J Mater Sci (2010) 45:6732–6738
DOI 10.1007/s10853-010-4767-y

Grain refinement of AM60B magnesium alloy by SiC particles

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Received: 15 March 2010 / Accepted: 12 July 2010 / Published online: 23 July 2010

Abstract AM60B alloy has been refined by SiC particles and the corresponding refining mechanism has been mainly discussed. The results indicate that the addition of 0.2 wt% SiC particles in form of mixture with Mg powder decreases the grain size from 317 μm of the not refined alloy to 46 μm. The decrease of β phase and formation of Mg_2Si and Al_4C_3 phases well demonstrate that the reactions of $3SiC + 4Al = Al_4C_3 + 3Si$ and $2Si + Mg = Mg_2Si$ occur during refining treatment. In addition, the crystal nuclei are composed of two kinds of elements, Al and C. All of these imply that the formed Al_4C_3 particles are the actual heterogeneous nucleation substrates.

Introduction

Mg alloys have large application potential in automobile industry due to their high specific strength and are receiving increased attention. Al bearing alloys, such as AZ91D, AZ31, AM60B and so on, are the most commonly used ones among them. However, they often suffer from the challenge in meeting the requirements of strength, ductility, fatigue, and creep resistance [1]. It is well known that grain refinement can improve mechanical properties of most of alloys. So a fine microstructure should be very important for overcoming the low mechanical properties of these Mg alloys. In addition, a fine microstructure is also important for the properties of semi-fabricated products, e.g., ingots for extrusion and semisolid forming [2, 3].

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Unfortunately, there is no a commercially suitable grain refiner for the Al-bearing Mg alloys although several approaches have been developed. These approaches mainly include four categories, superheating, carbon inoculation, the Elfinal process, and grain refinement by other additives [4–22]. In addition, there are other alternative methods, such as severe deformation induced grain refinement, stirring cast and so on [23–26]. Comparatively, the carbon inoculation not only has significant refining effect but also has good adaptability to the alloys' compositions [19–22, 27]. Furthermore, the resources of some of environment-friendly carbon-containing additives, such as graphite, SiC, $MgCO_3$, and $MnCO_3$, are very abundant and their costs are quite cheap. Finally, their addition temperatures are also relatively low, which is beneficial to decrease oxidation during melting. So this method has larger application potential than the other approaches. The key of this method is how to accurately and reliably introduce a certain quantity of C into the Mg melts. Among these additives, SiC particles are always used as reinforcements in metal matrix composites and the methods to add them into metal melts have been well known. Moreover, the existing investigations show that the grain-refining effect is very remarkable, the resulting product of Mg_2Si phase is beneficial to improve mechanical properties of the treated alloys and there is no pollution to the melts and environment [19–22]. So the inoculation by SiC particles is a competitive technology for the Al bearing alloys. However, the existing references have not investigated the details of treating technique and the refining effect is not reliable for each operation. In addition, there is dispute on refining mechanism and a final conclusion has not been achieved for which is the real heterogeneous nucleation substrates among the potential candidates of Al_4C_3, Al_2CO, and SiC particles [19–22, 28].

Therefore, in the present work, the effect of addition amount of SiC particles, one of the main grain refining parameters, on the grain size of AM60B Mg alloy has been investigated. Especially, the refining mechanism has been mainly discussed.

Experimental procedure

The material used in this work is commercial AM60B magnesium alloy and its composition is Mg–5.98Al–0.343Mn–0.023Si (in wt%). The size of the used SiC particles is 1–2 μm. A quantity of AM60B alloy was first remelted at 740 °C and degassed by C_2Cl_6. The melt then was heated to 790 °C and a given amount of SiC particles was added and mechanically stirred for 30 s every 10 min (stirred for two times). Following, the melt was held for 10 min, and then cooled to 740 °C and poured into a permanent mold to form some rods with diameter of 16 mm. To easily introduce the SiC particles into the melt and enhance their absorptivity, the SiC particles were mixed with Mg powder according to weight rate of 1:3 and then pressed into small blocks. During experiment, a quantity of the prepared refiner blocks was enwrapped by aluminum foil and then added into the melt. Repeating the above experimental procedures, the alloys refined by different amounts of SiC particles were obtained.

