Mechanical Properties and Microstructure of Mg–Al–Zn–Si-base Alloy

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Magnesium alloys containing Mg₂Si particles, as a promising low cost heat-resistant magnesium alloy for automobile engine applications, are attracting more and more attention of both material scientists and design engineers. Refinement of the Chinese script Mg₂Si particle is a key for using this kind of alloy in sand casting or permanent mould casting. In the present work, a new type of heat-resistant magnesium alloy with low cost based on Mg–Al–Zn–Si was developed. The effect of Sb addition and mischmetal (MM, a mixture of rare-earth, RE elements) microaddition to a Mg–Al–Zn–Si alloy was investigated systematically from the viewpoints of microstructure, solidification process, mechanical properties and corrosion resistance. Microstructure observation revealed that Sb promoted the formation of fine polygonal type Mg₂Si particles by providing the nucleation sites. Meanwhile, the grain sizes of modified Mg–Al–Zn–Si–Sb alloy are much finer than those of base alloy. Such improved microstructure brings about the significant improvement in tensile properties, toughness and creep resistance at elevated temperatures up to 200°C, which is superior to or comparable to AE42 alloy. Moreover, the corrosion resistance of the new alloy is improved significantly by the MM microaddition.

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1. Introduction

The growing demand for more fuel-efficient vehicles to reduce energy consumption and air pollution is a challenge for the automotive industry. The characteristic properties of magnesium alloys, low density, high strength stiffness to weight ratio, good damping capacity and diecastability, and recycling potential make it the ideal candidate for heavier materials (steel, aluminum) to reduce the weight of the car. The widely used magnesium alloys are Mg–Al series, such as AZ91 and AM60, which have excellent castability, good mechanical properties at room temperature and low cost. However, the use of these magnesium alloys have been limited because of their poor heat resistance.¹⁾ The previous investigation²⁾ showed that the grain boundary sliding is an important part of the deformation mechanism at elevated temperatures in Mg–Al based alloys. Therefore, to improve heat resistance in Mg–Al based alloy, it seems an effective method to develop an alloy containing thermal stable intergranular phases, which can suppress the grain boundary sliding.

Recent studies indicate that addition of silicon to Mg–Al–Zn alloy can achieve substantial increases in strength, toughness, etc. because Mg₂Si formed by the addition of Si is the substantially effective strengthening particles, which exhibit a high melting temperature (1085°C), low density (1.9 g/cm³), high elastic modulus (120 GPa), and a low thermal expansion coefficient ($7.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$).³⁾ However, the magnesium alloys containing Si are only limited to the diecasting, which has a rapid solid rate. Mg₂Si compounds are prone to forming undesirable coarse Chinese script under conventional (or slower) solidification process. To use of magnesium alloys containing Mg₂Si particles for sand casting or permanent mould casting, microstructural refine-

ment should be achieved.

It has been reported that the as-cast microstructure of Mg alloys containing Mg₂Si particles could be refined by P or Ca addition.⁴⁾ However, addition of phosphor can produce ignition and result in large quantity of sick smoke. In recent studies,⁵⁾ we found a more effective modifier of Sb than Ca in Mg–Al–Zn–Si alloys. This paper reports the results of our preliminary experiments on the effects of Sb and MM simultaneous additions on the microstructural development, tensile strength, creep properties and corrosion resistance of Mg–5Al–1Zn–1Si alloy obtained by a permanent mould gravity casting process.

2. Experimental Procedure

Three alloys of which the compositions are listed in Table 1 were prepared in mild steel crucible under the protection of mixed gas of CO₂/0.5%SF₆ using commercial stock. Tensile specimens with a gauge section of 15 mm × 3.5 mm × 2 mm were cut by electric spark machining from the bottom of ingots. Before testing all the specimens were solution heat-treated at 410°C for 10 hours, water quenched, and then aged at 200°C for 2 hours. All specimens for microstructural characterization were cut from the same positions on the ingots at 10 mm from the castings. Phases in the Mg–5Al–1Zn–1Si–X alloys were analyzed by D/MaxIII A-12KW-Cu type XRD analyzer operated at 40 kV and 120 mA. Chemical analysis of the cast experimental alloys was performed by inductively coupled plasma (ICP). The electropolished samples were examined in a Philip-505 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS) to investigate the microstructures and second phases in the alloys. The grain size was determined using a line intercept method from a large number of non-overlapping measurements.

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Table 1 Chemical composition of the alloys (mass%).

