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As-cast microstructure and Sr-containing phases of AZ31 magnesium alloys with high Sr contents

WU Lu[1], PAN Fu-sheng[1], YANG Ming-bo[2], WU Ju-ying[1], LIU Ting-ting[1]

1. National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400044, China;
2. College of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400050, China

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Abstract: The as-cast microstructure and Sr-containing phases in the AZ31 magnesium alloys with different Sr contents (0%, 0.3%, 2.5% and 5.0%, mass fraction) were investigated. The results indicate that after adding Sr to the AZ31 magnesium alloy, the dendrite/grain size is decreased, and with the Sr content increasing from 0 to 5.0%, the dendrite becomes finer, the dendrite morphology becomes more passive and the distribution of alloying phases at dendrite/grain boundary is dispersed. Furthermore, the morphology of the β-$Mg_{17}Al_{12}$ phase in the alloy with addition of 0.3%Sr changes from continuously irregular strip-like shape to discontinuously irregular strip-like shape and/or fine granule-like shape. At the same time, some lamella-like eutectic phases are found in the alloys with additions of 2.5% Sr and 5.0% Sr, and the lamella spacing in the alloy with addition of 5.0% Sr is finer. Adding high Sr content to the AZ31 alloy can bring the new ternary eutectic and/or divorced eutectic phase of $Mg_{11}Al_5Zn_4$ in the alloy, and the $Mg_{17}Sr_2$ and Mg_2Sr phases are formed in the alloys with additions of 2.5% Sr and 5.0% Sr.

Key words: magnesium alloy; AZ31 magnesium alloy; Sr-containing phase; Sr

1 Introduction

In recent years, the annual output of magnesium has increased remarkably in China, and magnesium alloys are being applied to motorcycles, automobiles, electric devices and so on[1]. As one significant member of the big family, the Mg-Al-Zn system 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[2−6]. Therefore, many methods are being investigated in the world in order to improve mechanical properties and processing performances of Mg-Al-Zn system alloys. It has been reported that the Sr addition to the Mg-Al-Zn system alloys can refine the microstructures, improve the strength and creep resistance. ALIRAVCI et al[7−8] and NUSSBAUM et al[9] found that adding minor Sr to the Mg-9Al-1Zn alloy can decrease the grain size and improve the shrinkage micro-porosity. In addition, YANG et al[10−11] reported that different Sr-containing master alloys such as Mg-9Sr and Al-10Sr, have different grain refining efficiencies to the Mg-3Al-1Zn alloy. In spite of the above works, the previous investigations mainly focus on the effect of minor Sr on the grain refinement and mechanical properties of the Mg-Al-Zn system alloys. The effect of Sr addition on the alloying phases of the Mg-Al-Zn system alloys is very scarce in the literature, especially the effect of high Sr content. Since the alloying phases are very important to the mechanical properties of the engineering alloys, it is very necessary to investigate the effect of Sr addition on the alloying phase in the Mg-Al-Zn system alloys, especially the effect on the Sr-containing alloying phases. Based on the above reasons, the as-cast microstructure and the Sr-containing phases in the AZ31 magnesium alloys with different Sr contents (0, 0.3%, 2.5% and 5.0%, mass fraction) were investigated in this work.

2 Experimental

The experimental alloys were prepared from pure Mg, Al and Zn (≥99.9%), Mg-4.6%Mn and Mg-38.89%Sr

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Corresponding author: PAN Fu-sheng; Tel: +86-23-65112635; E-mail: fspan@cqu.edu.cn
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master alloys. The pure Mg was first melted in an electrical resistance furnace using a graphite crucible and protected by a flux addition. When the melt temperature reached 730 °C approximately, the pure Al, pure Zn and the master alloys were added to the melt. After being held for 40 min at 700 °C, the melt was poured into a permanent mould in order to obtain a casting. Table 1 lists the chemical compositions of the experimental alloys.