Some small specimens were cut from the cast rods, and finished and polished by standard metallographic technique. They then were etched by aqueous solution (containing glycerol, nitric acid, hydrochloric acid, and acetic acid) and observed on an optical microscope (OM). In order to delineate the grain boundaries and quantitatively examine the grain size, these specimens were solution-treated for 8 h at 420 °C and then again processed according to the above procedures for preparing metallographic specimen. The mean linear intercept method was used to measure the average grain size. On each specimen, 3–7 images with magnification of 100 or 200 times were examined.

After the metallographic observation, X-ray diffraction (XRD) analysis was carried out using the metallographic specimens. To clarify the grain-refining mechanism of SiC inoculation, the specimen with addition of 0.2 wt% SiC particles was analyzed by energy dispersive spectroscopy (EDS) equipped with scanning electron microscope (SEM). In addition, in order to obviously show the products formed from the reactions between the SiC particles and Mg melt, and thus deduce the detailed reactions and the refining mechanism, a specific experiment with addition of 5 wt% SiC particles was carried out. The resulting alloy was observed on SEM and analyzed by XRD and electron microprobe analyzer (EPMA).

Results and discussion

Effect of addition amount of SiC particles on grain size

Figure 1 presents the microstructures of the AM60B alloys refined by different amounts of SiC particles. It shows that the primary grains of the unrefined alloy are in developed dendrite form and their secondary dendrite arms are up to several hundred micrometers (Fig. 1a). After being treated by 0.1 wt% SiC particles, the primary grains are significantly refined and they become fine equiaxed dendrites (Fig. 1b). As the addition amount of SiC particles increases, the dendrites are further refined (Fig. 1c). But when it exceeds 0.2 wt%, the dendrites gradually become more and more developed again (comparing Fig. 1c, d). This change can be more obviously seen in Fig. 2.

Figure 3 gives the result of quantitative examinations. It shows that the addition of 0.2 wt% SiC particles decreases the grain size from 317 μm of the not refined alloy to 46 μm, which implies that SiC particles are an effective grain-refiner for the AM60B alloy. It also indicates that the number of the heterogeneous nucleation substrates formed due to the addition of SiC particles is saturated when 0.2 wt% SiC particles is added. If the addition amount is further increased, the substrates will merge and settle, resulting in the decrease of the effective substrate number and thus the increase of the grain size. All of these results imply that adding 0.2 wt% SiC particles at 790 °C in form of the mixture with Mg powder and subsequent pouring at 740 °C are appropriate for AM60B alloy.

Mechanism of grain refinement

Figure 4 presents the micrographs with relatively high magnification of the as-cast AM60B alloys refined by different amounts of SiC particles. It gives two main phenomena: one is that the amount of interdendritic β phase ($Mg_{17}Al_{12}$) decreases with increasing the addition amount of SiC particles; the other is that two new phases with different morphologies (one is in Chinese script morphology and the other is in polygonal particle shape) form and both of them grow up with the addition amount. These two phenomena imply that the formation of the two new phases generate by exhaustion of the β phase and SiC particles.

Figure 5 shows the typical XRD results of the alloys. It indicates that the unrefined alloy is composed of α-Mg and β phases, but for the refined alloys, a new phase of Mg_2Si forms besides the α-Mg and β. It also indicates that the diffraction intensities of Mg_2Si phase are enhanced as the SiC particle amount increases while those of the β phase are weakened (comparing the corresponding peaks of (a)–(c) diffractograms). Together with the above discussion, it can

