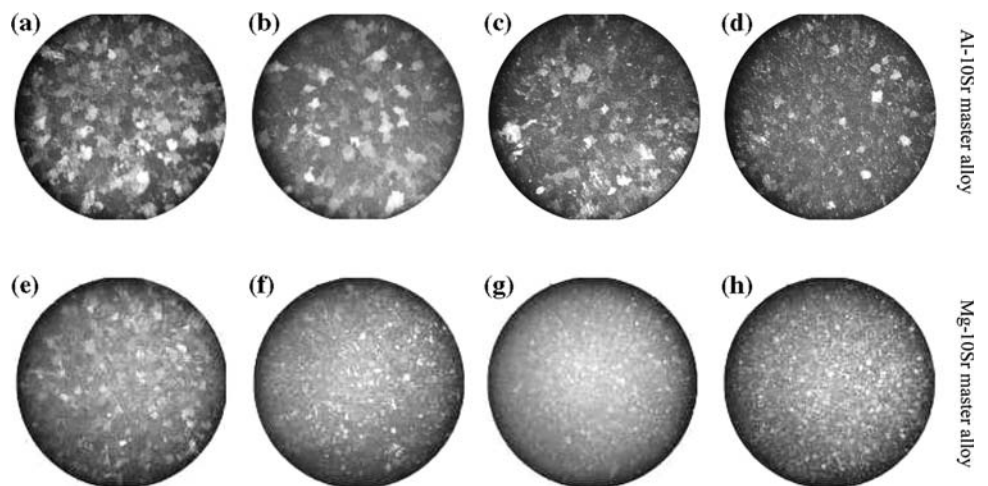
## Discussion

In general, the grain refinement in industrial applications usually involves adding nucleants and solute elements, and the effect of a solute element on grain refinement is

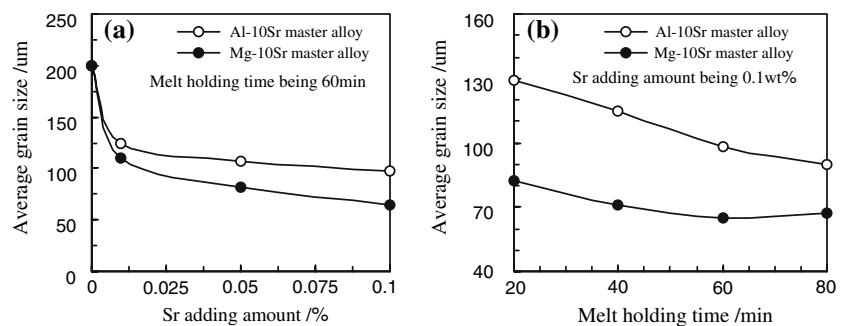
**Fig. 4** Effects of Sr adding amount on the macrostructure of AZ31 magnesium alloy under the melt holding time being 60 min: (a) untreated, (b) and (e) 0.01 wt% Sr; (c) and (f) 0.05 wt% Sr; (d) and (g) 0.1 wt% Sr; The diameter of each polished section is ~25 mm



**Fig. 5** Effects of melt holding time on the macrostructure of AZ31 magnesium alloy under the Sr adding amount being 0.1 wt%: (a) and (e) 20 min, (b) and (f) 40 min, (c) and (g) 60 min, (d) and (h) 80 min; The diameter of each polished section is ~25 mm



**Fig. 6** Effects of Sr adding amount and melt holding time on average grain sizes of AZ31 magnesium alloy: (a) Sr adding amount, and (b) melt holding time



explained in terms of the growth restriction factor GRF (Eq. (1)) [5, 6, 16]. At the same time, according to the research results obtained by Lee and Gruzleski [5, 6], the solid solubility of Sr in magnesium is relatively limited (about 0.11 pct) [16], and thus rapid enrichment of Sr in the liquid ahead of the growing interface will restrict the grain growth during solidification. So the mechanism of grain refinement by Sr in magnesium alloys is mainly believed to be the GRF mechanism. Bigger the GRF value is, then higher the refinement efficiency of Sr in magnesium alloys is.