Table 1 Chemical compositions of experimental alloys (mass fraction, %)

Alloy	Al	Zn	Mn	Sr	Mg
AZ31	3.0	1.0	0.3	0	Bal.
AZ31+0.3%Sr	3.0	1.0	0.3	0.3	Bal.
AZ31+2.5%Sr	3.0	1.0	0.3	2.5	Bal.
AZ31+5.0%Sr	3.0	1.0	0.3	5.0	Bal.

The samples of the experimental alloys were etched with a 8% nitric acid distilled water solution, and then examined by an Olymous optical microscope and TESCAN VEGA Ⅱ LMU type scanning electron microscope (SEM) equipped with an Oxford energy dispersive spectrometer (EDS). The phases in the experimental alloys were analyzed by Rigaku D/MAX−2500PC type X-ray diffractometer (XRD) with Co K_{α}.

3 Results and discussion

3.1 Microstructure of alloys

Figure 1 shows the optical images of the AZ31 alloy with different Sr contents (0, 0.3%, 2.5% and 5.0%). It is found that the microstructure of the AZ31 alloy without Sr is mainly composed of the primary α-Mg and β-$Mg_{17}Al_{12}$ phases which precipitate along interdendritic; the dendritic arm spacing and grain size of the AZ31 alloy without Sr (Fig.1(a)) are obviously bigger than those of the other alloys (Figs.1(b))−(d)). The above results indicate that Sr added to the AZ31 alloy can refine the grains of the alloy. The difference is that the dendrite in the alloy with addition of 0.3% Sr just only gets slender, but the dendrite is finer and dendritic arm spacing is obviously decreased in the alloy with addition of 5.0% Sr. In addition, with additions of 2.5% and 5.0% Sr the curvatures of dendrite tips are found to become smaller and the dendrite becomes more passive in the alloys (Figs.1(c) and (d)).

In general, the grain refinement in industrial applications usually involves adding nucleant and solute elements，and the effect of a solute element on grain refinement is explained in terms of the growth restriction factor (GRF) (Eq.(1))[7, 12−13]. At the same time, according to the research results obtained by LEE et al[12] and ALIRAVCI et al[7], the solid solubility of Sr in magnesium is relatively limited. The solidification process belongs to non-equilibrium freezing because of the high solidification rates. During the solidification process, the primary α-Mg crystals first formed and grew, and the remaining Sr solute atoms in the melts diffused to the liquid/solid interface, restricting the grain growth. Therefore, the Sr element addition contributes to the significant grain refinement in the AZ31 alloy, as illustrated in Fig.1. And the mechanism of grain

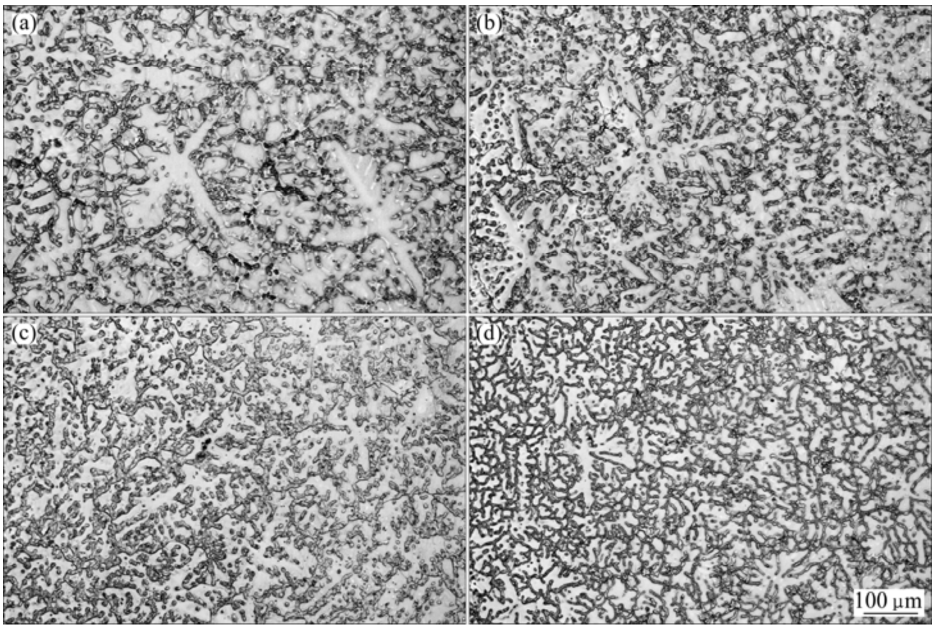

Fig.1 As-cast microstructures of AZ31 magnesium alloys with different Sr contents: (a) Without Sr; (b) 0.3% Sr; (c) 2.5% Sr; (d) 5.0% Sr

