Effect of Sb and Sr Additions on the Microstructural Evolution of Mg-Sn-Al-Si Based Alloys

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A study has been made on the effect of Sb and Sr on the microstructure and mechanical properties of Mg-Sn-Al-Si based (TAS) alloy. When Sb is added to TAS alloy, the morphology of second phase particles changes to fine radial shape by the formation of nucleation cores. Refined microstructure of TAS-Sb alloys results in higher yield strength and larger elongation with lower creep resistance than those of TAS alloy. Sr addition induces the formation of large amount of thermally stable second phase particles. Due to the large amount of thermally stable second phase particles, TAS-Sr alloys show superior creep resistance and higher yield strength at both room and high temperatures than those of TAS alloy. [doi:10.2320/matertrans.MC200751]

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1. Introduction

Magnesium alloys have a great potential for high performance structural applications due to their excellent properties such as low density, high specific strength, superior damping capacity, etc.¹⁻⁶⁾ Since they also have good castability and machinability, Mg alloys have been mostly used as cast products in aerospace and automobile applications.^{7,8)} The typical alloys are Mg-Al based alloys such as AZ91 and AM60 alloys. They are currently used extensively in automotive components due to their improved corrosion resistance and moderate mechanical properties at room temperature.⁷⁻¹⁰⁾ In recent years, however, improving the elevated temperature properties has become a critical issue to extend their applications to powertrain components which are generally used at high temperatures.^{2,7,11-13)} Since the conventional Mg alloys have shown large decrease in mechanical properties at high temperatures over 100°C, several approaches have been taken to improve the elevated temperature properties of Mg alloys. The most common way of improving the elevated temperature properties is the utilization of thermally stable second phase particles in the microstructure.¹¹⁻¹⁴⁾ In our previous studies, Mg-Sn-Al-Si based (TAS) alloys which have thermally stable particles within matrix as well as along the grain boundaries have shown highly improved elevated temperature properties.¹⁵⁻¹⁸⁾ In the present study, the effect of additional alloying elements, Sb and Sr, on the microstructure and mechanical properties of TAS alloys have been investigated. Sb and Sr have been chosen since they are known to form thermally stable second phase particles in Mg alloys.

2. Experimental Procedures

Various TAS alloys with 1, 3, 5 mass% of Sb or Sr were investigated in the present study. Analyzed chemical compositions are summarized in Table 1. The alloys were melted at 750°C under an inert atmosphere of CO₂ and SF₆ mixture. The melt was injected into Cu mold where the cooling water

Table 1 Analyzed chemical compositions of the alloys.

Alloy	Mg	Sn (mass%)	Al (mass%)	Si (mass%)	Sb (mass%)	Sr (mass%)
TAS	Bal.	7.79	2.73	0.70	0.54	
TAS-1Sb	Bal.	7.76	2.60	0.51	0.81	
TAS-3Sb	Bal.	6.83	2.91	0.57	2.89	
TAS-5Sb	Bal.	7.06	2.70	0.62	4.44	
TAS-1Sr	Bal.	8.80	3.34	0.88		0.77
TAS-3Sr	Bal.	7.00	2.95	0.67		1.91
TAS-5Sr	Bal.	8.12	3.06	0.51		4.77

is circulating to obtain fast cooling rate similar to that of high pressure die casting process. Microstructure of the alloys was characterized using SEM and TEM. Tensile properties were measured by using flat tensile specimens with 12.6 mm gage length, 1 mm gage thickness and 5 mm gage width at a strain rate of $6.4 \times 10^{-4} \text{ s}^{-1}$. High temperature creep tests were performed in a horizontal creep tester at 150°C in an applied stress of 50 MPa. Creep specimens were cylindrical ones with gage length of 18 mm and gage diameter of 4 mm.

3. Results

3.1 Microstructure

Figure 1 shows the SEM micrographs of TAS alloy and Sb added TAS alloys. It shows that Sb added TAS alloys have a finer grain size than the TAS alloy (20 μm vs. 28 μm). As can be seen in Fig. 1(a), TAS alloy has shown semi-continuous particles along the grain boundaries. It has been shown that these particles consist of thermally stable Mg₂Sn and Mg₂Si with a small amount of Mg₁₇Al₁₂ particles.¹⁵⁻¹⁸⁾ Although Mg₂Si particles generally form as coarse Chinese-script shape in a slow cooling rate, having quite detrimental effect on the tensile properties of the alloys, they form in TAS alloy as a globular shape due to fast cooling rate.^{12,19)} The microstructure of TAS alloy with 1 mass% of Sb is essentially similar to that of TAS alloy (Fig. 1(b)). However, when higher amounts (3 and 5 mass%) of Sb are added in TAS alloy (Figs. 1(c) and (d)), the morphology of second

