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Transactions of Nonferrous Metals Society of China

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Trans. Nonferrous Met. Soc. China 25(2015) 22-29

Microstructures and mechanical properties of Mg–Al–Sm series heat-resistant magnesium alloys

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Received 8 January 2014; accepted 5 March 2014

Abstract: The microstructures and phase compositions of the as-cast and die-cast Mg-6.02Al-1.03Sm, Mg-6.05Al-0.98Sm-0.56Bi and Mg-5.95Al-1.01Sm-0.57Zn alloys were investigated. Meanwhile, the tensile mechanical and flow properties were tested. The results show that the as-cast microstructure of Mg-6.02Al-1.03Sm alloy is composed of α -Mg matrix, discontinuous β -Mg₁₇Al₁₂ phase and small block Al₂Sm phase with high thermal stability. Rod Mg₃Bi₂ phase precipitates when Bi is added, while the added metal Zn dissolves into α -Mg matrix and β -Mg₁₇Al₁₂ phase. The as-cast alloys exhibit the excellent tensile mechanical property. The tensile strength (σ_b) and elongation (δ) can reach 205–235 MPa and 8.5%–16.0% at ambient temperature, respectively. Meanwhile, they can also exceed 160 MPa and 14.0% at 423 K, respectively. The die-cast microstructures are refined obviously, and meanwhile the broken second phases distribute dispersedly. The die-cast alloys exhibit better tensile mechanical properties with the values of σ_b and δ of 240–285 MPa and 8.5%–16.5% at ambient temperature, respectively, and excellent flow property with the flow length of 1870–2420 mm. The die-cast tensile fractures at ambient temperature exhibit a typical character of ductile fracture.

Key words: heat-resistant magnesium alloy; Mg-Al-Sm alloy; microstructure; mechanical property; flow property; fracture morphology

1 Introduction

Magnesium alloys, one of the most important structural materials with high specific strength, are used widely in the automotive, communicated, electronic and aerial industries [1]. Mg-Al series alloys such as AZ91D and AM60B are the most widely used commercial heat-resistant magnesium alloys. However, the main strengthening phase β -Mg₁₇Al₁₂ exhibits low thermal stability owing to the low melting temperature of 710 K. When the temperature rises, the microstructure will become soft and coarse easily, and then the strength and creep resistance will decrease significantly. Thus, the alloys cannot usually be fabricated to the parts used under high temperature condition above 393 K for long time. Researchers often enhance the elevated temperature performance through precipitating the phases with high thermal stability such as Al₂Ca, Al₂Sr, Mg₂Si and Al-RE by adding alkaline earth metal [2–4], Si [5,6] and rare earth (RE) [7-13], respectively. RE with unique atomic electron and chemical property can purify the alloy melt, ameliorate the microstructure, and then enhance the mechanical property and corrosion resistance. Compared with other RE, the effects of cheaper Sm on the microstructure and mechanical properties of Mg–Al series alloys have been rarely studied yet [9,10]. Meanwhile, the addition of Bi can also enhance the elevated temperature performance effectively through precipitating the Mg₃Bi₂ phase with high thermal stability. Therefore, in this work, the microstructures, mechanical and flow properties of the as-cast and die-cast Mg–6.02Al–1.03Sm, Mg–6.05Al–0.98Sm–0.56Bi and Mg–5.95Al–1.01Sm–0.57Zn alloys were investigated, and the strengthening mechanism was discussed.

