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Effects of antimony addition on the microstructures of ZA84 magnesium alloy

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ABSTRACT

The effects of antimony (Sb) on the microstructures of as-cast Mg–8Zn–4Al (ZA84) magnesium alloy were investigated by using optical microscopy, SEM, EDX, and XRD, etc. The results indicated that the microstructures of as-cast alloys containing Sb consisted of solid solution α(Mg), ternary phases τ [$Mg_{32}(Al, Zn)_{49}$] and φ ($Al_2Mg_5Zn_2$), eutectic mixture phase [α(Mg) + τ], a newly formed dual phase $MgZn_2$, and a newly formed needle-like phase Mg_3Sb_2. After adding Sb, the morphologies of ternary phase on the grain boundaries have been changed from quasi-continuous-net shape to uniformly dispersed particles, and the sizes of grains were decreased from 120–130 μm to 50–60 μm. In this experiment conditions, the optimal addition amount of Sb was 0.3 wt%. Meanwhile, the microhardness of the matrix of ZA84 magnesium alloy was found to increase with the increases of Sb additions. As the phase Mg_3Sb_2 with high melting point and the dual phase $MgZn_2$ were formed, the high-temperature strength of ZA84 magnesium alloy was increased.

1. Introduction

Magnesium alloys are the lightest structural metallic materials, magnesium alloys have been widely used in automobile and electronic industry because of their low density, high specific strength, good damping and electromagnetic shielding capacities. But the lower allowable service temperature in the engineering applications is one of the main disadvantages of magnesium alloys. For example, the highest allowable temperature for a commonly-used magnesium alloy AZ91 in long period service is only 120 °C [1]. Although Mg–Al–Si and Mg–Al–RE magnesium alloys with better high-temperature performance have been developed, their worse castability and high-cost constrict their engineering applications [2]. Hence, it is very important to develop a new magnesium alloy possessing better performance at both higher and lower temperatures. As shown by other's researches, the adoption of rare earth element modifiers or Al5TiB modifier can improve the mechanical properties and castabilities of many magnesium alloys [3,4]. However, compared to rare earth element modifiers or Al5TiB modifier, Sb is a modifying alloy element with much lower price. And Sb is adopted simply by magnesium alloys. So far, some researchers have successfully applied Sb as a modifier in magnesium alloy AZ91 [5]. Nevertheless, the influence of Sb on the ZA84 magnesium alloy has not gotten enough emphasis. In the present paper, the modification effects of Sb on the microstructures and microhardnesses of ZA84 magnesium alloy were systematically investigated and the effect mechanisms were discussed.

2. Sample preparation and testing methods

2.1. Sample preparation

The chemical compositions of the prepared alloys are given in Table 1. The raw materials used in the experiment are Mg ingots (its purity ≥99.95%), Zn ingots (its purity ≥99.5%), Al ingots (its purity ≥99.5%), and Al–10% Mn intermediate alloy. Alloys were smelted in a pot-shaped crucible, and the melt surface being protected with flux. The Sb was added to the melt at 780 °C and held at 780 °C for 30 min to make sure the Sb element could be completely dissolved. The testing samples were cast with the metal moulds.

2.2. Testing methods

The etching agent for preparing metallographic samples was acetic–picral (10 ml acetic acid, 4.2 g picric acid, 10 ml H_2O, 70 ml ethanol (95%)) [6]. The microstructures of the samples were characterized by an optical microscope (Olympus B-51RF). The compositions of each phase were analyzed with the EDX method by using a scanning electron microscope (JSM-5610LV) and an X-ray diffractometer (Philips PW-1700). The microhardnesses of the samples were mensurated by a hardness tester (HV-1000), with a load of 100 g force and duration of 20 s, and the average value of the readings from 3 samples was taken as the resulting point.