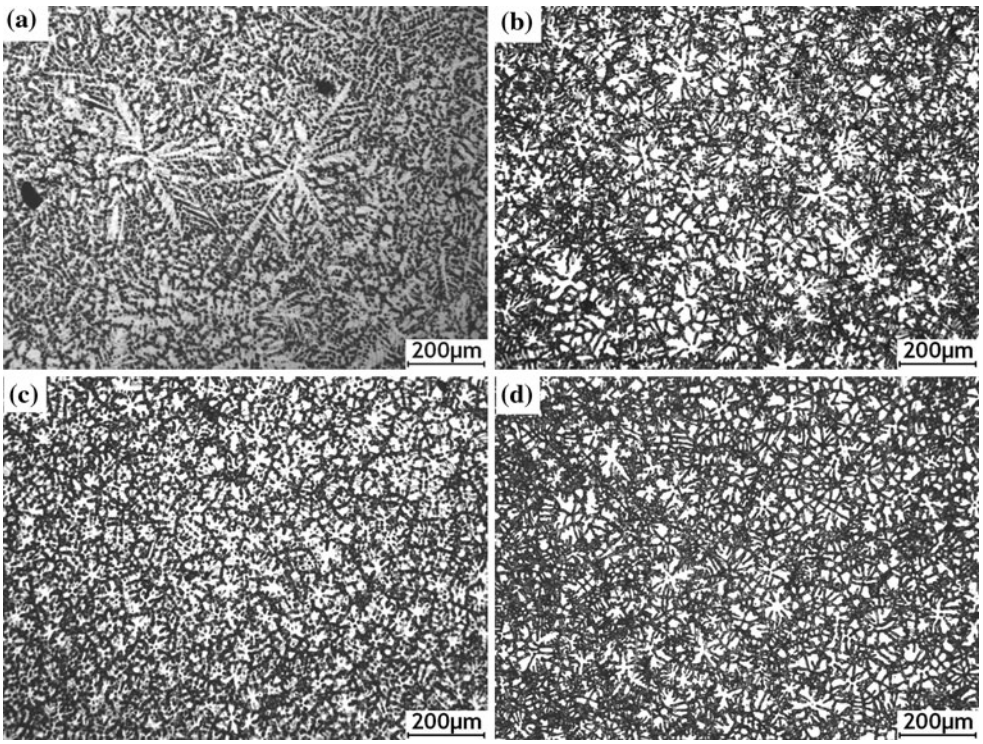


Fig. 1 Microstructures of the AM60B alloys refined by **a** 0 wt%, **b** 0.1 wt%, **c** 0.2 wt%, and **d** 0.3 wt% SiC particles

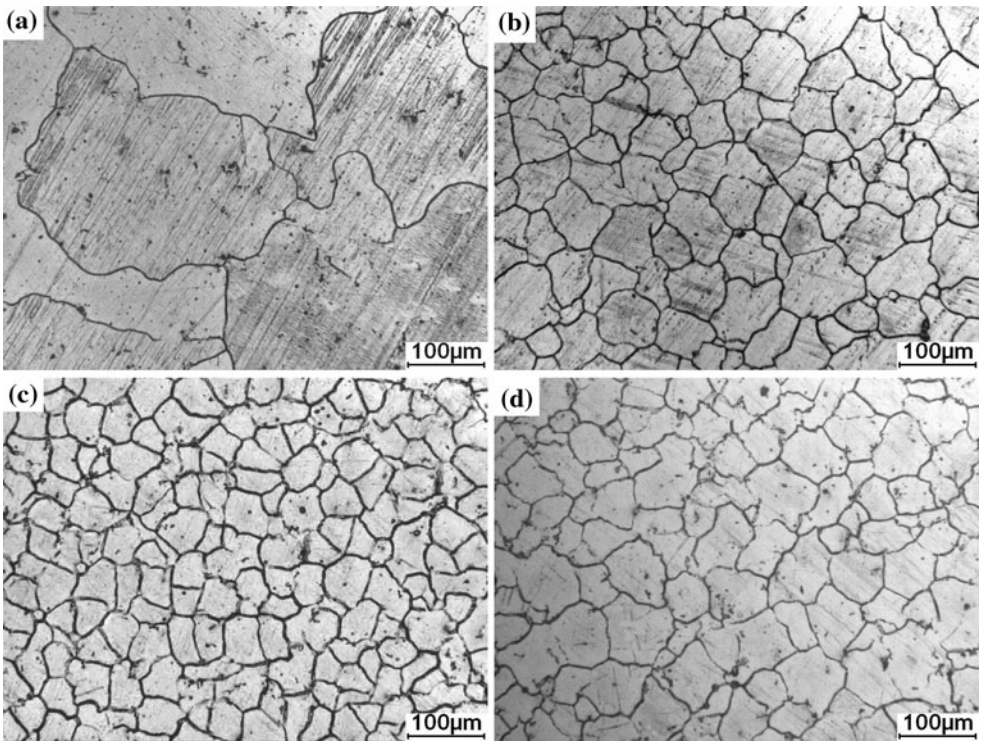


Fig. 2 Microstructures of the AM60B alloys refined by **a** 0 wt%, **b** 0.1 wt%, **c** 0.2 wt%, and **d** 0.3 wt% SiC particles and followed by solution treatment at 420 °C for 8 h

be suggested that these two phases with different morphologies, shown in Fig. 4c, d, belong to one phase and should be the Mg_2Si. Previous investigations about in situ Mg_2Si/Mg or Al matrix composites indicated that primary Mg_2Si phase sometimes was in polygonal particles and eutectic Mg_2Si was in Chinese script forms [29–32], which

