Effect of Al-5Ti-1B on the microstructure of near-eutectic Al-13.0%Si alloys modified with Sr

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The addition of Sr in Al-Si alloys as a modifier causes a transition of the morphology of eutectic silicon from coarse plate-like or acicular to fine fibrous. However, it may also lead to the formation of long columnar dendritic α-Al phase. Al-5Ti-1B master alloy is often used as a grain refiner to achieve the fine equiaxed grains in aluminum and aluminum alloys. The aim of the present study is to highlight the effect of Al-5Ti-1B master alloy additions on the microstructure of near-eutectic Al-Si alloys modified with Sr. When the addition of Al-5Ti-1B master alloy was below 0.82 mass%, the dendritic α-Al phase changed from long columnar to equiaxed, and there were no noticeable changes of the morphology and size of eutectic silicon, while the size of eutectic cells decreased slightly. However, when the addition was above 0.82 mass%, the deleterious influence of Al-5Ti-1B master alloy on the modification effect of Sr emerged and with further increases in addition level a fully unmodified microstructure was finally produced. The results indicate that the effective Sr in the melt decreases with increased addition of Al-5Ti-1B. The poisoning event of Al-5Ti-1B master alloy on the modification of Sr is supposed to be related with the interaction between Sr and Ti. © *2002 Kluwer Academic Publishers*

1. Introduction

Near-eutectic Al-Si alloys exhibit excellent castability, good mechanical properties, good corrosion resistance and weldability, and low thermal expansion [1]. The commercial importance of these alloys has attracted many researchers. The eutectic silicon in unmodified Al-Si alloys is present as coarse flakes and consequently, has a detrimental effect on the ductility. With small additions of sodium or strontium, the eutectic silicon undergoes a morphological transition from coarse flakes to fine fibers. Two explanations have been put forward for the mechanism of modification, and these have been the subject of many investigations. The first is based on a restriction of the nucleation of the eutectic Si by the modifying elements [2–5], whereas in the second it is believed that a restriction of crystal growth takes place [2, 6–13].

The modification behavior in the Al-Si system was firstly reported by Pacz [6, 14] in 1921, following an accidental introduction of sodium fluoride to a flux. Since then, a number of researchers have studied the effect of numerous elements on the modification process [1, 6, 11, 15–21], of which, however, only sodium and strontium exhibit a strong effect at low concentrations, which make them suitable for commercial applications. The recovery rate of strontium in the melt is usually

of the order of 90% [15, 22]. It has been established that the rate of oxidation and the loss of strontium from the melt is much slower than that of sodium, and apparently strontium does not lead to over-modification [1, 19, 22–24]. In recent years, the use of strontium as a modifier, instead of sodium, has become widely accepted, although strontium has been reported to have an "incubation time" problem [1, 19, 24–26].

Al-5Ti-1B master alloy, an effective grain refiner for commercial pure aluminum and wrought aluminum alloys, is often used in Al-Si cast alloys to achieve fine equiaxed grains. TiB_2 or/and $TiAl_3$ particles from Al-5Ti-1B master alloy are thought to be capable of acting as the nuclei of primary α-Al [27]. However, in the high silicon level Al-Si alloys (Si content more than 7 mass%), the grain refining power of Al-5Ti-1B master alloy was less than that of Al-3B and Al-3Ti-3B master alloys [27–30]. It was thought that Si poisoned the nuclei due to the formation of titanium silicide over the $TiAl_3$ particles [28], and Kori *et al.* [31] pointed out that this poisoning effect could be neutralized by increasing the addition level of Al-5Ti-1B master alloy.

Sr addition to near-eutectic Al-Si alloys could promote the growth of columnar dendrite and also result in a considerable increase of the amount of dendritic α phase [32] (i.e. the area percent of the dendritic α-Al

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TABLE I The composition of Al-13.0%Si alloy

Elements	Si	Mg	Cu	Fe	Mn	Zn	Ti	Ca	Al
Content, mass%	13.02	0.05	0.03	0.15	≤0.10	≤0.08	≤0.10	≤0.10	balance

phase in the total field of view). In order to obtain good mechanical properties, both dendrite refinement and eutectic modification are necessary. However, these two effects have received little attention and interactions between the modifier (Sr) and the refiner (Al-5Ti-1B) have not been reported in details. Thus the aim of this paper is to investigate the effect of Al-5Ti-1B addition on the microstructure of Al-13.0%Si alloys modified with Sr.

2. Experimental procedure

Al-13.0%Si alloy, the composition of which is shown in Table I, was melted in an electrical resistance furnace using a graphite crucible. The details of the additions of Sr, in the forms of Al-4Sr (Al-4.16mass%Sr), and Al-5Ti-1B master alloy (Al-4.92mass%Ti-0.96mass%B) are given in Table II. The Al-4Sr master alloy was added to the melt at ∼730°C. After holding for 20 minutes, hexachlorethane (C_2Cl_6) flux was introduced for degassing, then, the Al-5Ti-1B master alloy was added to the melt. After 5 minutes holding at ∼720°C, the melt was poured into a metallic mold (grey iron, preheated to 250°C) with a wall thickness of 5 mm. Cylindrical castings of 20 mm diameter and 60 mm height were produced. Metallographic samples were prepared from the vertical center of the castings. The recovery of Sr in the melt is low, due to the degassing with hexachloroethane (C_2Cl_6) flux, was about 50% as found by ICP-Spectrometer. The Sr content reported in the present paper is equal to the addition level of Sr multiplied by the recovery. The degassing had no significant influence on the recovery of Ti in the melt.

