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ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) 1367−1373
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effect of Sb on microstructure and mechanical properties of Mg_2Si/Al-Si composites

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Received 8 September 2009; accepted 23 March 2010

Abstract: The effect of Sb on the microstructure and mechanical properties of Mg_2Si/Al-Si composites was investigated. The results show that Sb can improve the microstructure and mechanical properties of Mg_2Si/Al-Si composites. When the content of Sb is 0.4%, the morphology of primary Mg_2Si changes from dendrites to fine particles, the average size of Mg_2Si particles is refined from 52 to 25 μm, and the ultimate tensile strength and elongation of the composites increase from 102.1 MPa and 0.26% to 138.6 MPa and 0.36%, respectively. The strengthening mechanism can be attributed to the fine-grain strengthening. However, excessive Sb is disadvantageous to the modification of the composites.

Key words: Mg_2Si/Al-Si composite; Sb; mechanical property; fine-grain strengthening

1 Introduction

Particulate-reinforced aluminum and magnesium metal matrix composites (MMCs) have attractive advantages of high specific tensile strength, modulus, high wear resistance and improved mechanical properties[1−2], which makes them potential materials in the field of automotive industry, such as cylinder blocks, cylinder heads, pistons and valve lifters[3]. In situ Mg_2Si/Al composites have a high wear resistance since the intermetallic compound Mg_2Si has a high melting temperature, low density, high hardness, low thermal expansion coefficient and reasonably high elastic modulus[4−8]. However, these expected excellent properties of Mg_2Si/Al composites can be seriously affected by the coarse Mg_2Si particles and brittle eutectic matrix[5, 8]. Therefore, controlling the primary and eutectic Mg_2Si phase is a key problem for acquiring excellent mechanical properties.

It was reported that the microstructure and mechanical properties of the Mg_2Si/Al composites can be improved by advanced processing techniques, such as hot extrusion, rapid solidification processing, directional solidification, mechanical alloying, electromagnetic stirring and electromagnetic separation[9−10]. However, these processing methods lead to the increase of production cost. Recently, the primary and eutectic Mg_2Si phase in Mg_2Si/Al composites have been modified by means of adding modification elements, and desirable mechanical properties are obtained.

The physical properties of Mg_2Si and Si are very similar, and the solidification characteristics of Al-Mg_2Si and Al-Si systems are also considerable similar (see Tables 1 and 2)[11]. Modification elements, such as Sr, Ba, P, RE, Sb and Ti, can be used to modify primary Si and eutectic structure in Al-Si alloy systems (including hypoeutectic, eutectic and hypereutectic alloys) effectively[12−18], and they can be used as refiners to modify primary Mg_2Si in Al-Mg_2Si composites. It has been also reported that Na salts, K_2TiF_6, mischmetal, P, extra Si，La, Li and Sr can refine the primary Mg_2Si in Al-Mg_2Si or Mg-Mg_2Si alloy systems [1−3, 5, 19−27]. Recently, Sb has been used to modify the primary Mg_2Si

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DOI: 10.1016/S1003-6326(09)60306-X

Table 1 Physical properties of Mg_2Si and Si[11]

Phase	Crystal structure	Lattice parameter/nm	Density/($g\cdot cm^{-3}$)	Coefficient of thermal expansion/$10^{-6}K^{-1}$	Elastic modulus/GPa	Melting point/°C
Mg_2Si	Cubic	0.635 2	1.99	7.5	120	1 085
Si	Cubic	0.542 8	2.33	3.06	112	1 414

Table 2 Solidification characteristics of Al-Mg_2Si and Al-Si systems[11]

System	Equilibrium diagram	Growth character	Eutectic composition (mass fraction)/%	Eutectic temperature T_E/K	Solubility at T_E (mass fraction)/%
Al-Mg_2Si	Pseudoeutectic	Non-faceted-faceted	13.9	856.5−867	1.91
Al-Si	Eutectic	Non-faceted-faceted	12.6	850	1.65

in Mg-Al-Si-Zn alloy and Mg-Si alloy, which changes the morphology of Mg_2Si particles from coarse dendrites to fine particles [28−29]. However, few investigations were carried out on the modification of Mg_2Si by the addition of Sb in Mg_2Si/Al composites. In this study, the in situ 20Mg_2Si/Al-5Si composites were produced by means of common gravity casting process. The effect of Sb on the microstructure and mechanical properties of the composites were investigated. In addition, the modification mechanism of Sb on the primary Mg_2Si is analyzed.