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Fig. 1 SEM micrographs: (a) TAS, (b) TAS-1Sb, (c) TAS-3Sb, and (d) TAS-5Sb alloys.

phase particles gradually changes into radial shape consisting of core, branches and outer parts. It can be seen in Fig. 1(c) that fine cores start to emerge at the center of large amount of second phase particles in 3 mass% Sb containing TAS alloy. In the TAS alloy with 5 mass% of Sb, all the particles have fine radial shape as shown in Fig. 1(d). Figure 2 shows TEM bright field image, EDS spectra and diffraction patterns from core and outer part of the second phase particles of TAS-5Sb alloy. TEM EDS results show that core part contains Si and Sb, while outer part contains mostly Sn with a small amount of Si. SAD analyses show that core and outer parts have same FCC structure with lattice parameters of 0.670 and 0.645 nm, respectively. It suggests that Mg_2Si particles containing Sb form as primary particles during solidification, which then act as nucleation sites for Mg_2Sn particles.

As compared to Sb added TAS alloys, Sr addition has resulted in quite different microstructure as shown in Fig. 3. When 1 mass% of Sr is added to TAS alloy, a large amount of needle-shaped particles form in the microstructure (Fig. 3(a)). As the Sr content increases, needle-shaped particles become more dominant. 5 mass% of Sr addition has generated a fairly large amount of various second phase particles in the microstructure. Since it is well known that Sr can form several kinds of second phases with Al, Mg and Sn,^{13,20)} it is expected that Sr containing TAS alloys would also have various second phase particles in the microstructure. TEM bright field images and diffraction patterns of some second phase particles are shown in Fig. 4. The phases have been identified as SiSr_2 (orthorhombic), MgSi_2Sr (orthorhombic), and Sr_5Sn_3 (BCT), besides Mg_2Sn and

Mg_2Si . It is quite obvious that these microstructural changes by Sb and Sr addition will affect on the mechanical properties of the alloys. In addition, it is expected that high melting temperatures of second phases might be beneficial to the elevated temperature properties of TAS alloy.

3.2 Tensile and creep properties

Room and elevated temperature tensile properties of the alloys are summarized in Table 2. Properties of AZ91 are also included for comparison purposes. When Sb is added to TAS alloy, there are large increases in ultimate tensile strength and elongation with a small increase in yield strength at room temperature. Higher strengths of Sb added TAS alloys than those of TAS alloy are also maintained at higher temperatures. With the addition of Sr, there are large increases in yield strength at both room and high temperatures. However, increases in ultimate tensile strength by the addition of Sr are rather small at both room and high temperatures. More importantly, Sr-added TAS alloys show smaller elongation than TAS and Sb added TAS alloys at both room and high temperatures, suggesting that a large volume fraction of second phase particles in Sr-added TAS alloys are detrimental to the ductility of the TAS alloy systems.

Minimum creep rates of the alloys are shown in Table 3. It shows that the addition of Sb results in the increase in the minimum creep rates of the alloys. On the other hand, the addition of Sr has greatly decreased the minimum creep rates of the alloys. Even with the addition of 1 mass% Sr, creep elongation becomes too small to be measured and thus the minimum creep rate could not accurately be calculated.

Fig. 2 TEM micrographs of TAS-5Sb alloy: (a) TEM bright field image, (b) EDS spectrum and SAD pattern of core, and (c) EDS spectrum and SAD pattern of outer part.

4. Discussion

It has been shown in the present study that the microstructural changes by Sb and Sr additions have large effects on mechanical properties. The interesting feature of Sb added TAS alloys is the formation of radial shape second phase particles consisting of core Mg_2Si phase containing Sb and outer Mg_2Sn phase. Since Sb has very low solubility in molten Mg and Mg_3Sb_2 phase has very high melting temperature, it can be expected that Mg_3Sb_2 phase might form at the first stage of solidification in the microstructure of Sb added TAS alloy. However, the present study shows that

Fig. 3 SEM micrograph: (a) TAS-1Sr, (b) TAS-3Sr, and (c) TAS-5Sr alloys.