2 Experimental

The chemical compositions of the fabricated alloys were measured by inductively coupled plasma analyzer (ICP, JY Ultima2). The alloy ingots were prepared by melting Mg, Al, Bi, Zn and Mg-30%Sm (mass fraction) master alloy in an electric resistance furnace under the

Foundation item: Project (2013AA031001) supported by the National High-tech Research and Development Program of China; Project (2011A080403008) supported by the Major Science and Technology Project of Guangdong Province, China
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DOI: 10.1016/S1003-6326(15)63574-9

mixed atmosphere of CO_2 and 0.1% SF₆ (volume fraction). When the melt temperature of Mg reached 1003 K, the pure metals and master alloy were added into the melt in turn. Then, the melt was stirred twice within 1 h to ensure the compositional homogeneity. After adding the refine agent, the melt was held at 1023 K for 25 min. When the temperature was cooled to 988 K, the melt was poured into the wedge permanent and spiral flow molds with the preheated temperature of 523 K, and then the samples for testing as-cast tensile and flow properties were obtained, respectively. The die-cast samples were obtained by a 400T die-casting machine with the injection force, injection time, cooling time and mold temperature of 370 kN, 4.0 s, 5 s and 463 K, respectively.

The specimens were etched with 4% HNO₃ (volume fraction) in ethanol. The microstructural observation was

carried out on an optical microscope (OM, Leica DM IRM) and a scanning electron microscope (SEM, JEOL JXA–8100) with an energy dispersive spectroscope (EDS, OXFORD 7412). The phase analysis was carried out on an X-ray diffractometer (XRD, D/MAX-RC) with Cu K_{α} radiation. The tensile test at temperatures of 298 and 423 K was performed on a material test machine (GP–TS2000) at a rate of 2 mm/min. The tensile fractograph at ambient temperature was observed using SEM.

3 Results and discussion

3.1 Microstructure and mechanical property of as-cast alloys

Figure 1 shows the optical and SEM micrographs of the as-cast alloys. All as-cast microstructures consist



Fig. 1 Optical (a, c, e) and SEM (b, d, f) micrographs of as-cast alloys (arrows denote small block and rod compounds): (a, b) Mg=6.02Al=1.03Sm; (c, d) Mg=6.05Al=0.98Sm=0.56Bi; (e, f) Mg=5.95Al=1.01Sm=0.57Zn

of α -Mg matrix, few discontinuous β -Mg₁₇Al₁₂ phase and small block compound. In addition, rod compound can be observed in the microstructure of Mg–6.05Al– 0.98Sm–0.56Bi alloy.

Figure 2 shows the EDS spectra of the as-cast alloys, and the results are listed in Table 1. It is seen that the gray phase is Mg–Al phase, i.e. β -Mg₁₇Al₁₂ for the three alloys. Small block compound is Al–Sm phase (spectrum 1 in Figs. 2(a) and (c) and spectrum 3 in Fig. 2(b). Rod compound is Mg–Bi phase containing few Al and Sm for Mg–6.05Al–0.98Sm–0.56Bi alloy (spectrum 1 in Fig. 2(b)). The added metal Zn dissolves into α -Mg matrix and β -Mg₁₇Al₁₂ phase.



Fig. 2 EDS spectra of as-cast alloys: (a) Mg=6.02Al=1.03Sm; (b) Mg=6.05Al=0.98Sm=0.56Bi; (c) Mg=5.95Al=1.01Sm= 0.57Zn

Figure 3 shows the XRD patterns of the as-cast alloys. It is seen that all XRD patters consist of peaks of α -Mg, β -Mg₁₇Al₁₂ and Al₂Sm phases. In addition, the peak of Mg₃Bi₂ phase can be observed among the XRD pattern of as-cast Mg=6.05Al=0.98Sm=0.56Bi alloy.

Combined with the above mentioned EDS results, the small block and rod compounds are considered Al_2Sm and Mg_3Bi_2 phases, respectively.

| Table 1 | EDS | results | of | as-cast | alloy | 79 |
|---------|-----|---------|----|---------|-------|----|
| Lable L | LDO | results | U1 | as-cast | ano | 1. |