2 Experimental

Industrial pure Al, Mg, Si and Al-3Sb master alloy were used to produce 20Mg_2Si/Al-5Si (mass fraction, %) composites. An excess of 20% (mass fraction) Mg was added in order to balance the oxidation loss. All the alloys were melted in a 7.5 kW resistance furnace. The melt of Al-Si alloy was degassed in Ar at 750 °C. The Mg and Al-3Sb master alloy were added into the Al-Si melt at 765 °C and 780 °C, respectively. The Addition amount of Sb was 0, 0.2%, 0.4% and 0.6% (mass fraction), respectively. After cleaning the slag, the melts were poured into a steel mold preheated at 200 °C. Two kinds of composites billets were cast, which were named tensile test billets and analysis billets, respectively. The tensile test billets were machined to cylindrical samples with a diameter of 8 mm and a gauge length of 80 mm. The tensile tests were conducted on an MTS810 tester at a strain rate of 5×10^{-4}/s. The microstructure of the tested composites was observed and quantitatively analyzed using an Olympus BX51 metallographic microscope with an image collection and analysis system, and JSM6700F scanning electron microscope (SEM). The chemical compositions of these alloys were analyzed by energy dispersive spectrometer (EDS) assembled in SEM. X-ray diffractometer (XRD, X'Pert PROX) was used to identify the crystalline structures with scanning area ranging from 20˚ to 100˚ at a speed of 6 (˚)/min.

3 Results

3.1 Microstructure of Mg_2Si/Al-Si composites

The XRD patterns of Mg_2Si/Al-Si composites are presented in Fig.1. The microstructures of these composites consist of α(Al), primary Mg_2Si and (Mg_2Si+Si +Al) eutectic.

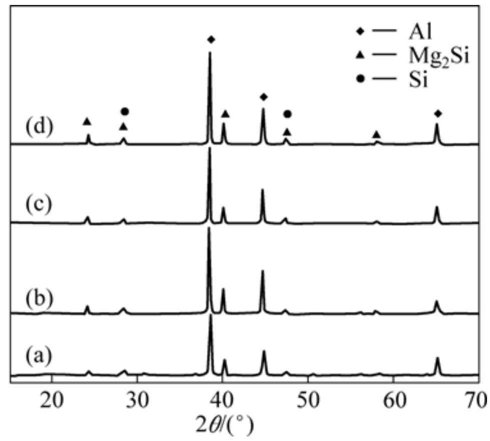

Fig. 1 XRD patterns of Mg_2Si/Al-Si composites with different Sb content: (a) 0; (b) 0.2%; (c) 0.4%; (d) 0.6%

The microstructures of Mg_2Si/Al-Si composites are shown in Fig.2. Many coarse dendritic or Chinese script type of primary Mg_2Si can be found in the unmodified composites (Fig.2(a)). The average size of primary Mg_2Si decreases with increasing Sb content, and the edges and angles are passivated (Fig.2(b−d)). Moreover, α(Al) phase becomes finer. The primary Mg_2Si changes into fine particles when the content of Sb increases to 0.4%, while excessive Sb results in coarsening of primary Mg_2Si.

Fig.3 presents the effects of Sb on the volume fraction, average size and roundness of primary Mg_2Si. We can see that the volume fraction of primary Mg_2Si and the particles roundness C^2/A (C and A are the circumference and area of primary Mg_2Si particles,