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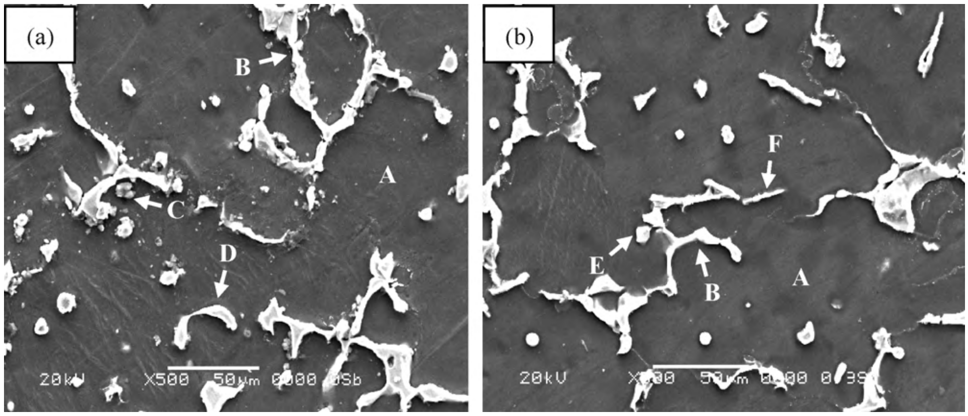

Fig. 1. SEM micrographs of as-cast ZA84 magnesium alloy: (a) un-modified; (b) modified with 0.3 wt% Sb.

Table 1
Compositions of the experimental alloys (wt%).

Zn	Al	Mn	Sb	Mg
8	4	0.3	0.0	Bal
8	4	0.3	0.1	Bal
8	4	0.3	0.3	Bal
8	4	0.3	0.5	Bal

3. Results and discussions

3.1. Microstructures

The SEM micro-morphologies of ZA84 magnesium alloy both unmodified and modified by adding 0.3 wt% Sb are shown in Fig. 1. The XRD patterns for ZA84 magnesium alloy both unmodified and modified by adding 0.3 wt% Sb are shown in Fig. 2. And the compositions analyzed by EDX for points labeled in Fig. 1 are listed in Table 2. Consulting Table 2, it can be known from Figs. 1 and 2 that point A represents the matrix, a solid solution α(Mg); point B is phase τ [$Mg_{32}(Zn, Al)_{49}$]; point C is an eutectic mixture [α(Mg) + τ] formed due to non-equilibrium solidification; point D is phase φ ($Al_2Mg_5Zn_2$); point E is a newly formed phase $MgZn_2$ due to the addition of Sb, which assumes island-shape and uniformly distributed at the grain boundaries; point F is another newly formed phase Mg_3Sb_2 after adding Sb, which assumes needle-shape and located at the grain boundaries.

The metallographs of ZA84 magnesium alloy with different amount of Sb are shown in Fig. 3. It can be seen from Fig. 3(a) that the grain size of the matrix is coarser and the ternary phase assumes semi-continuous-net shape in the unmodified ZA84 magnesium alloy. After being modified by adding 0.1 wt% Sb, the grain size of the matrix is obviously reduced, and the ternary phase net has been interrupted although the semi-continuous-net shape for the most of the phase is still maintained (Fig. 3(b)). When the content of the modifier gets up to 0.3 wt%, the grain size gets even smaller, and the ternary phase has become totally interrupted-net shape (Fig. 3(c)). But when the addition of the modifier reaches 0.5 wt%, the grain size of the matrix is obviously coarsened again (Fig. 3(d)). However, the addition of the modifier Sb has little influence on the eutectic α(Mg), the variation of volume fraction of eutectic α(Mg) with the change of Sb content cannot be seen in the metallographs.

The as-cast microstructures of ZA84 magnesium alloy have been fairly improved by adding suitable amount of the modifier Sb. The main reason for the improvement is that the melting temperature of the inter-metallic compound Mg_3Sb_2 which formed from

Table 2
The phases and their compositions for the labeled points in Fig. 1 determined by XRD patterns and EDX analysis.

Points	Mg/at%	Al/at%	Zn/at%	Sb/at%	Phases
A	97.13	1.11	1.75	0.00	Matrix [α(Mg)]
B	46.53	21.03	32.44	0.00	$Mg_{32}(Al, Zn)_{49}$
C	93.00	3.70	3.30	0.00	Eutectic [α(Mg) + τ]
D	52.15	12.83	35.02	0.00	$Al_2Mg_5Zn_2$
E	29.68	4.22	57.10	0.00	$MgZn_2$
F	59.80	1.39	2.47	36.34	Mg_3Sb_2