refinement of Sr in magnesium alloys is mainly believed to be the GRF mechanism. The larger the GRF value, the higher the refinement efficiency of Sr in magnesium alloys.

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

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 work, i is Al, Zn and Sr elements, respectively.

According Eq.(1), the GRF value will be increased with increasing the $c_{0\mathrm{Sr}}$, which is due to adding much more amount of Sr element. Thus the dendrite/grain size of the AZ31 alloy decreases with increasing the Sr content from 0 to 5.0% based on the GRF mechanism which tallys with Fig.1 by and large.

3.2 Morphology and distribution of alloying phases

Figure 2 shows the SEM images of the AZ31 alloys with Sr showing of morphology and distribution of alloying phases. It is found from Fig.2 that with the addition of more than 2.5% Sr, the volume fraction of alloying phases at the dendrite/grain boundary is quite more than AZ31 alloy without Sr, and the alloying phases in the alloy with the addition of 5.0% Sr are more uniform and dispersed than those in the alloy with the addition of 2.5% Sr. And the similar phenomena can be found in Figs.2(b) and (a).

Figure 3 shows SEM images of the AZ31 alloy with Sr showing the morphology of alloying phases. It is found from Fig.3 that the morphology of the β-$Mg_{17}Al_{12}$ phase in the alloy with addition of 0.3% Sr changes from continuously irregular strip-like shape to discontinuously irregular strip-like shape and/or fine granule-like shape. At the same time, some lamella-like eutectic phases are found in the alloys with 2.5% Sr and 5.0% Sr, and the lamella spacing in the alloy with 5.0% Sr is finer. The energy dispersive spectrometry (EDS) results of the lamella-like shape phases, which are shown in Table 2, indicate that the mole ratios of Mg to Al to Zn and to Sr are about 67:24:6:3 and 67:26:4:3 at points A and B (Fig.3(c)) and (d)), respectively.