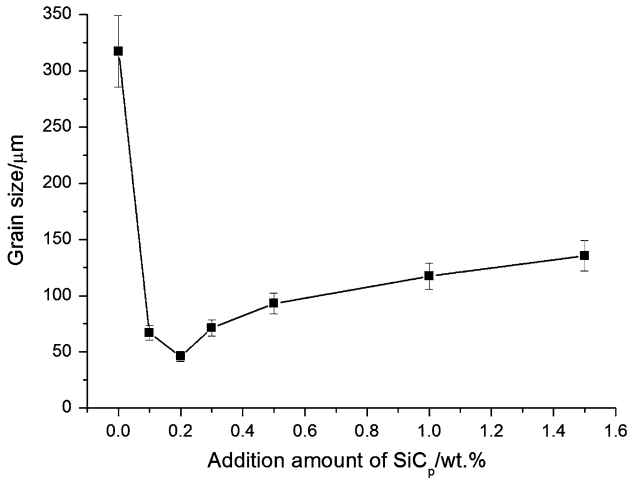


Fig. 3 Variation of grain size of the AM60B alloy with addition amount of SiC particles

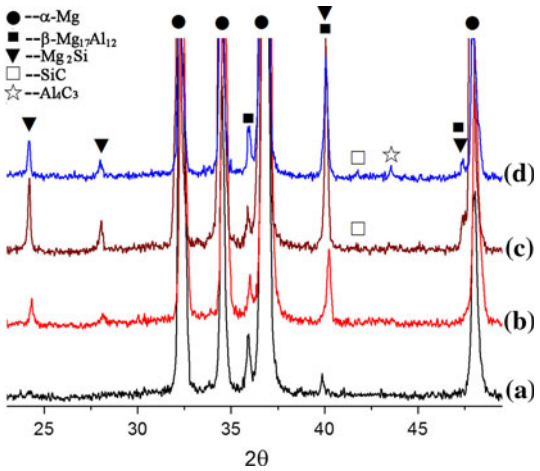


Fig. 5 X-ray diffractograms of the AM60 alloys refined by different amounts of SiC particles. **a** 0 wt%, **b** 0.2 wt%, **c** and **d** 5 wt%

just correspond to the two morphologies of the new phase in the present work. The result from EPMA indicates that the compositions of these two phases are also same and both of them contain two elements of Mg and Si (Fig. 6). This further demonstrates that the two phases belong to one phase, i.e., Mg_2Si. Figure 5 also shows only a little SiC phase is detected for the alloy refined by 5 wt% SiC particles, which implies that most of the added SiC particles have reacted with the melt. Based on the above discussion, it can be concluded that at least one of the reaction product is the Mg_2Si phase and the reactions operate by exhaustion of the β phase. In addition, the effective nucleation substrates are not the added SiC particles.

As indicated in the "Introduction" section, several possible nucleation substrates, such as Al_4C_3, Al_2CO, and SiC (refined by SiC), have been suggested for the carbon inoculation [19–22, 27]. Besides this hypothesis of heterogeneous nucleation mechanism, Jin et al. [28] consider that the introduced carbon element diffuses out from the primary α-Mg phase during solidification and then generate