$$GRF = \sum_i m_i c_{0i} (k_i - 1) \tag{1}$$

where  $m_i$  is the slope of the liquidus line,  $c_{0i}$  is the initial concentration of element  $i$ ,  $k_i$  is the partition coefficient. Under the experimental condition of this article,  $i$  are Al, Zn, and Sr elements respectively. According to the reference [16],  $m_{Al} = -6.87$ ;  $m_{Zn} = 6.04$ ;  $m_{Sr} = -3.53$ ;  $k_{Al} = 0.37$ ;  $k_{Zn} = 0.12$ ;  $k_{Sr} = 0.006$ ;  $c_{0Al}$ ,  $c_{0Zn}$ , and  $c_{0Sr}$  of parts of the experimental alloys are listed in Table 2.

**Fig. 7** Solutionized microstructures of AZ31 magnesium alloy treated by the Al–10Sr and Mg–10Sr master alloys: (a) Al–10Sr alloy, and (b) Mg–10Sr alloy

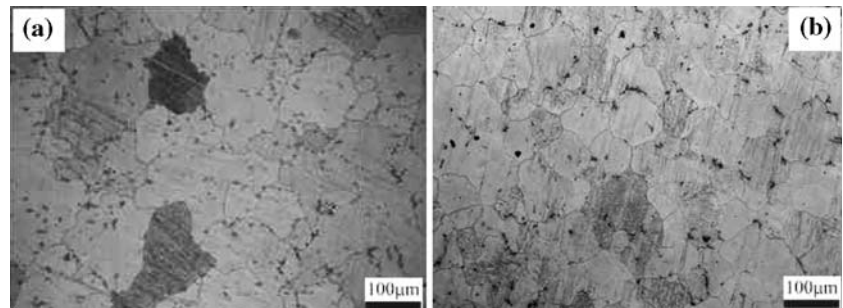
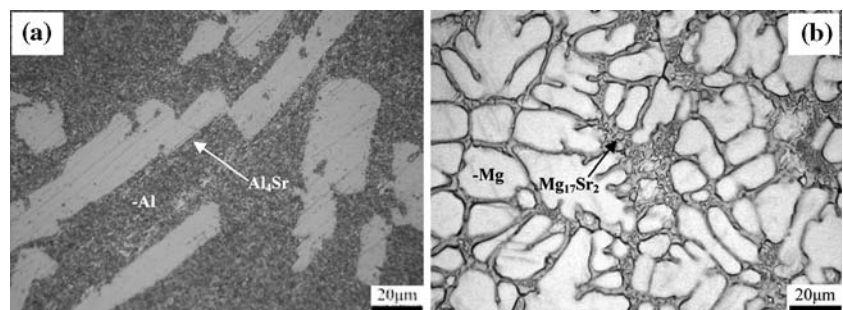


Figure 8 shows the microstructures of Al–10Sr and Mg–10Sr master alloys. As shown in Fig. 8, the Al–10Sr master alloy is composed of  $\alpha$ -Al and  $\text{Al}_4\text{Sr}$  phases, the Mg–10Sr master alloy is composed of  $\alpha$ -Mg and  $\text{Mg}_{17}\text{Sr}_2$  phase. It is well known that the  $\text{Al}_4\text{Sr}$  phases in Al–10Sr master alloy is a body centered tetragonal structure ( $\text{DI}_3$  type with  $a = 4.46$  nm and  $c = 11.07$  nm) [18], the  $\text{Mg}_{17}\text{Sr}_2$  phases in Mg–10Sr master alloy is a hexad structure ( $\text{Ni}_{17}\text{Th}_2$  type with  $a = b = 10.468$  nm and  $c = 10.300$  nm) [19], the  $\alpha$ -Mg phase is a Hexagonal Close-Packed crystal structure with  $a = 0.320$  nm and  $c = 0.520$  nm [20]. Obviously, the  $\text{Al}_4\text{Sr}$  and  $\text{Mg}_{17}\text{Sr}_2$  phases could not directly influence the grain refinement unless the free Sr could be obtained by the dissolution of  $\text{Al}_4\text{Sr}$  and  $\text{Mg}_{17}\text{Sr}_2$  phases.