Metallographic samples were etched in an aqueous solution of potassium hexacyanoferrate ($K_3Fe(CN)_6$). An optical microscope (OLYMPUS BX-60M) and a scanning electron microscope (SEM) (JEOL-JSM 6300), fitted with an Energy Dispersive X-ray Analyser, were used. An improved aqueous solution of $K_3Fe(CN)_6$ was prepared for observing the eutectic cells. The linear intercept method was adopted to measure the size of the eutectic cells. In order to achieve representative results, every cell size given is the arithmetic mean from 100 arbitrary cell counts.

TABLE II The details of compositions used in the present study

| Heat No.	Sr content in melts, mass%	Al-5Ti-1B master alloy addition level, mass%
1	–	–
2	0.03	–
3	0.03	0.37
4	0.03	0.62
5	0.03	0.82
6	0.03	0.92
7	0.03	1.02
8	0.03	1.20
9	0.03	1.52

3. Results and discussion

Dendritic α-A1, primary silicon and α-Al + Si eutectic commonly co-existed in ummodified near-eutectic Al-Si alloys. In the microstructure of Al-13.0wt%Si alloys modified with 0.03mass% Sr content, the primary Si disappears and the eutectic silicon is present as uniformly distributed fine fibers. The addition of strontium also causes the formation of columnar dendritic α-Al, as seen in Fig. 1.

3.1. Effect of Al-5Ti-1B addition on the microstructure
3.1.1. Dendritic α-Al phase

By comparison with Fig. 1b, Fig. 2a shows that the trunk of the dendrites shortens with an increase in addition level of A1-5Ti-1B master alloy, but the refinement effect of A1-5Ti-1B is not as remarkable as expected. When the addition level increases above 0.82 mass%, the amount of dendritic α-A1 phase decreases (shown in Fig. 2b). It has been found that the amount of the dendritic α-A1 phase increases with the addition of Sr in near-eutectic A1-11.6%Si and A1-11.6%Si-0.4%Mg alloys [33]. These previous investigations indicate that addition of Sr to A1-Si cast alloys will increase the difference in the eutectic temperature between the modified and unmodified
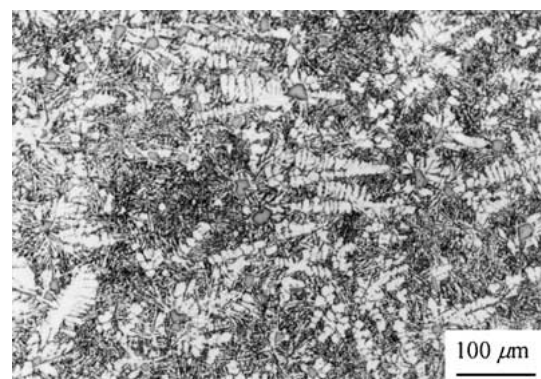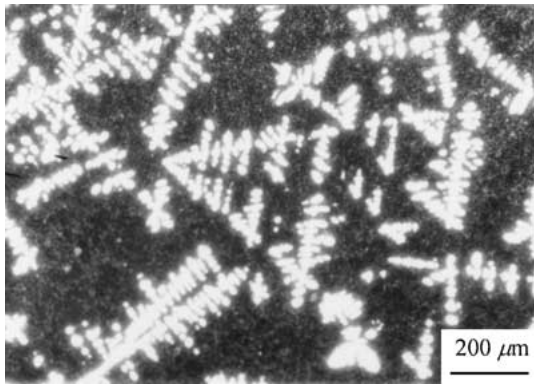

(a)
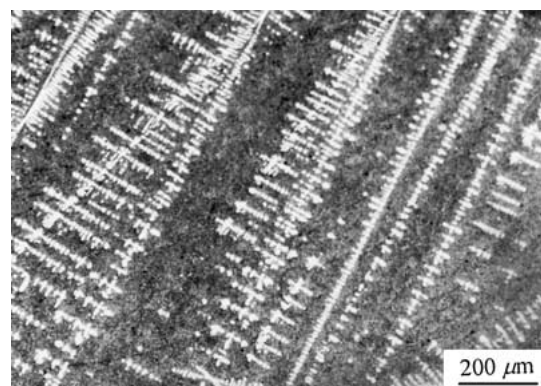
(b)

Figure 1 Change of dendritic α-Al in Al-13.0%Si alloy (a) without and (b) with 0.03 mass% Sr modification.

(a)

(b)

Figure 2 Morphology of α-Al dendrites in Al-13.0%Si alloy modified by 0.03 mass%Sr (a) with 0.82% Al-5Ti-1B addition (b) with 1.02% Al-5Ti-1B addition.