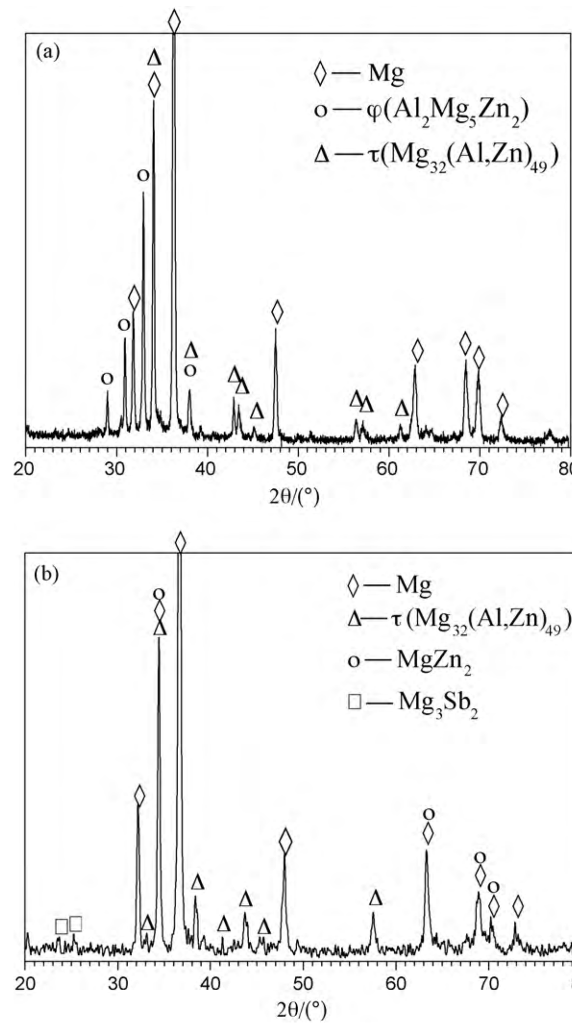

Fig. 2. XRD patterns of as-cast ZA84 magnesium alloy: (a) un-modified; (b) modified with 0.3 wt% Sb.

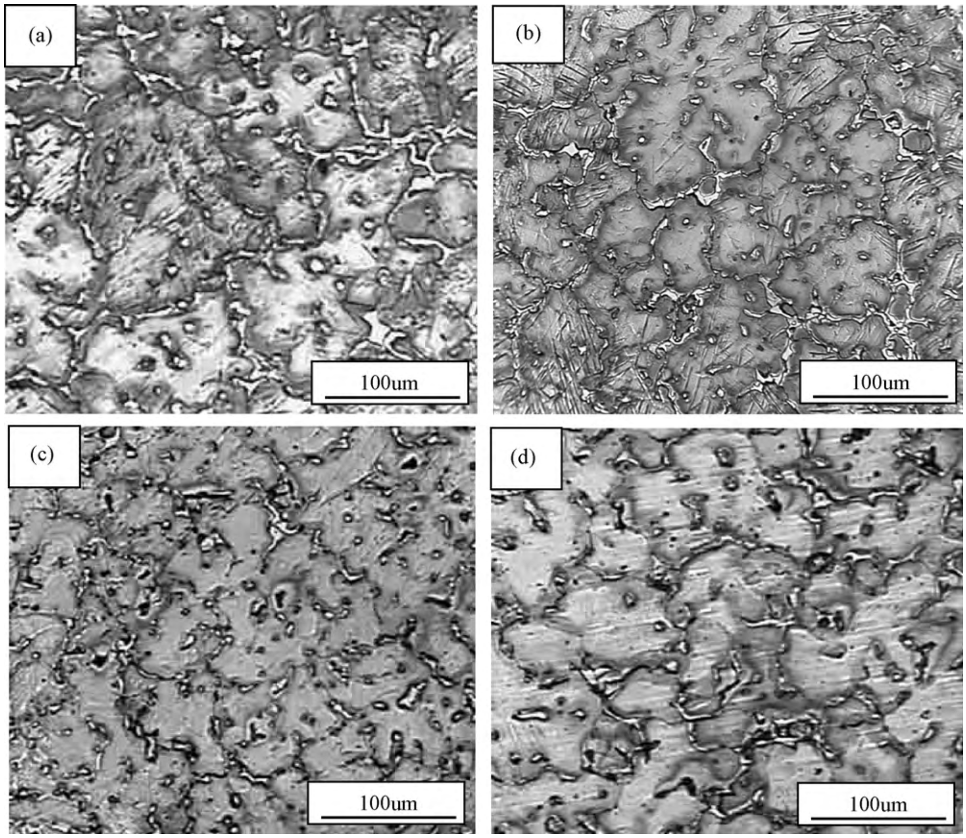

Fig. 3. Optical microstructures of as-cast ZA84 magnesium alloy with different Sb additions: (a) 0.0 wt%; (b) 0.1 wt%; (c) 0.3 wt%; (d) 0.5 wt%.