Alloy code	Mg	Al	Zn	Si	Sb	Mn	Re	Grain size (μm)
Mg–5Al–1Zn–1Si	Bal.	5.1	0.93	0.72	—	—	—	134 $\pm$ 5
Mg–5Al–1Zn–1Si–0.5Sb	Bal.	5.0	0.95	0.70	0.45	—	—	68 $\pm$ 5
SJTU-HM1	Bal.	5.0	0.90	0.71	0.40	—	0.20	70 $\pm$ 5
AZ51	Bal.	5.0	0.80	—	—	0.20	—	—
AE42	Bal.	4.0	—	—	—	0.20	2.5	—
AZ91	Bal.	9.0	0.80	—	—	0.20	—	—

3. Results and Discussion

3.1 Microstructure

The typical microstructure of the permanent mould cast Mg–5Al–1Zn–1Si based alloys is illustrated in Fig. 1. The microstructure consisted of Chinese-script type Mg_2Si particles with interdendritic $\text{Mg}_{17}\text{Al}_{12}$ phases in matrix (α -Mg). When the as-cast specimens of the alloys were solution treated at 420°C for 10 hours (T4 condition), almost all of β phase dissolved in the matrix and only Chinese-script type Mg_2Si particle existed, as shown in Fig. 1(b), which indicated that Mg_2Si has excellent thermal stability at elevated temperatures. With the addition of Sb, two microstructural changes can be observed clearly: (1) morphology of the Mg_2Si particles changed from coarse Chinese script shape to the fine polygonal shape. (2) the average size of grain decreased from 134 to 68 μm (Figs. 1(b) and (c)). With the mischmetal microaddition to Mg–5Al–1Zn–1Si–0.5Sb alloy, the microstructure was not influenced obviously. The refinement may be due to the formation of lots of finely distributed polygonal type Mg_2Si particles in the interface of liquid-solid former during solidification.

Figure 2 is the XRD results of Mg–5Al–1Zn–1Si–0.5Sb alloy. It is recognized peaks from Mg_3Sb_2 phase in the Sb-containing alloys.

3.2 Mg_2Si phase heterogeneous nucleation

Figure 3(a) shows micrograph of Mg_2Si particles in the alloy containing 0.5Sb. It is interesting that Mg_2Si particles contain small particles inside (labeled “A”), which presumably act as nucleation sites for Mg_2Si particles. Figure 3(a) shows a typical result on crystallization center in the Sb-containing alloy obtained by magnified secondary electron image (SEI) of nucleus. Figure 3(b) shows the EDS spectra for the nucleus. It shows that the nucleus is enriched with Mg, Sb and Si. Combining the information from XRD and EDS spectrum shows that the nature of nucleus is possible to be Mg_3Sb_2 .

In classical nucleation theory, nucleating can be facilitated when the foreign particle displays a small lattice mismatch ($<6\%$) with the nucleating solid phase.⁶⁾ The results of calculation for some possible crystallographic orientations for Mg_2Si nucleation on the Mg_3Sb_2 particles show that when the orientation relationship between Mg_2Si phase and Mg_3Sb_2 phase is $(0001)_{\text{Mg}_3\text{Sb}_2} \parallel (111)_{\text{Mg}_2\text{Si}}$, the planar disregistry is the lowest (5.1%).⁵⁾ Therefore, Mg_3Sb_2 can act as the heterogeneous nucleation for the Mg_2Si phase by this orientation relationship.

3.3 Solidification process of Mg–Al–Zn–Si-base alloys

Figure 4 shows a typical cooling curve for the Mg–5Al–1Zn–X based alloys under a cooling rate of 0.5°C/s. From the curves of solidification, the following information could be obtained: the practical temperature of the liquid metal at the moment of entry to the mold was 648°C and 621°C respectively, which was measured with a high sensitivity thermocouple. The wall of mold cavity chilled the liquid metal, causing the temperature of the liquid metal to rapidly drop. A little platform appeared in the curve at about 616°C for AZ51 and 606°C for SJTU-HM1 (The liquidus temperature of SJTU-HM1 is lower by 10°C than that of AZ51, which may be beneficial to the castability). With the decrease of temperature, the liquid metal starts to solidify. Owing to the high melting point of Mg_2Si particles, the Mg_2Si primarily precipitated. Followed by the onset of $\text{Mg}(\alpha)$ formation, and then the further growth of Mg_2Si phase and $\text{Mg}(\alpha)$ phase and ends at 407°C (another platform, as arrowhead shown in Fig. 4), which is actually the non-equilibrium eutectic temperature for $\text{L} \rightarrow \text{Mg}(\alpha) + \text{Mg}_{17}\text{Al}_{12}$, forming the divorced eutectic structure of $[\text{Mg}(\alpha) + \text{Mg}_{17}\text{Al}_{12}]$ as shown in Fig. 1(a).