Mg_3Sb_2 phase does not exist and core phase is Mg_2Si phase containing Sb. It has been reported that two of Mg-Sb phases, $\alpha\text{-Mg}_3\text{Sb}_2$ and $\beta\text{-Mg}_3\text{Sb}_2$, have solubility in Mg_2Sn and Mg_2Si phases and they can make a complete solid solution with these phases.^{21,22} Thus the formation mechanism of the microstructure of TAS-Sb alloys can be explained as follows. When the melt is solidified, Mg_3Sb_2 phase forms as primary phase in the melt. These Mg_3Sb_2 particles then act as nucleation sites for other phases during solidification and Mg_2Si phase forms around the Mg_3Sb_2 nuclei, forming the core part of the second phase particles. At this stage, Mg_3Sb_2 phase dissolves into the core, which eventually becomes Mg_2Si phase containing Sb. This phase continuously grows to the outside along a crystallographic direction forming branches. As the solidification continues, there is an additional precipitation of Mg_2Sn at the branch of Mg_2Si -rich phase. Detailed TEM SAD analysis indicates that Mg_2Sn and

Fig. 4 TEM bright field images and SAD patterns obtained from the second phase particles: (a) SiSr_2 , (b) MgSi_2Sr and (c) Sr_5Sn_3 phases.

Mg_2Si have the orientation relationship such as $(011)_{\text{Mg}_2\text{Sn}} // (013)_{\text{Mg}_2\text{Si}}$, $[100]_{\text{Mg}_2\text{Sn}} // [100]_{\text{Mg}_2\text{Si}}$. It also shows that the growth directions of branch are $[100]$ and $[031]$ for Mg_2Si . Such various growth directions of Mg_2Si phase possibly explain the occurrence of Chinese script Mg_2Si particles in numerous Mg alloy systems. Since Mg_2Sn and Mg_2Si phases have the same crystal structure with only a small difference in the lattice parameters, they can form a completely miscible structure.^{23,24)} However, inter-solution of these phases has not been found in the present study. Further study is necessary to understand the exact formation mechanism of these particles. Although the addition of Sb to TAS alloy imparts significant and interesting changes in the micro-

Table 2 Room and elevated temperature tensile properties of the alloys.

Alloy	Room temp.			150°C		
	YS(MPa)	UTS(MPa)	El.%	YS(MPa)	UTS(MPa)	El.%
AZ91	104	141	2.4	83	125	12.0
TAS	110	152	3.0	87	138	12.5
TAS-1Sb	111	186	5.5	95	147	10.0
TAS-3Sb	115	194	6.5	102	149	8.6
TAS-5Sb	117	198	5.8	106	148	8.0
TAS-1Sr	146	168	2.1	125	143	4.4
TAS-3Sr	147	165	1.9	123	142	4.4
TAS-5Sr	153	167	1.7	130	145	3.7

Table 3 Minimum creep rates of the alloys.

Alloy	Min. creep rate ($\times 10^{-9} \text{ s}^{-1}$)
AZ91	34.0
TAS	2.2
TAS-1Sb	3.7
TAS-3Sb	3.6
TAS-5Sb	3.4
TAS-1Sr	<0.01
TAS-3Sr	<0.01
TAS-5Sr	~0

structure as mentioned above, it does not improve the creep resistance of the alloys. Sb has been initially added to the alloy to utilize the high thermal stability of Mg_3Sb_2 phase, which might have a beneficial effect on creep resistance. However, Mg_3Sb_2 phase dissolves into Mg_2Si , making the microstructure of the alloys basically similar to that of non-Sb containing TAS alloy. Moreover, there is an overall refinement of grain size and particle size with Sb addition. Such microstructural changes induced by Sb addition result in improvement of tensile properties but decrease in the creep resistance of Sb containing alloys as compared to those of TAS alloy. As compared to Sb added alloys, Sr added alloys have much more complex microstructure due to the formation of many types of second phase particles such as Mg_2Sr , SnSr_2 , SiSr , Si_2Sr , Al_4Sr , etc. besides Mg_2Si and Mg_2Sn . Formation mechanism of these phases in the alloy system could not be understood at this time since there are no thermodynamic data and phase diagram available. However, since all the second phase particles present in the current alloys have higher melting temperatures above 500°C , it can be expected that these phases are thermally stable, improving the creep resistance of TAS-Sr alloys as shown in the present study. However, a large increase in the volume fraction of second phase particles by Sr addition results in a decrease in tensile ductility.

5. Conclusion

When Sb is added to TAS alloy, the microstructure becomes refined and the morphology of second phase particles changes to radial shape particles consisting of Mg_2Si phase containing Sb in the core region and Mg_2Sn phase in the outer region. Refined microstructure of Sb

containing TAS alloys has resulted in decrease in creep resistance as compared to TAS alloy. On the other hand, Sr addition has induced the formation of a large amount of thermally stable second phase particles in the microstructure, resulting in a large increase in creep resistance as compared to TAS and other commercially available Mg alloys.

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