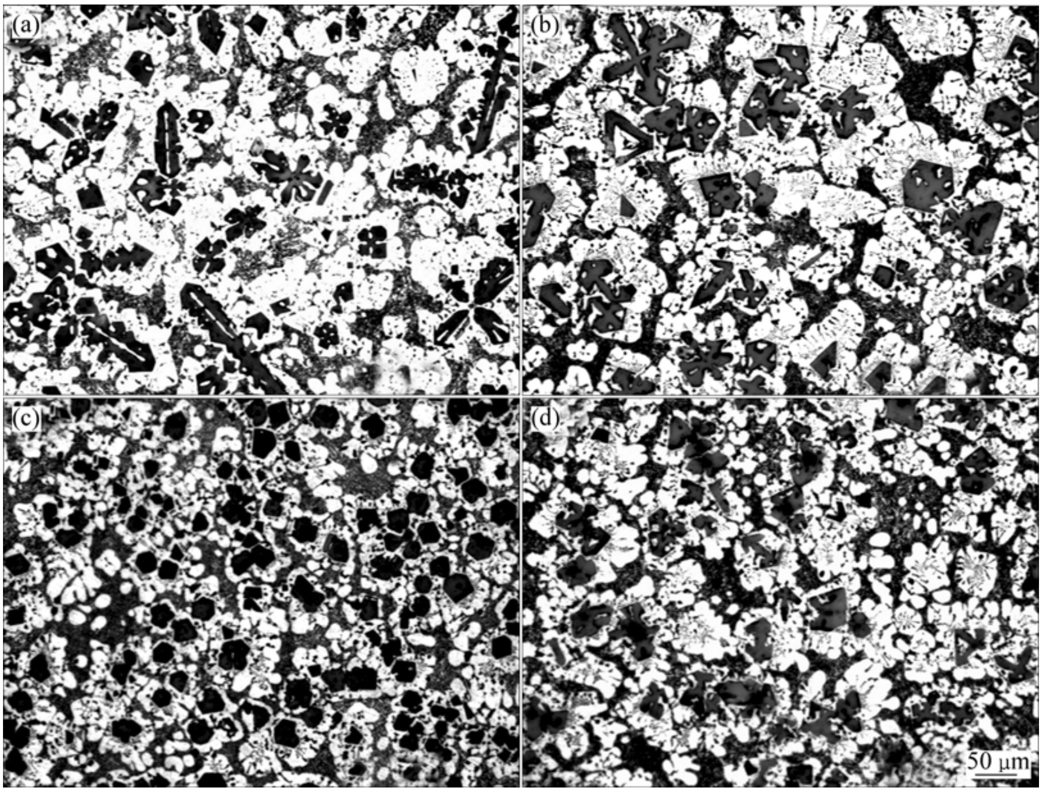

Fig.2 Microstructures of Mg_2Si/Al-Si composites with different Sb additions: (a) 0; (b) 0.2%; (c) 0.4%; (d) 0.6%

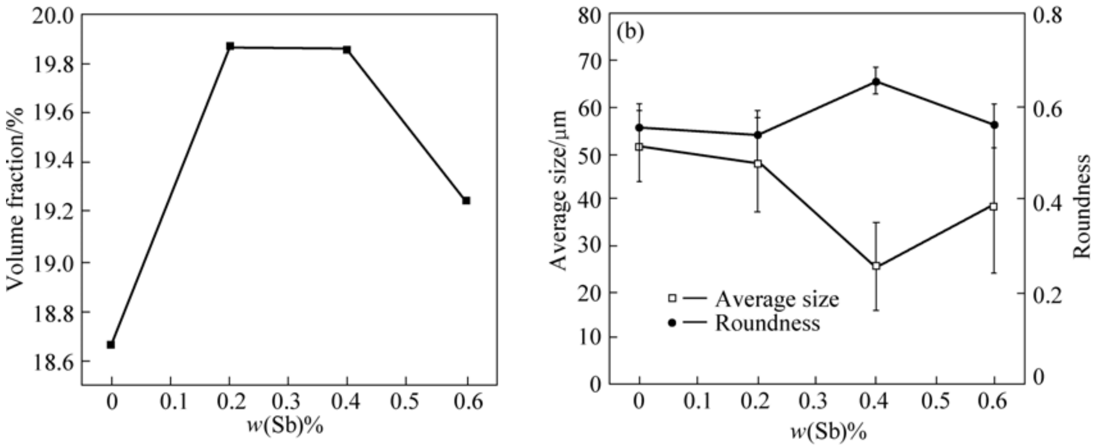

Fig.3 Correlation parameters of primary Mg_2Si particles as function of Sb content: (a) Volume fraction; (b) Roundness and average size

respectively) have a slightly increase with the increase of Sb; on the contrary, the average size of primary Mg_2Si is refined to 25 μm after adding 0.4% Sb. However, when the content of Sb exceeds 0.4%, the variation tendency of volume fraction, roundness and average size moves to the opposite direction.

3.2 Tensile properties

The ultimate tensile strength (UTS) and elongation of Mg_2Si/Al-Si composites with different Sb content are shown in Fig.4. It can be seen that the UTS and elongation increase from 102.1 MPa and 0.26% to 138.6 MPa and 0.36%, respectively, with increasing Sb content. When the Sb content exceeds 0.4%, however, the UTS and elongation begin to decrease and the tendency is similar to that of the modifications of primary Mg_2Si.