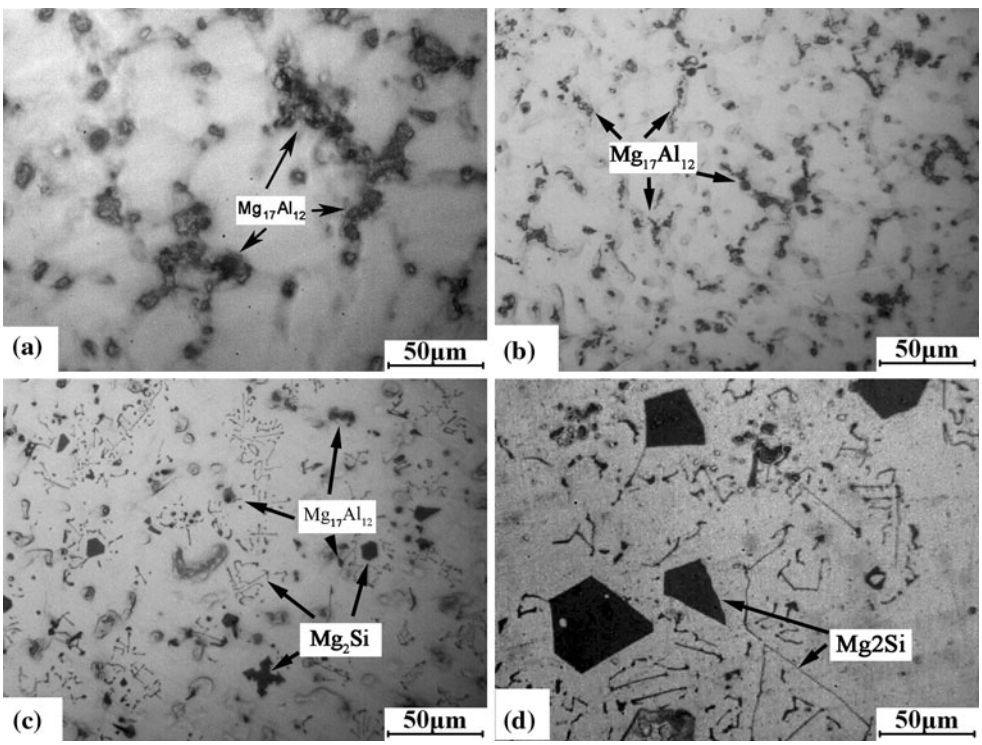


Fig. 4 Microstructures of the as-cast AM60B alloys refined by **a** 0 wt%, **b** 0.2 wt%, **c** 1.5 wt%, and **d** 5 wt% SiC particles

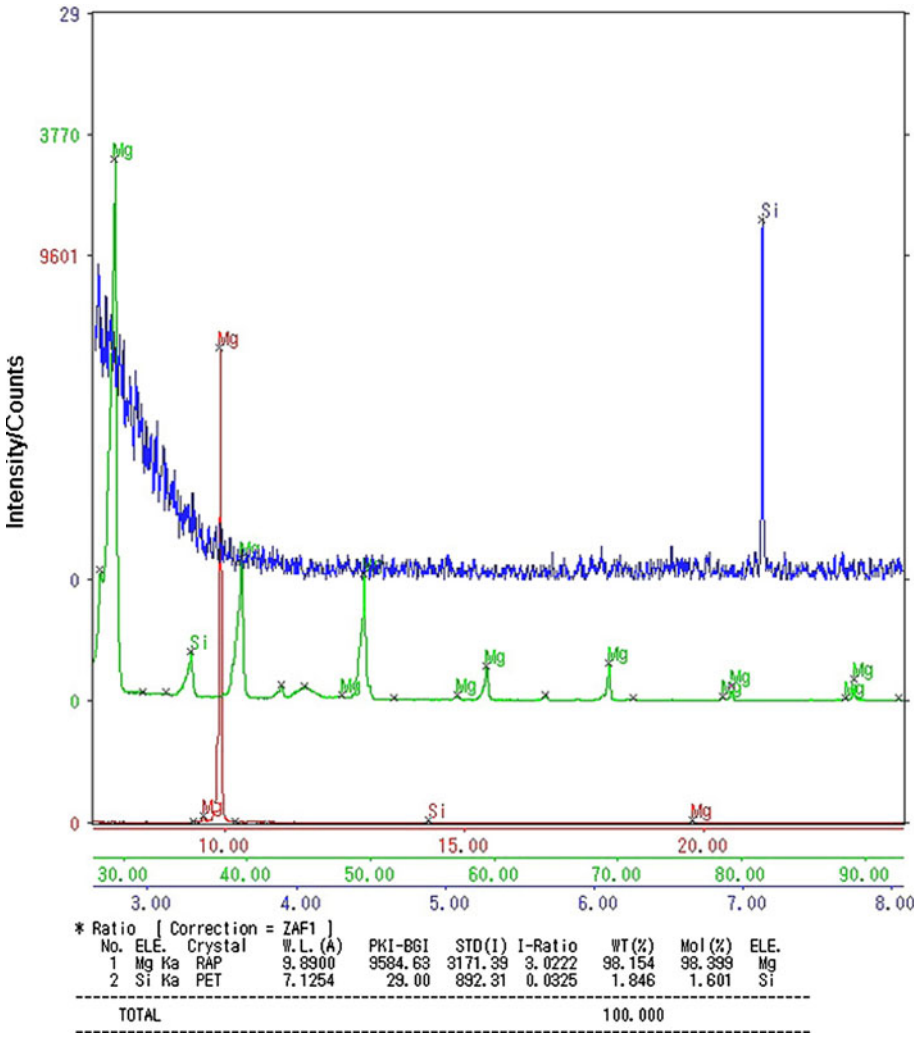


Fig. 6 Result from EPMA for the polygonal particle phase in the AM60B alloy refined by 5 wt% SiC particles