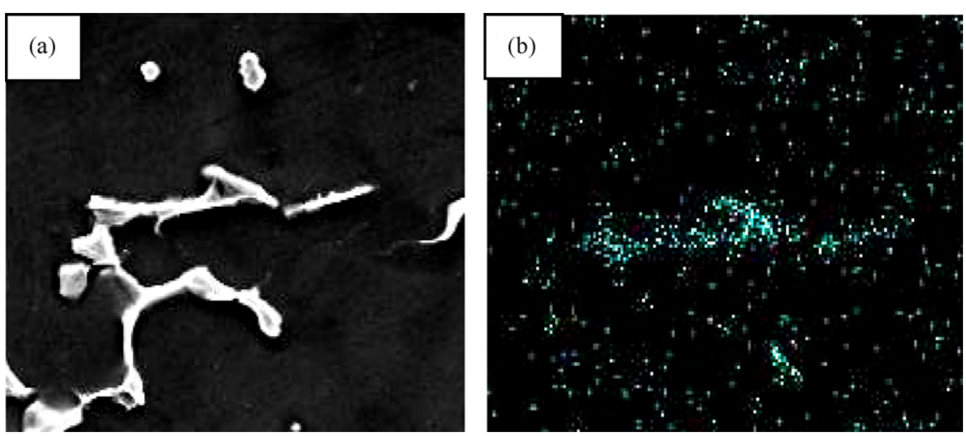

Fig. 4. SEM image (a) and EDX patterns of Sb element (b) in (a) of ZA84 magnesium alloy with 0.3 wt% Sb.

Sb and Mg is rather high (t_m = 1228 °C) [5], thus, it precipitates and crystallize first from the melt during the molten metal solidification. Then, as the temperature decreases, a part of the precipitated particles (Mg_3Sb_2) can act as the nuclei during the heterogeneous nucleation of the matrix phase α(Mg). Another part of the particles congregate at the front of the firstborn phase α(Mg) to impede the growth of the dendrite, hence, the as-cast microstructures of ZA84 magnesium alloy is refined. The SEM metallographs of ZA84 magnesium alloy with 0.3 wt% Sb and the EDX patterns of Sb element are shown in Fig. 4. It can be seen that the Sb element is mostly located at the grain boundaries, and this result also confirms the above conclusions.

Table 3
Grain sizes of ZA84 magnesium alloy with different Sb additions.

Sb wt%	0	0.1	0.3	0.5
Grain sizes range/μm	120–130	80–90	50–60	70–80

The ranges of grain size for ZA84 magnesium alloy with different contents of Sb are listed in Table 3. It can be seen that the grain size decreases at first, and then increases, as the Sb content increases. And when the content of Sb equals 0.3 wt%, the grain size is at its minimum.

Generally speaking, there must be an optimum addition for any modifier to refine microstructures of an alloy. In the case of this experiment, when the addition of Sb is less than 0.3 wt%, the effect of refinement for the microstructures of the alloy is not the optimum, since there are not enough heterogeneous nuclei for the

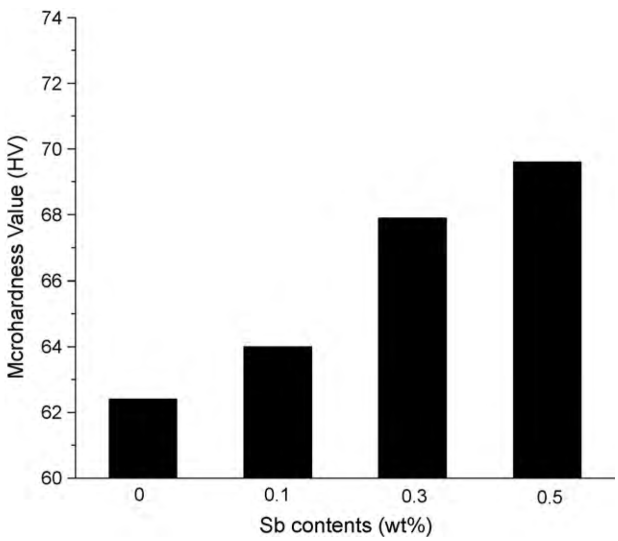

Fig. 5. Microhardnesses of the matrix of ZA84 magnesium alloy with different Sb additions.