Fig.5 shows the fractograph difference between primary and modified composites. In Fig.5(a), there are many coarse dark inhomogeneous distributed cleavage facets in the fracture. For modified composites, however, the size of cleavage facets is smaller and the distribution is very homogeneous, as seen in Fig.5(b). These fractured particles are identified as Mg_2Si particles according to the EDS analysis.

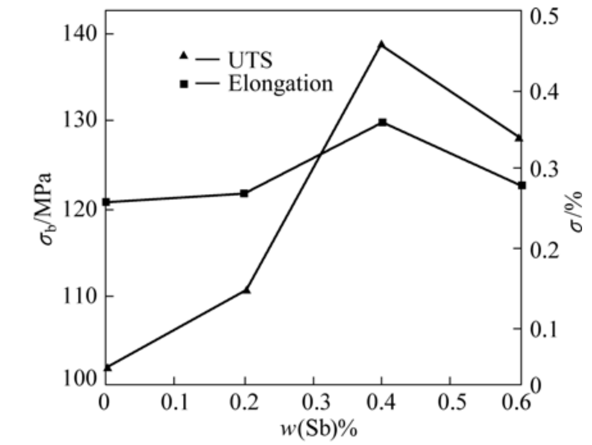

Fig.4 Mechanical properties of composites as function of Sb content

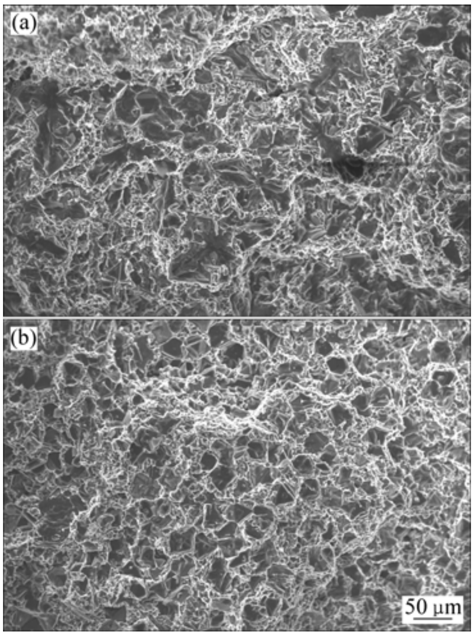

Fig.5 Fractographs of Mg_2Si/Al-Si composites with different Sb addition: (a) 0% Sb; (b) 0.4% Sb

4 Discussion

4.1 Evolution of phase structure

According to Ref.[5], there is a narrow ternary phase region of (liquid + α(Al) + Mg_2Si) between 583.5 and 594 ℃ at the pseudo-eutectic point in equilibrium diagram of Al-Mg_2Si system. The composition of the pseudo-eutectic is 13.9% Mg_2Si and the solubility of Mg_2Si in the α(Al) at 583.5 ℃ is 1.91%. However, the pseudo binary eutectic is converted to ternary eutectic system when excessive Si is added into the alloys. Fig.6 shows the vertical section of the Al-Mg_2Si-Si equilibrium ternary phase diagram[30]. It can be found that the equilibrium solidification paths of the alloys depend on the alloys' compositions:

Mg_2Si/Al:

$$L \to L_1 + (\mathrm{Mg_2Si})_\mathrm{P} \to (\mathrm{Mg_2Si})_\mathrm{P} + (\mathrm{Al} + \mathrm{Mg_2Si})_\mathrm{E} \quad (1)$$

Mg_2Si/Al-5Si:

$$L \to L_1 + (\mathrm{Mg_2Si})_\mathrm{P} \to L_2 + (\mathrm{Mg_2Si})_\mathrm{P} + (\mathrm{Al} + \mathrm{Mg_2Si})_\mathrm{E} \to (\mathrm{Mg_2Si})_\mathrm{P} + (\mathrm{Al} + \mathrm{Mg_2Si})_\mathrm{E} + (\mathrm{Al} + \mathrm{Mg_2Si} + \mathrm{Si})_\mathrm{E} \quad (2)$$

where P and E represent the primary and eutectic phase, respectively. Accordingly, primary Mg_2Si solidifies first from the liquid in all cases followed by binary eutectic reactions to form either Al or Si eutectic with Mg_2Si. Afterwards, the ternary eutectic forms if extra Si is added into the alloys in the range from A to C in Fig. 6. It is clear that the components of the obtained alloys are primary Mg_2Si, α(Al) and ternary eutectic (Al+Mg_2Si+Si), which is consistent with the XRD analyses.