3.4 Mechanical properties

The mechanical properties of the alloys with and without Sb and microaddition of RE are compared in Table 2. It can be seen that Sb and RE microaddition to the alloy (SJTU-HM1) resulted in beneficial influence on improving the mechanical properties. It shows that the Sb- and RE-containing alloys have improved yield strength, ultimate tensile strength, elongation and apparent fracture toughness over the base alloy. It is obvious that the improvement of tensile strength was ascribed to three aspects: (1) small grain strengthening, (2) the change of morphology of Mg_2Si from Chinese-script type to polygonal type, since long cracks can easily nucleate along the interface between Chinese-script Mg_2Si particles and Mg matrix, and (3) the dispersion strengthening of fine particles (Mg_2Si and Mg_3Sb_2).

In addition, owing to its high melting point (1228°C) of those Mg_3Sb_2 particles which can not act as nucleus of Mg_2Si in Mg–5Al–1Zn–1Si are also effective strengthening phases for Mg alloy application at elevated temperatures,⁷⁾ which may be contributed to the improvement of tensile strength at elevated temperatures.

3.5 Creep behavior

Figure 5 is several typical creep strain vs. time curves obtained from the constant-load and constant-temperature test (200°C/50 MPa) for the four kinds of alloys. The

Fig. 1 Optical micrographs showing the effect of Sb addition on the microstructure of alloys; (a) as-cast Mg-5Al-1Zn-1Si alloy, (b) solution heat-treated Mg-5Al-1Zn-1Si alloy, (c) solution heat-treated Mg-5Al-1Zn-1Si-0.5Sb alloy.

Fig. 2 X-ray diffraction patterns of as-cast Mg-5Al-1Zn-1Si-0.5Sb alloy.

Fig. 3 Crystallization nuclei observing shows (a) SEI of Mg_2Si particles in permanent mould cast Mg-5Al-1Zn-1Si-0.5Sb alloy (b) EDS spectrum from the nucleus area 'A' in (a).

simultaneous additions of Sb and mischmetal (MM) to Mg-5Al-1Zn-Si alloy reduced the steady state creep rate significantly. Moreover, the creep strain for the alloys after 100 hours decreased from 5.2% for Mg-5Al-1Zn-1Si to 2.6% for SJTU-HM1, even lower than that of AE42 (2.7%). It showed that tensile creep property of the newly developed SJTU-HM1 alloy is better than that of AE42 alloy, which is the benchmark creep-resistant magnesium die casting alloy for automobile powertrain application.

Fig. 4 Solidification cooling curves for alloys studied.

Fig. 5 Creep curves of alloys at 200°C, 50 MPa.

Table 2 Mechanical properties of permanent mould-cast Mg–Al–Zn–Si–X alloys.

Alloy	RT tensile			150°C tensile			Apparent fracture toughness A_k (J)
	Ulti. (MPa)	Yield. (MPa)	Elong. (%)	Ulti. (MPa)	Yield. (MPa)	Elong. (%)	
SJTU-HM1	235	108	9	178	99	14	28
AE42	202	97	12	165	91	22	20
AZ91	234	110	3	175	96	20	15

3.6 Corrosion resistance properties

Figure 6 shows the salt spray corrosion test result of the alloys. Si shows an adverse effect on corrosion properties. Single addition of Sb shows a similar effect like Si. On the other hand, with both additions of Sb and MM microaddition, SJTU-HM1 shows higher corrosion resistance than those of AZ51 and AE42 alloys. This showed that Misch metal (Ce, La, Nd, Pr) improved the corrosion resistance for Mg–Al based alloys in chloride solutions. The solubility of rare earths in the magnesium matrix is limited in the presence of aluminum, but the intermetallic Al-RE phase formed is electrochemically passive and does not affect the corrosion rate much.⁸⁾ The high corrosion resistance of the STJU-HM1 appears to be related to a certain positive synergism of aluminum and RE elements in the aluminum rich zones along

Fig. 6 Corrosion rate compared with standard die casting alloys.

the grain boundaries, impeding the propagation of localized corrosion attack. The improved passivity of SJTU-HM1 under the conditions is possibly due to the enrichment of trace amounts of RE in the oxide film. Further investigation is under way.

4. Summary

Microstructure and mechanical properties and corrosion resistance for the developed SJTU-HM1 alloy were investigated and summarized as follows:

- (1) Addition of Sb was found to be efficient in refining the microstructure of the Mg–5Al–1Zn–1Si-base alloy. The morphology of Mg_2Si particles changed from coarse Chinese-script shape to small polygonal type. The modification mechanism of Sb is the formation of the polygonal type Mg_2Si particles nucleate from Mg_3Sb_2 particles.
- (2) Refined microstructure in the modified alloy by simultaneous additions of Sb and mischmetal results in significant improvement in tensile properties and toughness, creep resistance at high temperatures as compared to the base alloy of Mg–5Al–1Zn–1Si. The mechanical properties at room temperature are similar to or better than those of AZ91 alloy and the high temperature properties are even better than those of AE42 alloy.
- (3) With simultaneous additions of Sb and mischmetal, the corrosion resistance of the Si-containing Mg alloy is improved significantly and even better than that of AE42 alloy.

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