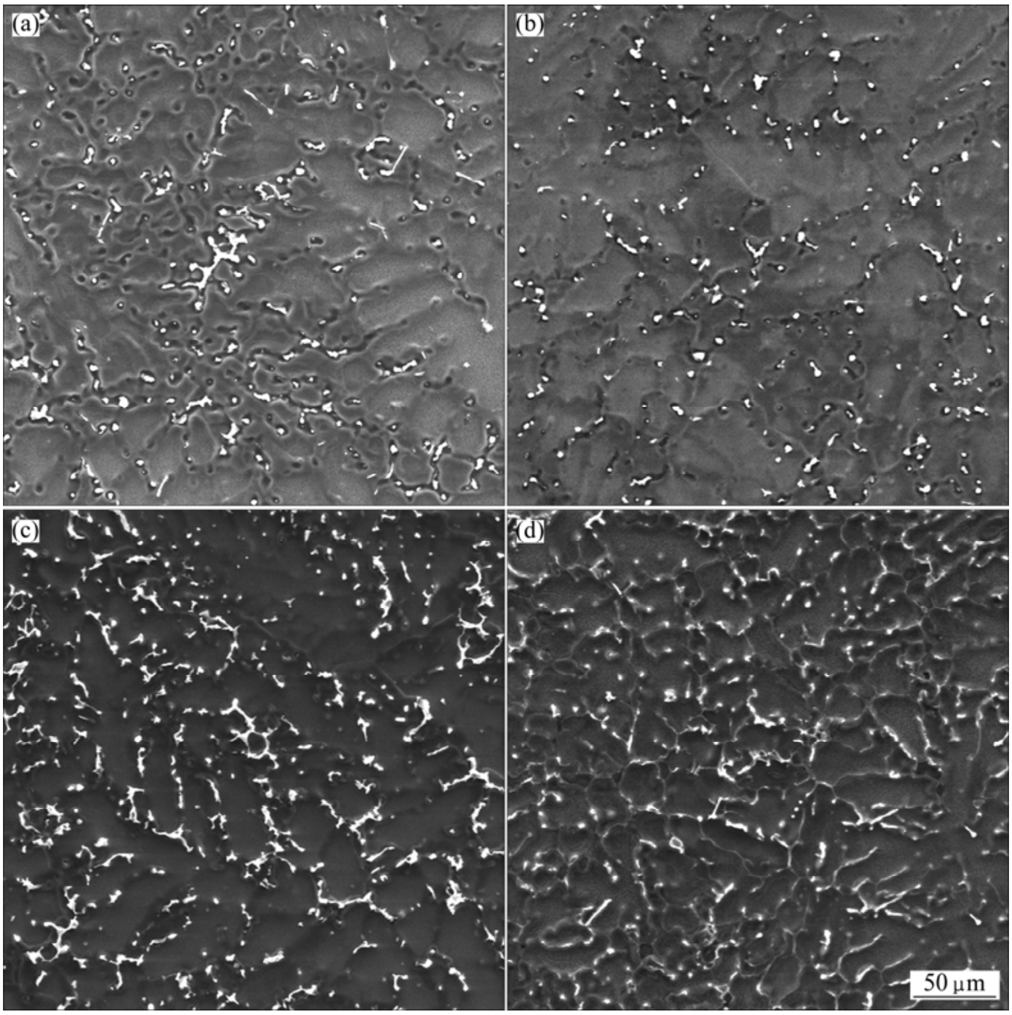

Fig.2 SEM images of AZ31 magnesium alloys with different Sr contents: (a) Without Sr; (b) 0.3% Sr; (c) 2.5% Sr; (d) 5.0% Sr