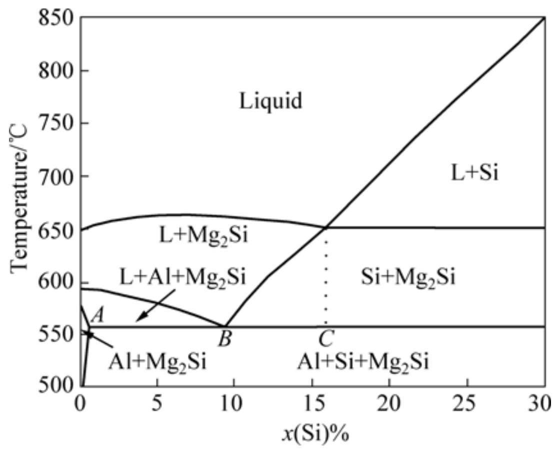

Fig.6 Phase diagram of Al-Mg_2Si-Si equilibrium ternary alloy[30]

It is noticed that some α(Al) phase around Mg_2Si particles can be found in the microstructure. According to the solidification paths of (1) and (2), no α(Al) phase is produced under equilibrium solidification[30]. But the high cooling rate in experiments restrains the diffusion of Mg and Si in liquid aluminum. There is an Al-rich region around each Mg_2Si particle. Once the under-cooling at the solid-liquid interface is large enough, α(Al) may nucleate on the facets of the Mg_2Si crystals. The growth of Mg_2Si may be restrained, which is similar to the α(Al) haloes around primary Si in hypereutectic Al-Si alloys and halos around primary Mg_2Si in Mg-Si alloys [6].

4.2 Effects of Sb on primary Mg_2Si

Usually, the modification mechanism of Sb in Al-Si alloys is related to the AlSb compounds which act as heterogeneous crystallization nucleus for the eutectic silicon, hence resulting in fine lamellar morphology of eutectic silicon[14]. However, the reason of primary Mg_2Si refined in Mg-Si alloys and Al-Mg_2Si systems is still not clear. As for Mg-Si alloys, it is believed that Sb on the surface not only prompts the formation of homogeneous nucleation but also restrains the growth of primary Mg_2Si, because Sb aggregates on the interface between Mg_2Si and melt [28]. As for the Al-Mg_2Si composites, the above mentioned modification mechanism may be one reason for the formation of refined Mg_2Si particles.

Fig.7(a) shows the microstructure of Mg_2Si in the composites. We can see that some Mg_2Si particles contain small white particles which may act as nucleation sites for Mg_2Si particles.

The results of area scanning and EDS (as shown in Fig.8) indicate that the nucleus are enriched in Si, Mg and Sb. It is believed that the nucleus should be Mg_3Sb_2 compounds. Similar results were observed in Mg-Al-Zn-Si alloys, and the heterogeneous crystallization nucleus Mg_3Sb_2 was also observed inside the Mg_2Si particles [25]. It is found that the misfit between lattice parameters of Mg_3Sb_2 and Mg_2Si is the lowest (5.1%) when the orientations relationship between Mg_2Si and Mg_3Sb_2 phase is $(0001)_{Mg_3Sb_2}$ // $(0001)_{Mg_2Si}$. Therefore, Mg_3Sb_2 can act as the heterogeneous crystallization nucleus for the Mg_2Si phase, which results in the modification of primary Mg_2Si.