| Alloy | Position | x(Mg)/ | x(Al)/ | x(Sm)/ | <i>x</i> (Bi)/ | x(Zn)/ |
|---------------------------------|------------------|--------|--------|--------|----------------|--------|
| Mg-6.02Al- 1.03Sm | 1 1 1 1 <u>1</u> | 0 | 64.52 | 35.48 | 0 | 0 |
| | 2 | 59.11 | 40.89 | 0 | 0 | 0 |
| | 3 | 99.82 | 0.18 | 0 | 0 | 0 |
| Mg-6.05Al- 0.98Sm- 0.56Bi | 1 | 75.12 | 4.95 | 5.53 | 14.40 | 0 |
| | 2 | 71.30 | 27.53 | 0 | 1.17 | 0 |
| | 3 | 0 | 67.07 | 32.93 | 0 | 0 |
| Mg-5.95Al- 1.01Sm- 0.57Zn | 1 | 0 | 66.69 | 33.31 | 0 | |
| | 2 | 65.11 | 30.06 | 0 | 0 | 4.83 |
| | 3 | 99.10 | 0 | 0 | 0 | 0.90 |
| | 4 | 37.59 | 44.51 | 17.90 | 0 | 0 |



Fig. 3 XRD patterns of as-cast alloys

The degree of difficulty in forming compounds between different elements can be judged by electronegativity difference $\Delta \chi$. The greater the value of $\Delta \chi$ is, the larger the binding force is, and then the easier the formation of compounds is [14]. Electronegativities χ are 1.31, 1.61, 1.17 and 1.9 for elements Mg, Al, Sm and Bi, respectively [15]. Adding the RE into Mg-Al series alloys may form Al-RE, Mg-RE or Mg-Al-RE compounds. Sm-Al exhibits the larger value of $\Delta \chi$ (0.44) than Sm-Mg (0.14), which indicates the greater binding force between Sm and Al. From the thermodynamic point of view, small block Al₂Sm rather than Mg-Sm or Mg-Al-Sm phase precipitates on the priority when Sm is added into Mg-Al alloy. Meanwhile, Bi-Mg alloy exhibits larger value of $\Delta \chi$ (0.59) than Bi-Al alloy (0.29). Therefore, rod Mg₃Bi₂ compound can precipitate on the priority when Bi is added.

The as-cast alloys exhibit the excellent tensile mechanical property at ambient and elevated

temperatures, respectively (Table 2). For Mg–6.02Al– 1.03Sm alloy, tensile strength (σ_b) can reach 220 and 162 MPa at 298 and 423 K, respectively, and the corresponding elongation (δ) can reach 12.5% and 14.5%, respectively. At ambient temperature, σ_b and δ slightly decrease to 205 MPa and 8.5%, respectively when 0.56%Bi is added, while they slightly increase to

 Table 2 Tensile mechanical properties of as-cast and die-cast alloys

| A 11 | Condition | $\sigma_{ m b}/{ m MPa}$ | | δ/% | |
|---------------|-----------|--------------------------|-------|-------|-------|
| Alloy | | 298 K | 423 K | 298 K | 423 K |
| Mg-6.02Al- | As-cast | 220 | 162 | 12.5 | 14.5 |
| 1.03Sm | Die-cast | 285 | 145 | 16.5 | 19.0 |
| Mg-6.05Al- | As-cast | 205 | 162 | 8.5 | 19.5 |
| 0.98Sm-0.56Bi | Die-cast | 240 | 144 | 8.5 | 10.0 |
| Mg-5.95Al- | As-cast | 235 | 171 | 16.0 | 20.0 |
| 1.01Sm-0.57Zn | Die-cast | 275 | 149 | 14.0 | 17.5 |

235 MPa and 16.0%, respectively when 0.57%Zn is added. Meanwhile, the two alloys exhibit the slightly higher comprehensive tensile mechanical property at elevated temperature.

All as-cast tensile fractures at ambient temperature exhibit a complex mode of ductile and brittle fractures (Figs. 4(a), (c) and (e)). Dimples and cleavage steps exist simultaneously for Mg-6.02Al-1.03Sm alloy. Cleavage steps increase slightly when 0.56% Bi is added, which is consistent with the rapid decrease in the elongation. Dimples still increase slightly when 0.57% Zn is added, which is consistent with the slightly increasing comprehensive tensile mechanical property. Meanwhile, few fine second phase particles can be observed at the bottom of dimples for the three alloys (see illustrations).