a constitutional undercooling region, which not only prevents the α-Mg from growth but also facilitates the formation of new stable nucleation particles. But the experimental result from Qian et al. [22] shows that only Mg–Al alloy can be refined when pure Mg, Mg–Zn, and Mg–Al contain the same amount of carbon (20 ppm) and disproves the standpoint from Jin et al. [28]. From the existing experimental and analysis results, it can be achieved that the heterogeneous nucleation mechanism using the Al_4C_3 particles as nucleation substrates has been commonly accepted [7, 19–22, 27]. But so far, there is no direct evidence to demonstrate it.

Considering from thermodynamic aspect, SiC can only react with Al in the molten Al bearing alloys, such as AZ91D, AZ31, and AM60B [22, 28]. This reaction can be expressed as follows: [20, 33]

$$3SiC + 4Al = Al_4C_3 + 3Si \quad (1)$$

The reduced Si element then reacts with Mg to form Mg_2Si phase through the reaction: [20]

$$2Si + Mg = Mg_2Si. \quad (2)$$

In fact, the reaction (1) is always found during preparation of SiC particle reinforced Al matrix composites by compocasting [34, 35]. Just due to this reaction, the added SiC particles dissolve into the Mg melts and they are difficult to be detected by XRD. Also due to this reaction, the Al element in the melt that is necessary to form β phase is exhausted, and thus the β phase amount in the resulting alloys is decreased. The formation of Mg_2Si phase in the alloys well demonstrates that the reaction (2) has also occurred. It can be expected that the more the added SiC particles, the less the β phase and the more the Mg_2Si phase, which are completely consistent with the present results.

It is found that there is always a small white particle in the center of each equiaxed dendrite as shown by A in Fig. 7a and it should be the nucleus of the dendrite. The EPMA result shows that the nucleus is rich in C and Al, but lacks Si (Fig. 7b–d). The EDS result indicates that it is