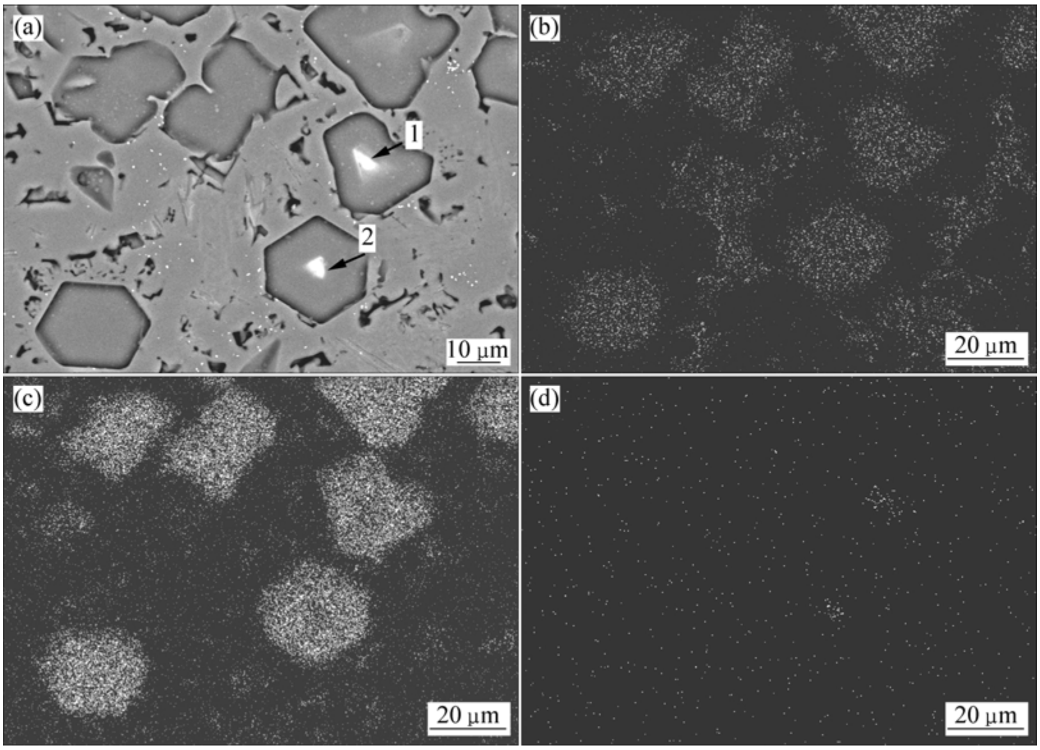

Fig.7 SEM image (a) of modified Mg_2Si particles with 0.4 % Sb and area scanning: (b) Si element; (c) Mg element; and (d) Sb element

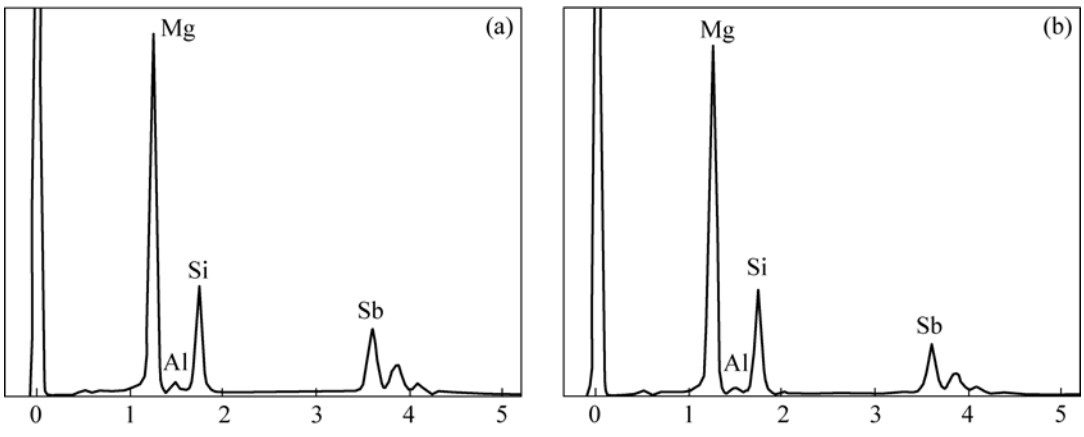

Fig.8 EDS analysis of Mg_2Si particles: (a) Spect 1 and (b) Spect 2

4.3 Effects of Sb on tensile properties

The investigations of hypereutectic Al-Si alloys showed that their mechanical properties are mainly determined by some metallurgical factors such as [14]: 1) the morphology, size and distribution of the primary silicon crystal particles; 2) the cohesion between the silicon crystal particles and the matrix; and 3) the ease with which the particles crack. The strengthening mechanism of Al-Mg_2Si composites is very similar to the hypereutectic Al-Si alloys. The mechanical properties of Mg_2Si/Al-Si composites are determined by the size, morphology and distribution of primary Mg_2Si particles.

As for the unmodified or inadequate modified Mg_2Si/Al-Si composites, the high stress concentration on the coarse dendritic Mg_2Si particles is produced by the tensile load. The microcrack is easily initiated from the primary Mg_2Si particles by debonding Mg_2Si particles from matrix or self-cracking of Mg_2Si particles, which results in the decrease of mechanical properties of the composites. As for the modified composites, the fine particles and perfect shape make the particles subject to less stress concentration and have higher resistance of crack comparatively. The initiation probability of microcrack also decreases effectively. Moreover, the increasing volume fraction of Mg_2Si particles and the excellent bonding between fine Mg_2Si particles and Al matrix may further increase the strength of the composites. Therefore, the strengthening mechanism of Mg_2Si/Al-Si composites is mainly fine-grain strengthening.