The strengthening mechanism of magnesium alloys mainly includes the grain-refinement strengthening, solid–solution strengthening, precipitation strengthening, dispersion strengthening and strain hardening. During the



Fig. 4 SEM morphologies of tensile fractures of as-cast and die-cast alloys at ambient temperature (Illustrations indicate local enlarged regions): (a) Mg-6.02Al-1.03Sm, as-cast; (b) Mg-6.02Al-1.03Sm, die-cast; (c) Mg-6.05Al-0.98Sm-0.56Bi, as-cast; (d) Mg-6.05Al-0.98Sm-0.56Bi, die-cast; (e) Mg-5.95Al-1.01Sm-0.57Zn, as-cast; (f) Mg-5.95Al-1.01Sm-0.57Zn, die-cast

solidification process of Mg-6.02Al-1.03Sm alloy, Sm participates in the eutectic reaction to form small block Al₂Sm phase with high thermal stability, which can form the eutectic microstructure together with α -Mg and β -Mg₁₇Al₁₂ phases. Al₂Sm phase can be pushed into the growth interface, and then the free growth of dendrite can be impeded. Meanwhile, the second phases distribute dispersedly. The phase with high thermal stability can pin the grain boundary, and inhibit the sliding of the grain boundary and the movement of the dislocation at the elevated temperature effectively. Therefore, the as-cast alloy exhibits the excellent tensile mechanical property at ambient and elevated temperatures, respectively. When 0.56% Bi is added, the as-cast microstructure is not refined significantly. Meanwhile, new rod phase Mg3Bi2 plays a weaker strengthening effect than small block Al₂Sm phase. Therefore, the tensile mechanical property at ambient temperature decreases slightly. When 0.57% Zn is added, metal Zn dissolves into α -Mg matrix and β -Mg₁₇Al₁₂ phase, which leads to a slight increase in the tensile mechanical property at ambient and elevated temperatures owing to the solid-solution strengthening.

The as-cast alloys exhibit the relatively excellent flow property (Fig. 5(a)). The flow length can reach 460 mm for Mg-6.02Al-1.03Sm alloy. It decreases to 430 and 320 mm when 0.56% Bi and 0.57% Zn are added, respectively.

3.2 Microstructure and mechanical property of diecast alloy

Figures 6 and 7 show the optical and SEM micrographs of the die-cast alloys, respectively. Obviously, the die-cast microstructures are different from those of the as-cast. The microstructures are refined significantly owing to the higher cooling rate. Meanwhile, the broken and refined second phases including discontinuous β -Mg₁₇Al₁₂, small block Al₂Sm and rod Mg₃Bi₂ phases mainly distribute along the grain boundary dispersedly.

The die-cast alloys exhibit better tensile mechanical properties at ambient temperature (Table 2). $\sigma_{\rm b}$ can increase to 285, 240 and 275 MPa for Mg-6.02Al-1.03Sm, Mg-6.05Al-0.98Sm-0.56Bi and Mg-5.95Al-1.01Sm-0.57Zn alloys with the increasing amplitude of 35-65 MPa, respectively. Meanwhile, the three alloys still exhibit the better plasticity, where δ is equal to or slightly higher than that of the as-cast value. This is owing to the grain-refining strengthening by the obviously refined microstructure and dispersion strengthening by the refined and dispersed second phases. Because gas cannot be exhausted opportunely and effectively during the commercial die-cast process, more or less gas cavities exist in the die-cast microstructures (see arrows in Fig. 7). They can expand during the tensile process at elevated temperature. Therefore, $\sigma_{\rm b}$ decreases to about 150 MPa at 423 K for the three alloys,



Fig. 5 Flow samples of as-cast (a) and die-cast (b) alloys

(b)





Fig. 6 Optical micrographs of die-cast alloys: (a, b) Mg-6.02Al-1.03Sm; (c, d) Mg-6.05Al-0.98Sm-0.56Bi; (e, f) Mg-5.95Al-1.01Sm-0.57Zn

which is even lower than that of the as-cast. How to reduce the gas cavities for the die-cast sample is a task to be resolved urgently. Researchers often ameliorate the problem by optimizing the die-cast process parameters or using advanced die-cast technology such as vacuum die casting.