Table 4
Compositions of the matrixes of the alloys without Sb and with 0.3 wt% Sb analyzed by EDX.

Sb wt%	Mg/at%	Al/at%	Zn/at%
0.0%	97.14	1.11	1.75
0.3%	94.91	1.93	3.16

solidification. But when the addition of Sb is more than 0.3 wt%, because of the rapid growth of the nuclei of Mg_3Sb_2 phase, part of them cannot act as the heterogeneous nuclei anymore, thus the grains begin to be coarsen (Table 3). Besides, since Sb is also a surface active agent, it may concentrates on the crystallizing front to prevent the ternary phase from growing during the solidification, hence, the semi-continuous-net shaped ternary phase becomes into interrupted-net shaped.

3.2. Microhardness

The influences of the addition of the modifier Sb on the microhardness of ZA84 magnesium alloy is as shown in Fig. 5. It can be clearly seen that the microhardness of the alloys with 0.1 wt%, 0.3 wt%, and 0.5 wt% Sb is 2.6%, 8.8%, and 11.5% higher, compared with the unmodified alloy, respectively.

As suggested in other's research [7], the strength and hardness of an alloy will increase after some alloying elements dissolve into the base metal to form a solid solution. The reason for the increase is that the lattice of base metal is distorted by the dissolving of alloying elements, causing the increase of resistance for dislocation's glide, hence the alloy is strengthened. Since the solubility of Al and Zn in magnesium is considerably large, being 12.7% and 6.2% respectively, Al and Zn will play an important role in strengthening the base of the magnesium alloy.

Compositions of the matrixes of the alloy without Sb and with 0.3 wt% Sb analyzed by EDX are listed in Table 4. It can be seen that the contents of Al and Zn are higher in the matrix of the modified Mg-alloy than that in the matrix of the unmodified alloy. The reason is that the modifier Sb distributed at the grain boundaries acts as an active agent, facilitating the atoms of Al and Zn to diffuse into the matrix α(Mg). As well known, the more the solute atoms of Al and Zn there are in the matrix, the higher the hardness will be. Besides, The atoms of the modifier Sb themselves can also dissolve in the matrix α(Mg), causing the microhardness of the matrix to increase. But it should be pointed out that the solubility of Sb in magnesium is extremely small. Hence Sb itself strengthens the magnesium alloy not by alloying strengthening mechanism, but mainly by dispersion mechanism through the formation of tiny particles of the inter-metallic compound Mg_3Sb_2.

Although particles of the ternary phases (τ and φ) can also impede slide of dislocations when the alloy is deformed at ambient temperature, but when ZA84 magnesium alloy used in elevated temperatures, they will be coarsened and softened as temperature is elevated (the melting temperatures of τ and φ are 535 °C and 393 °C respectively [8]), hence the strengthening effect induced by them is gradually diminished. On the contrary, as mentioned above, Mg_3Sb_2 particles with fairly high melting temperature are thermally stable, particles of Mg_3Sb_2 are stable and can still resist glide of dislocations at elevated temperatures, thus the strengthening effect can be maintained at considerably high service temperature, and so the high-temperature strength of ZA84 magnesium alloy is increased.

4. Conclusions

(1) The micro-morphology of the ternary phases distributed on grain boundaries changes from semi-continuous-net shape to interrupted-net shape or particles in ZA84 magnesium alloy after the alloy is modified by Sb; meanwhile the grain size of the matrix is considerably refined. The grain size decreases from 120–130 μm to 50–60 μm with the addition of 0.3 wt% antimony modifier.
(2) The microhardness of the as-cast ZA84 magnesium alloy obviously increases with the addition of antimony modifier, and it goes up by 11.5% when the addition reaches 0.5 wt%.
(3) After adding Sb, an inter-metallic compound phase Mg_3Sb_2 with high melting point and a newly dual phase $MgZn_2$ are formed in ZA84 magnesium alloy, and thus the high-temperature strength of ZA84 magnesium alloy is increased.

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