5 Conclusions

1) When the mass fraction of Sb is 0.4%, the average size of primary Mg_2Si is refined to 25 μm, and the morphology of primary Mg_2Si changed from coarse Chinese script type or dendritic shape to fine particles. Excessive Sb content results in coarsening of primary Mg_2Si particles.

2) The refinement mechanism is related to the formation of Mg_3Sb_2, which is easy to act as the excellent heterogeneous crystallization nucleus of Mg_2Si particles and results in the modification of primary Mg_2Si particles.

3) As the Sb content increases to 0.4%, the ultimate tensile strength and elongation of Mg_2Si/Al-Si composites increase from 102.1 MPa and 0.26% to 138.6 MPa and 0.36%, respectively. The refined primary Mg_2Si particles subject to less stress concentration and have higher resistance of crack, which leads to the enhancement of mechanical properties. Therefore, the strengthening mechanism of Mg_2Si/Al-Si composites is mainly fine-grain strengthening.

Acknowledgments

The authors are grateful to the DDJT Aluminum alloys Co. Ltd. for providing testing materials and facilities.

References

[1] ZHANG J, FAN Z, WANG Y Q, ZHOU B. Microstrucral refinement in Al-Mg_2Si in situ composites [J]. Journal of Materials Science Letters, 1999, 18(10): 783−784.

[2] ZHAO Y G, QIN Q D, ZHAO Y Q, LIANG Y H, JIANG Q C. In situ Mg_2Si/Al-Si composite modified by K_2TiF_6 [J]. Materials Letters, 2004, 58(16): 2192−2194.

[3] ZHAO Y G, QIN Q D, ZHOU W, LIANG Y H. Microstructure of the Ce-modified in situ Mg_2Si/Al-Si-Cu composite [J]. Journal of Alloys and Compounds, 2005, 389(1/2): L1−L4 .

[4] QIN Q D, ZHAO Y G, CONG P J, LIANG Y H, ZHOU W. Multi-layer functionally graded Mg_2Si/Al composite produced by directional remelting and quenching process [J]. Materials Science and Engineering A, 2006, 418(1/2): 193−198.

[5] ZHANG J, FAN Z, WANG Y Q, ZHOU B L. Microstructural development of Al-15wt.%Mg_2Si in situ composite with mischmetal addition [J]. Materials Science and Engineering A, 2000, 281(1/2): 104−112.

[6] JIANG Q C, WANG H Y, WANG Y, MA B X, WANG J G. Modification of Mg_2Si in Mg-Si alloys with yttrium [J]. Materials Science and Engineering A, 2005, 392(1/2): 130−135.

[7] PAN Y C, LIU X F, YANG H. Microstructural formation in a hypereutectic Mg-Si alloy [J]. Materials Characterization, 2005, 55(3): 241−247.

[8] QIN Q D, ZHAO Y G, XIU K, ZHOU W, LIANG Y H. Microstructure evolution of in situ Mg_2Si/Al-Si-Cu composite in semisolid remelting processing [J]. Material Science and Engineering A, 2005, 407(1/2): 196−200.

[9] LI Ying-min, AI Xiu-lan. Influence of electromagnetic stirring on macro-segregation of in-situ Al/Mg_2Si composites [J]. Foundry, 2002, 51(12): 756−758. (in Chinese)

[10] SONG Chang-jiang, XU Zhen-ming, LIANG Gao-fei, LI Jian-guo. Study of in-situ Al/Mg_2Si functionally graded materials by electromagnetic separation method [J]. Materials Science and Engineering A, 2006(1/2), 424: 6−16.

[11] ZHANG J, FAN Z, WANG Y G, ZHOU B L. Microstructure and mechanical properties of in situ Al-Mg_2Si composites [J]. Materials Science and Technology, 2000, 16(7): 913−918.

[12] SUN Yu, WU Zhen-ping, LIU Bing-yi, SUN Guo-xiong. Grain refinement for near-hypoeutectic Al-Si alloys [J]. The Chinese Journal of Nonferrous Metals, 2004, 14(8): 1340−1347. (in Chinese)

[13] LIAO Heng-cheng, SUN Guo-xiong. Interaction between Sr and B in Al-Si casting alloys [J]. The Chinese Journal of Nonferrous Metals, 2003, 13(2): 353−359. (in Chinese)

[14] LIAO Heng-cheng, SUN Yu, SUN Guo-xiong, TANG Chong-xi. Effect of mischmetal on microstructures of near-eutectic Al-Si alloy modified with Sr [J]. The Chinese Journal of Nonferrous Metals, 2000, 10(5): 640−644. (in Chinese)

[15] CHEN Chong, LIU Zhong-xia, REN Bo, WANG Ming-xing, WENG Yong-gang, LIU Zhi-yong. Influence of complex modifications of P and RE on the microstructure and mechanical properties of hypereutectic Al-20%Si alloy [J]. Transactions of Nonferrous Metals Society of China, 2007, 17(2): 301−306.