(a)

Compared with the as-cast state, all die-cast tensile fractures at ambient temperature are different significantly (Figs. 4(b), (d) and (f)). Dimples occupy the majority, and meanwhile become deep. The dimples for Mg-6.05Al-0.98Sm-0.56Bi alloy are shallower than those for the other two alloys, which is consistent with its relatively poor tensile mechanical property.

Under the die-cast condition, the three alloys exhibit more excellent flow property (Fig. 5(b)). The flow

lengths reach 1870, 2420 and 2300 mm for Mg-6.02Al-1.03Sm, Mg-6.05Al-0.98Sm-0.56Bi and Mg-5.95Al-1.01Sm-0.57Zn alloys, respectively. Meanwhile, the change in the flow property for die-cast samples is different from that for as-cast samples. It may be related to different flow rules for each element and different microstructures under different cooling conditions.

4 Conclusions

1) The microstructure of as-cast Mg-6.02Al-1.03Sm alloy is composed of α -Mg matrix, discontinuous β -Mg₁₇Al₁₂ phase and small block Al₂Sm phase. The rod Mg₃Bi₂ phase precipitates when 0.56%Bi



Fig. 7 SEM images of die-cast alloys: (a, b) Mg=6.02Al=1.03Sm; (c, d) Mg=6.05Al=0.98Sm=0.56Bi; (e, f) Mg=5.95Al=1.01Sm=0.57Zn

is added, while the added metal Zn dissolves into α -Mg matrix and β -Mg₁₇Al₁₂ phase. The as-cast alloys exhibit excellent tensile mechanical properties. σ_b and δ reach 205–235 MPa and 8.5%–16.0% at ambient temperature, respectively. Meanwhile, they also exceed 160 MPa and 14.0% at 423 K, respectively.

2) The die-cast microstructures are refined obviously, and the broken second phases distribute along the grain boundary dispersedly. The die-cast alloys exhibit better tensile mechanical properties with σ_b and δ of 240–285 MPa and 8.5%–16.5% at ambient temperature, respectively, and excellent flow property with the flow length of 1870–2420 mm.

3) The die-cast tensile fractures at ambient temperature exhibit a typical character of ductile fracture. Deep dimples occupy the majority.

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Mg-Al-Sm 系耐热镁合金的显微组织和力学性能

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摘 要:分析铸态和压铸态 Mg-6.02Al-1.03Sm、Mg-6.05Al-0.98Sm-0.56Bi 和 Mg-5.95Al-1.01Sm-0.57Zn 合金的显微组织和相组成,测试其拉伸力学性能与流动性能。结果表明,Mg-6.02Al-1.03Sm 合金铸态组织由α-Mg 基体、半连续的β-Mg₁₇Al₁₂相和高热稳定性的小块状 Al₂Sm 相组成。添加 Bi 后生成杆状 Mg₃Bi₂相,而添加的 Zn 固溶于α-Mg 基体和β-Mg₁₇Al₁₂相中。铸态合金呈现优异的拉伸力学性能,室温时其抗拉强度(σ_b)和伸长率(δ)分别达到 205~235 MPa 和 8.5%~16.0%,而 423 K 时分别超过 160 MPa 和 14.0%。压铸态组织明显细化,第二相发生 破碎,且弥散分布。压铸态合金呈现更高的拉伸力学性能和优异的流动性能,室温σ_b和δ分别达到 240~285 MPa 和 8.5%~16.5%,流动长度可达 1870~2420 mm。压铸态室温拉伸断口呈现明显的断裂特征。 关键词:耐热镁合金; Mg-Al-Sm 合金;显微组织;力学性能,流动性能;断口形貌

(Edited by Wei-ping CHEN)