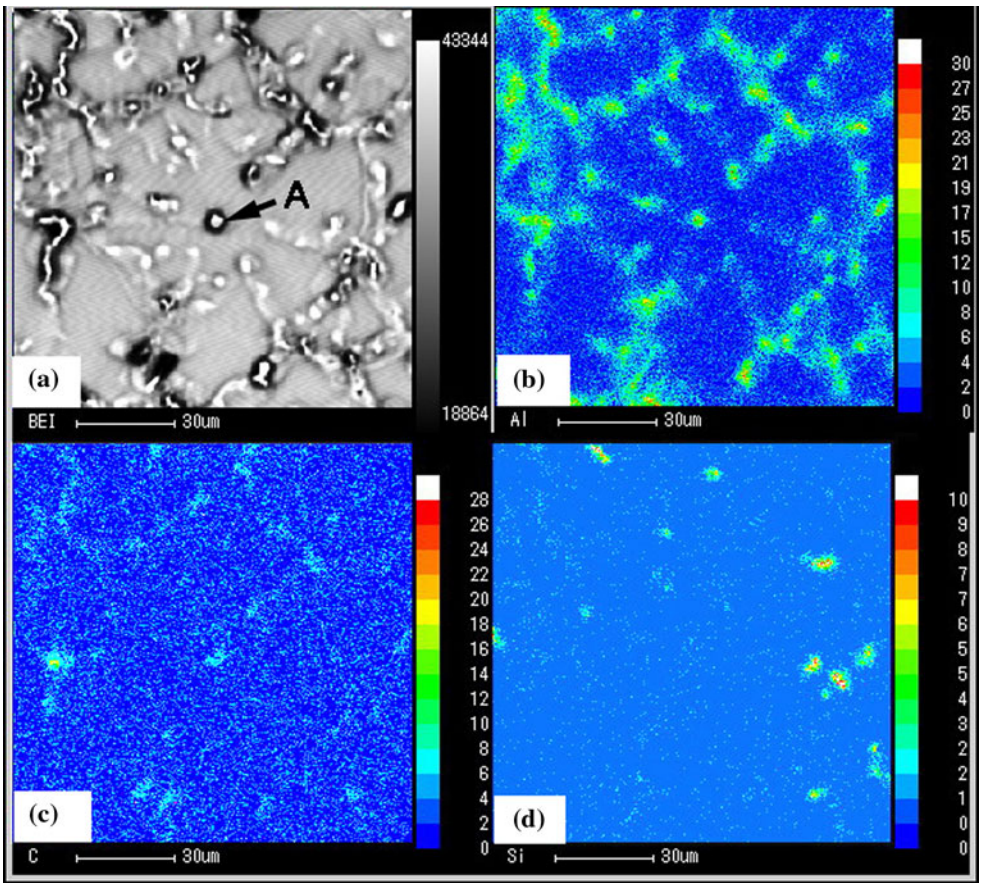
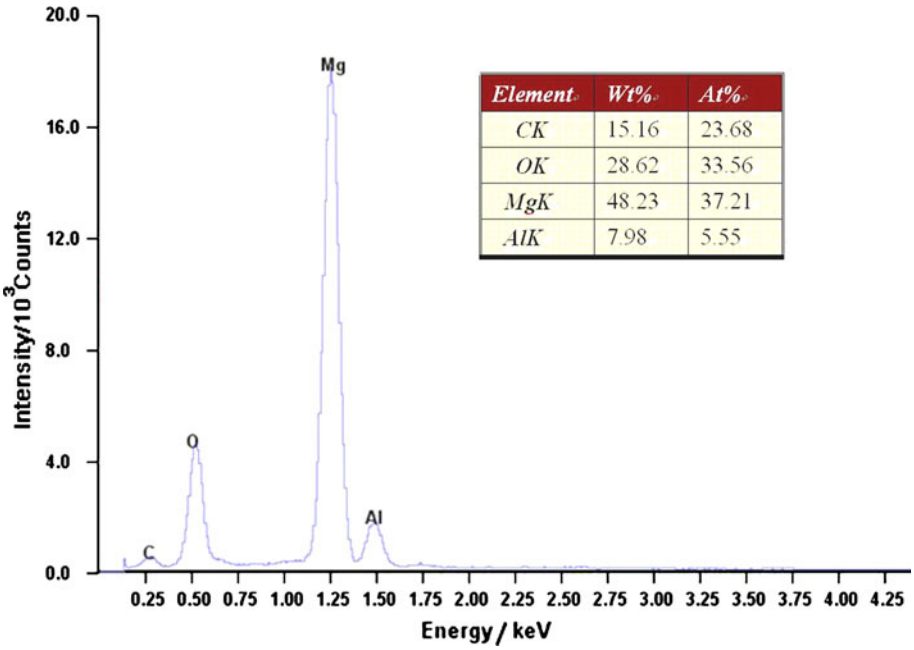


Fig. 7 **a** Back scattered electron image, and **b** Al, **c** C, and **d** Si maps of the AM60B alloy refined by 0.2% SiC particles

Fig. 8 EDS result of the white particle marked by *A* in Fig. 7a



composed of C, Al, O, and Mg (Fig. 8). The Mg peak is believed to be contributed by the Mg matrix. Therefore, it can be concluded that the particle A is consisted of C, Al, and O. But considering from thermodynamics, it is impossible to form Al–C–O compounds (such as Al_2OC particles that can also act as nucleation substrates for α-Mg

in view of crystal mismatch [22, 36]) due to low oxygen potential or small Al_2OC activity in the melt [21, 28]. It is known that Al_4C_3 is extremely reactive to water and it can react with water during polishing of the specimens through the reaction [7, 21],

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4 \quad (3)$$

which leads the Al_4C_3 to become into the Al–C–O compound. So the O element in the nucleus results from the reaction (3), its actual composition only includes two elements of Al and C. In order to avoid the reaction (3), a specimen cut from the alloy rod refined by 5 wt% SiC particles is not polished and only finished by metallographic abrasive paper prior to XRD analysis. The result is presented by Fig. 5d and it shows that Al_4C_3 phase has really formed. This not only implies that the reaction (3) can occur during preparation of the specimens but importantly demonstrates that the addition of SiC particles generates the Al_4C_3 phase through the reaction (1). So it can be concluded that the actual nucleation substrates are the Al_4C_3 particles.

Conclusions

(1) The addition of SiC particles in form of mixture with Mg powder can play a good grain-refining role for AM60B. Adding 0.2 wt% SiC particles can decrease the grain size from 317 to 46 μm.

(2) The addition of SiC particles decreases the amount of β phase and forms two new phases of Mg_2Si and Al_4C_3, which supply a credible proof for the occurrence of reactions of $3SiC + 4Al = Al_4C_3 + 3Si$ and $2Si + Mg = Mg_2Si$ during inoculation treatment by SiC particles. The nucleation substrates are composed of Al and C. All of these confirm that the actual nucleation substrates are the formed Al_4C_3 particles.