[16] SREEJA KUMARI S S, PILLAI R M, RAJAN T P D, PAI B C. Effects of individual and combined additions of Be, Mn, Ca and Sr on the solidification behaviour, structure and mechanical properties

of Al-7Si-0.3Mg-0.8Fe alloy [J]. Materials Science and Engineering A, 2007, 460/461: 561−573.

[17] KORI S A, MURTY B S, CHAKRABORTY M. Development of an efficient grain refiner for Al-7Si alloy and its modification with strontium [J]. Materials Science and Engineering A, 2000, 283(1/2): 94−104.

[18] SUÁREZ-PEÑA B, ASENSIO-LOZANO J. Microstructure and mechanical property developments in Al-12Si gravity die castings after Ti and/or Sr additions [J]. Materials Characterization, 2006, 57(4/5): 218−226.

[19] WANG H Y, JIANG Q C, MA B X, WANG Y, WANG J G, LI B. Modification of Mg_2Si in Mg-Si Alloys with K_2TiF_6, KBF_4 and KBF_4+K_2TiF_6 [J]. Journal of Alloys and Compounds, 2005, 387(1/2): 105−108.

[20] ZHANG J, FAN Z, WANG Y Q, ZHOU B L. Microstructural evolution of the in situ Al-15wt.%Mg_2Si composite with extra Si contents [J]. Scripta Materialia, 2000, 42(11): 1101−1106.

[21] WANG Qu-dong, ZHU Yan-ping, MA Chun-jiang, DING Wen-jiang. In situ surface composites of (Mg_2Si+Si)/ZA27 fabricated by centrifugal casting [J]. Materials Letters, 2003, 57(24/25): 3851−3858.

[22] CHANG J Y, NOGITA K, MOON I G, CHOI C S. Rare earth concentration in the primary Si crystal in rare earth added Al-21wt.%Si alloy [J]. Scripta Materialia, 1998, 39(3): 307−314.

[23] DAHLE A K, NOGITA K, mcDONALD S D, DINNIS C, LU L. Eutectic modification and microstructure development in Al-Si Alloys [J]. Materials Science and Engineering A, 2005, 413/414: 243−248.

[24] WANG Li-ping, GUO Er-jun, MA Bao-xia. Modification effect of lanthanum on primary phase Mg_2Si in Mg-Si alloys [J]. Journal of Rare Earths, 2008, 26(1): 105−109.

[25] LI Chong, WU Yu-ying, LIU Xiang-fa. Microstructural formation in hypereutectic Al–Mg_2Si with extra Si [J]. Journal of Alloys and Compounds, 2009, 477(1/2): 212−216.

[26] HADIAN R, EMAMY M, VARAHRAM N, NEMATI N. The effect of Li on the tensile properties of cast Al-Mg_2Si metal matrix composite [J]. Materials Science and Engineering A, 2008, 490(1/2): 250−257.

[27] QIN Q D, ZHAO Y G, CONG P J, ZHOU W. Strontium modification and formation of cubic primary Mg_2Si crystals in Mg_2Si/Al composite [J]. Journal of Alloys and Compounds. 2008, 454(1/2): 142−146.

[28] SUN Feng-quan, WANG Xiao-dong, YAN You-wei. The effect of Sb on microstructure in in-situ Mg_2Si/Mg composite [J]. Special Casting and Nonferrous Alloys, 2005, 25(1): 18−20. (in Chinese)

[29] YUAN G Y, LIU Z L, WANG Q D, DING W J. Microstructure refinement of Mg-Al-Zn-Si alloys [J]. Materials Letters, 2002, 56(1/2): 53−58.

[30] ZHANG J, FAN Z, WANG Y Q, ZHOU B L. Effect of cooling rate on the microstructure of hypereutectic Al-Mg_2Si alloys [J]. Journal of Materials Science Letters, 2000, 19(20): 1825−1828.

(Edited by FANG Jing-hua)