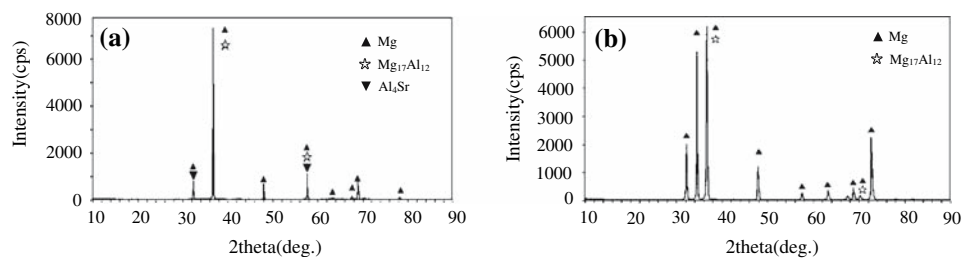
In this article, considering when the Al–10Sr and Mg–10Sr master alloys are used to refine the microstructure of AZ31 magnesium alloy, the treatment conditions such as melt treatment temperature, holding time and Sr adding amount (seeing Table 2) are same. Then if the initial concentration of free Sr in the melt of AZ31 magnesium alloys treated by Al–10Sr and Mg–10Sr master alloys were equal, the GRF values should be approximately equal according to the Eq. (1). Accordingly, the refinement efficiency of the two master alloys should be similar according to the GRF mechanism. However, the deducing conclusion does not agree with actual situation. Then it is inferred that the initial concentration of free Sr in the melt of AZ31 magnesium alloys treated by Al–10Sr and Mg–10Sr master alloys, could be different. Considering that the melt point of  $\text{Al}_4\text{Sr}$  and  $\text{Mg}_{17}\text{Sr}_2$  phases are 1,313 and 879 K respectively [19], so for a given melt treatment temperature of 1,013 K in this article, the obtaining modes of free Sr for Al–10Sr and

Mg–10Sr master alloys in the melt of AZ31 magnesium alloy should be different. The free Sr could be obtained by the dissolution and melting of  $\text{Mg}_{17}\text{Sr}_2$  phases for Mg–10Sr master alloy. Oppositely, the free Sr could be only obtained by the dissolution of  $\text{Al}_4\text{Sr}$  phases for Al–10Sr master alloy. Obviously, the obtaining rate of free Sr resulted from the  $\text{Mg}_{17}\text{Sr}_2$  phases dissolution and melting, is quicker than that of  $\text{Al}_4\text{Sr}$  phases dissolution. In addition, according to the results obtained by Zhang et al. [8, 10], the effect of morphology and size of  $\text{Al}_4\text{Sr}$  phase on its dissolution rate is obvious, thereinto high dissolution rate could be obtained for finer  $\text{Al}_4\text{Sr}$  phase in Al–Sr master alloys. In Fig. 8, the  $\text{Al}_4\text{Sr}$  phases in Al–10Sr master alloy mainly exhibit coarse block shape. Obviously, the dissolution rates of these  $\text{Al}_4\text{Sr}$  phases with coarse block shape are slower. This conclusion can be further confirmed from Fig. 9. Figure 9 shows the XRD results of as-cast AZ31 magnesium alloys treated by the Al–10Sr and Mg–10Sr master alloys under the condition of Sr adding amount being 0.1% (actual Sr content <0.1% in Table 2) and melt holding time being 60 min. Although the  $\text{Al}_4\text{Sr}$  phase is not found in the EDS result of as-cast microstructure for AZ31 magnesium alloy treated by the Al–10Sr master alloy, it is detected in Fig. 9a. Considering that small amounts of strontium (Sr <0.1%) do not cause the formation of any new phases in the microstructure of magnesium alloy [14], it is inferred that the  $\text{Al}_4\text{Sr}$  phases in the Al–10Sr master alloy do not completely dissolve into the melts of AZ31 magnesium alloy. Then the undissolved  $\text{Al}_4\text{Sr}$  phases are detected in Fig. 9a. Oppositely, the  $\text{Mg}_{17}\text{Sr}_2$  phases in the Mg–10Sr master alloy could completely dissolve and melt into the melt of AZ31 magnesium alloy thus are not detected in Fig. 9b.