Acknowledgements This work was supported by the National Basic Research Program of China (grant No. G2007CB613706), the Development Program for Outstanding Young Teachers in Lanzhou University of Technology and the Opening Foundation of Key Laboratory of Gansu Advanced Non-ferrous Materials.

References

1. Eliezer D, Aghion E, Froes FH (1998) Adv Perform Mater 5:201
2. Wang YX, Zeng XQ, Ding WJ, Luo AA, Sachdev AL (2007) Metall Mater Trans A38:1358
3. Chen TJ, Lu GX, Ma Y, Li YD, Hao Y (2009) J Alloys Compd 486:124
4. Chen B, Lin DL, Zeng XQ, Lu C (2010) J Mater Sci 45:2510. doi:10.1007/s10853-010-4223-z
5. Shepelev D, Bamberger M, Katsman A (2009) J Mater Sci 44:5627. doi:10.1007/s10853-009-3793-0
6. Cao P, Qian M, StJohn DH (2007) Scripta Mater 56:633
7. Motegi T (2005) Mater Sci Eng A 413–414:408
8. Cao P, Qian M, St John DH (2006) Scripta Mater 54:1853
9. Dahle AK, Lee YC, Nave MD, Schaffer PL, St John DH (2001) J Light Met 1:61
10. Cao P, Qian M, St John DH (2004) Scripta Mater 51:125
11. Kim YM, Wang L, You BS (2009) J Alloys Compd. doi:10.1016/j.jallcom.2009.10.141
12. Liu S, Zhang Y, Han H (2009) J Alloys Compd. doi:10.1016/j.jallcom.2009.10.161
13. Wang SC, Chou CP (2008) J Mater Proc Technol 197:116
14. Wang Y, Zeng X, Ding W (2006) Scripta Mater 54:269
15. Yang M, Pan F, Cheng R, Tang A (2008) J Alloys Compd 461:298
16. Ma G, Han G, Liu X (2009) J Alloys Compd. doi:10.1016/j.jallcom.2009.10.221
17. Suresh M, Srinivasan A, Ravi KR, Pillai UTS, Pai BC (2009) Mater Sci Eng A525:207
18. Fu HM, Qiu D, Zhang MX, Wang H, Kelly PM, Taylor JA (2008) J Alloys Compd 456:390
19. Gunther R, Hartig C, Bormann R (2006) Acta Mater 54:5591
20. Easton MA, Schiffl A, Yao J-Y, Kaufmann H (2006) Scripta Mater 55:379
21. Lu L, Dahle AK, St John DH (2005) Scripta Mater 53:517
22. Qian M, Cao P (2005) Scripta Mater 52:7415
23. He YB, Pan QL, Qin YJ, Liu XY, Li WB (2010) J Mater Sci 45:1655. doi:10.1007/s10853-009-4143-y
24. Figueiredo RB, Langdon TG (2009) J Mater Sci 44:4758. doi:10.1007/s10853-009-3725-z
25. Hou LF, Wei YH, Liu BS, Xu BS (2008) J Mater Sci 43:4658. doi:10.1007/s10853-008-2668-0
26. Park J, Kim M, Yoon U, Kim WJ (2009) J Mater Sci 44:47. doi:10.1007/s10853-008-3130-z
27. Liu S, Chen Y, Han H (2009) J Alloys Compd. doi:10.1016/j.jallcom.2009.12.064
28. Jin QL, Eom J-P, Lim S-G, Park W-W, You B-S (2005) Scripta Mater 52:421
29. Pan Y, Liu X, Yang H (2005) Mater Charact 55:241
30. Jiang QC, Wang HY, Wang Y, Ma BX, Wang JG (2005) Mater Sci Eng A392:130
31. Hadian R, Emamy M, Campbell J (2009) Metall Mater Trans B. doi:10.1007/s11663-009-9251-1
32. Li C, Wu Y, Li H, Liu X (2009) J Alloys Compd 477:212
33. Liu YH, Liu XF, Bian XF (2004) Mater Lett 58:1282
34. Sritharan T, Chan LS, Tan LK, Hung NP (2001) Mater Charact 47:75
35. Lee J-C, Byun J-Y, Park S-B (1998) Acta Mater 46:1771
36. Zhang MX, Kelley PM, Qian M, Taylor JA (2005) Acta Mater 53:3261