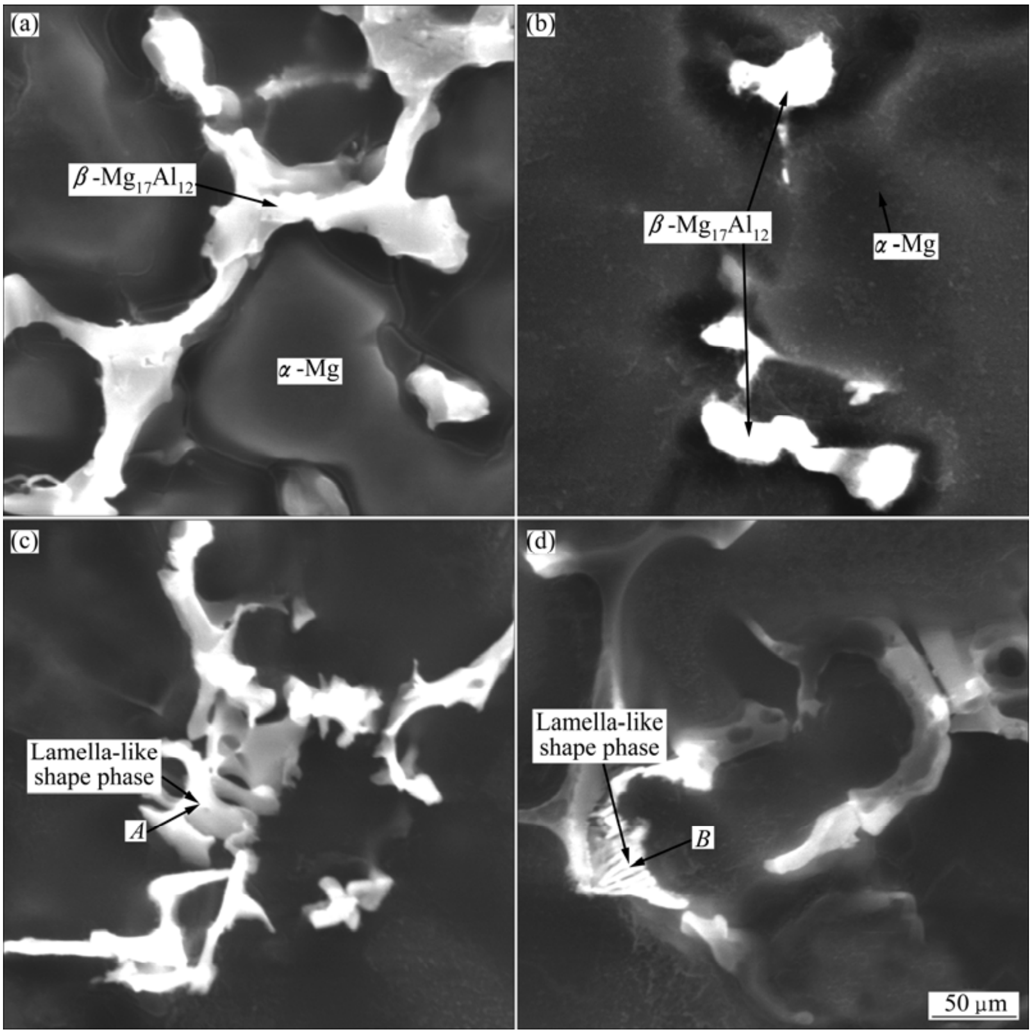

Fig.3 SEM images of alloying phases of AZ31 magnesium alloys with different Sr contents: (a) Without Sr; (b) 0.3% Sr; (c) 2.5% Sr; (d) 5.0% Sr

Table 2 Chemical compositions of lamella shape phases in Fig.3 (mole fraction, %)

Position	Mg	Al	Zn	Sr	Total
A	66.52	24.23	5.85	3.40	100
B	67.43	25.53	4.09	2.95	100

Figure 4 shows the X-ray diffraction (XRD) patterns of AZ31 alloy with different Sr contents (0, 0.3%, 2.5% and 5.0%). It is shown in Fig.4 that without or with the addition of 0.3% Sr in AZ31 magnesium alloy, there are primary α-Mg and β-$Mg_{17}Al_{12}$ divorced eutectic phases, furthermore a few of new Al_4Sr phases form in the microstructure with the addition of 0.3% Sr. Compared with them, β-$Mg_{17}Al_{12}$ divorced eutectic phase cannot be found in the alloys with 2.5% Sr and 5.0% Sr. In addition, combined with the EDS results, it is indicated that adding high Sr content to the AZ31 alloy can bring the new ternary eutectic and/or divorced eutectic phase of $Mg_{11}Al_5Zn_4$ in the alloy just like the lamella-like shape phase appears in Figs.3(c) and (d), and the $Mg_{17}Sr_2$ and Mg_2Sr phases are found in the alloys with 2.5% Sr and 5.0% Sr.

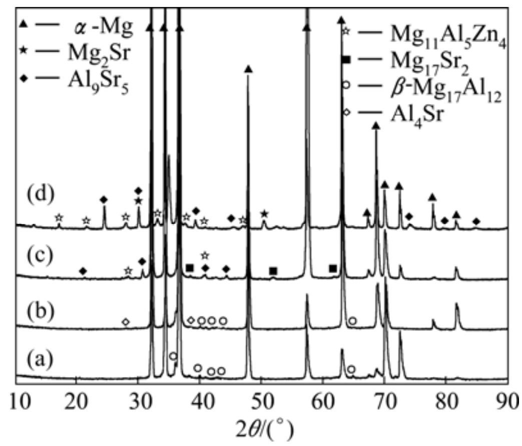

Fig.4 XRD patterns of AZ31 magnesium alloy with different contents of Sr: (a) Without Sr; (b) 0.3% Sr; (c) 2.5% Sr; (d) 5.0% Sr