**Fig. 8** Optical microstructures of the Al–10Sr and Mg–10Sr master alloys: (a) Al–10Sr alloy, and (b) Mg–10Sr alloy



**Fig. 9** XRD results of as-cast AZ31 magnesium alloys treated by the Al–10Sr and Mg–10Sr master alloys under the condition of Sr adding amount being 0.1% and melt holding time being 60 min: (a) Al–10Sr alloy, and (b) Mg–10Sr alloy



According to the above, when the treatment conditions such as melt treatment temperature, holding time and Sr adding amount are same, the concentration of free Sr in the AZ31 magnesium alloy melt treated by Mg–10Sr master alloy is higher than that of the AZ31 magnesium alloy melt treated by Al–10Sr master alloy. According to the GRF mechanism, the GRF value for Mg–10Sr master alloy is bigger. Accordingly, the refinement efficiency of Mg–10Sr master alloy to AZ31 magnesium alloy is higher than that of Al–10Sr master alloy.

In the melt of AZ31 magnesium alloy investigated, for the given Al–10Sr and Mg–10Sr master alloy, when the melt holding time keeps a constant, the amount of  $Al_4Sr$  and  $Mg_{17}Sr_2$  phases increase with Sr adding amount increasing. Accordingly, the amount of free Sr and the GFR value would increase. So as shown in Fig. 6a, with the Sr adding amount increasing, the refinement efficiency increases. However, when Sr adding amount keeps a constant, the dissolution time of  $Al_4Sr$  phases increase with melt holding time increasing. At the same time, considering that the dissolution of  $Al_4Sr$  phases is a continuous process and relatively slow, the increasing of free Sr amount and GFR value are a gradual process. Oppositely, due to the low melting point and fine size of  $Mg_{17}Sr_2$  phase, they would completely dissolve and melt into the melt of AZ31 magnesium alloy in a short time, then the concentration of free Sr and GFR value would keep a constant approximately. So as shown in Fig. 6b, with the melt holding time increasing, the refinement efficiency of Al–10Sr master alloy increases gradually, the changing of refinement efficiency for Mg–10Sr master alloy is not obvious.

## Conclusions

Adding Al–10Sr or Mg–10Sr master alloys to the AZ31 magnesium alloy could effectively reduce its grain size, but the refinement efficiency of Mg–10Sr master alloys is higher than that of the Al–10Sr master alloys. In addition, for a given melt holding time, the refinement efficiency of the two master alloys respectively increase with Sr adding amount increasing from 0 to 0.1%, and the increasing laws are similar. However, for a given Sr adding amount, the

refinement efficiency of Al–10Sr master alloy gradually increases with the melt holding time increasing from 20 min to 80 min, but its changing is not obvious for the Mg–10Sr master alloy. The difference of refinement efficiency for the Al–10Sr and Mg–10Sr master alloys might be related to the dissolution modes and rates of  $Al_4Sr$  and  $Mg_{17}Sr_2$  phases in the melt of AZ31 magnesium alloy.

**Acknowledgements** The present work was supported by both the High-tech Research and Development Program of China (863) (No. 2001AA331050) and Chongqing Science and Technology Commission (No. 2006AA4012-9-6).

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