According to the Mg-Sr phase diagram, the main phases in the as-cast Mg-38.89Sr are α-Mg and Mg_2Sr phases at the rapid solidification rate. And because of the large difference in crystal structure of Mg_2Sr phase and α-Mg phase, Mg_2Sr cannot be the core of heterogeneous nucleation. Unless free state Sr atoms are isolated and then new alloying phases are formed at the grain/detrite boundary to limit α-Mg dendrite to grow up, and to affect the microstructure of magnesium alloy further. It is reported that the electron negativities of Mg, Al, Zn and Sr are 1.31, 1.61, 1.65 and 0.95, respectively[14]. On the basis of the electron negativity theory[15] that the larger the difference between two elements in electron negativity is, the easier it is to form a compound. Thus Zn is the easiest to form a compound with Sr, Al, and Mg followed in turn. But for the limited amount and large solid solubility, most of the Zn atoms in AZ31 magnesium alloy become to be solute atoms, and solid-soluted into matrix. So they are hard to combine with the Sr atoms. Compared with Zn atoms, Al atoms are easy to combine with Sr for the high concentration to form stable Al_4Sr phase (Fig.4(b)) in minor Sr content alloy or metastable Al_9Sr_5 phase (Figs.4 (c) and d)) when adding much more Sr (>2.5%); otherwise, the surplus Sr atoms combine with Mg atoms to finally form $Mg_{17}Sr_2$ phase (Fig.4 (c)). And some Mg_2Sr phases left because of the high content of Sr addition (5.0%, Fig.4(d)). Combining with the Al atom, Sr element has reduced the Al atom concentration, and then causes the new ternary phase $Mg_{11}Al_5Zn_4$ phase formed when adding high Sr (>2.5%) to AZ31 magnesium alloy.

4 Conclusions

1) Adding Sr to the AZ31 magnesium alloy causes the dendrite/grain size to decrease, and with increasing the Sr content from 0 to 5.0%, the dendrite becomes finer, the dendrite morphology becomes more passive and the distribution of alloying phases at dendrite/grain boundary is dispersed. Furthermore, the morphology of the β-$Mg_{17}Al_{12}$ phase in the alloy with addition of 0.3%Sr changes from continuously irregular strip-like shape to discontinuously irregular strip-like shape and/or fine granule-like shape. At the same time, some lamella-like eutectic phases are found in the alloys with additions of 2.5% Sr and 5.0% Sr, and the lamella spacing in the alloy with addition of 5.0% Sr is finer.

2) Adding high Sr content to the AZ31 alloy can bring the new ternary eutectic and/or divorced eutectic phase of $Mg_{11}Al_5Zn_4$ in the alloy, and the $Mg_{17}Sr_2$ and Mg_2Sr phases occur in the alloys with additions of 2.5% Sr and 5.0% Sr.

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高锶含量 AZ31 镁合金的铸态组织及含锶相

吴 璐[1]，潘复生[1]，杨明波[2]，吴菊英[1]，刘婷婷[1]

1. 重庆大学 国家镁合金工程技术研究中心，重庆 400044；
2. 重庆理工大学 材料科学与工程学院，重庆 400050

摘　要：研究不同 Sr 含量(0, 0.3%，2.5%和 5.0%，质量分数)的 AZ31 镁合金的铸态组织及含锶相。结果表明：在 AZ31 镁合金中添加 Sr 后，枝晶/晶粒尺寸变小，并且在 0~5.0%的范围内，随着 Sr 含量的增加，枝晶细化且形态出现钝化现象，位于晶界/枝晶界的合金相分布更加弥散。添加 0.3%Sr 后，β-$Mg_{17}Al_{12}$ 相从未添加 Sr 的 AZ31 合金中的连续、不规则条状转变为不连续、不规则条状和/或细小颗粒状。在添加 2.5%Sr 和 5.0%Sr 的合金中发现了一些层片状共晶相，且后者的层片间距更加小。较高含量的 Sr 添加到 AZ31 镁合金中可以形成一种新的共晶和/或离异共晶三元 $Mg_{11}Al_5Zn_4$ 相，在添加 2.5%Sr 和 5.0%Sr 的合金中发现了 $Mg_{17}Sr_2$ 相和 Mg_2Sr 相。

关键词：镁合金；AZ31 镁合金；含锶相；锶

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