Figure 3 Fine particles phase containing Ti, Si and Al in Al-13.0%Si-0.03% Sr alloy with 1.52 mass% addition level of Al-5Ti-1B master alloy.

alloys, ΔT_E ($\Delta T_E = T_{EU} - T_{EM}$, where the subscripts E, U, and M denote eutectic, unmodified and modified respectively) [16, 20] and lead to a shift of the eutectic point toward a higher silicon level [6, 24]. So the solidification temperature interval increases and hence the amount of dendritic α-A1 rises. The decrease in the amount of dendritic α-A1 with increased additions of A1-5Ti-1B master alloy indicates that the effective Sr content in the melt decreases. Although A1-5Ti-1B master alloy is a strong grain refiner in pure aluminum and wrought aluminum alloys, it seems now to have only slight influence on promoting the Columnar-Equiaxed Transition (CET) in near-eutectic A1-Si alloy modified with Sr. Sigworth and Guzowski [28] proposed that a titanium silicide formed over the surface of the TiAl$_3$ particles in the melt and consequently poisoned the nuclei of the equiaxed dendrites, and this ideal was supported by Kori [31]. The presence of this compound haven't been confirmed. Mohanty and Gruzleski [27, 34] pointed out that Si might be dissolved in the TiAl$_3$, forming $(Ti_{1-x},Si_x)Al_3$ and high levels of Si (more than 7%) resulted in a shift of the peritectic reaction temperature (liquid + $(Ti_{1-x},Si_x)Al_3 \rightarrow \alpha$-Al) to a temperature so low that the Al-5Ti-1B master alloy had no power to refine the dendritic α-Al. In the present study, very fine particles, containing Ti, Si, Al and Sr, were found, as seen in Fig. 3. The energy-dispersive X-ray analysis of these particles is shown in Fig. 4 and provides support for the suggestion by Mohanty and Gruzleski. Kori *et al.* [31] deemed that increasing the addition of Al-5Ti-1B master alloy could neutralize the poisoning
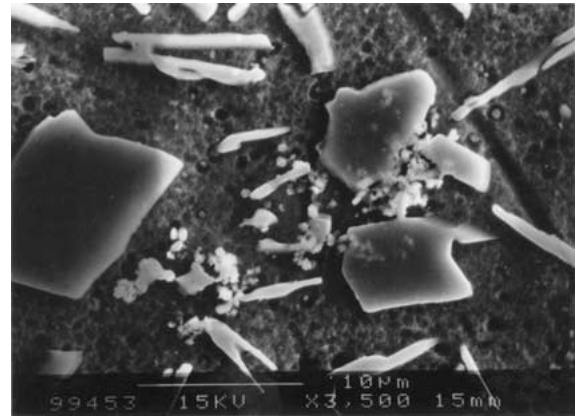
effect of silicon and recover the effectiveness as a strong refiner of dendritic α-Al. In the present study, however, when the addition of Al-5Ti-1B master alloy was 1.52 mass%, a fully unmodified microstructure was present, as shown in Fig. 5. From the above results, it is suggested that the Al-5Ti-1B master alloy cannot meet the requirement of refining the dendritic α-Al phase in Sr modified Al-13.0%Si alloy.

3.1.2. Silicon phase
Up to a 0.82 mass% Al-5Ti-1B addition level, there are no considerable changes of the size and morphology of the eutectic silicon. The eutectic silicon is in the form of fine fibers uniformly, as shown in Fig. 6a. When the addition of Al-5Ti-1B increases to 0.92 mass%, however, primary silicon phase appeared again. When the addition of Al-5Ti-1B master alloy is 1.2 mass%, a portion of eutectic silicon is present as flakes and there are a few primary silicon particles in the microstructure, as shown in Fig. 6b. 1.52 mass% addition produces a fully unmodified microstructure, as seen in Fig. 5. The change in the form of the eutectic silicon from fine fibers to coarse flakes demonstrates that the modification effect of strontium on eutectic silicon is poisoned by the addition of the Al-5Ti-1B master alloy. It is also indicates that the effective Sr content in the melts decreases with increased addition levels of Al-5Ti-1B master alloy.

3.1.3. Eutectic cells
The coupled growth of the α-Al + Si eutectic in the Al-Si eutectic system results in the formation of eutectic cells. In the unmodified case, the solid-liquid growth front of the eutectic seems to be non-isothermal with silicon flakes projecting ahead of the α-Al phase in a nearly random array [6, 35], so that it is difficult to observe the eutectic cells. In the case of alloys modified by Na or Sr, the eutectic silicon phase no longer protrudes and the coupled growth front is nearly isothermal and planar [1, 36], and hence the impurity elements may concentrate at the eutectic cell boundaries during solidification. As a result, the eutectic cells in Al-Si alloys may be seen clearly after etching in appropriate solutions. Investigations of eutectic cells in Al-Si alloy are scarce. Fig. 7 shows clearly the eutectic cells in Al-13.0%Si alloy. The variation in the value of the eutectic cell size with Al-5Ti-1B addition is given in
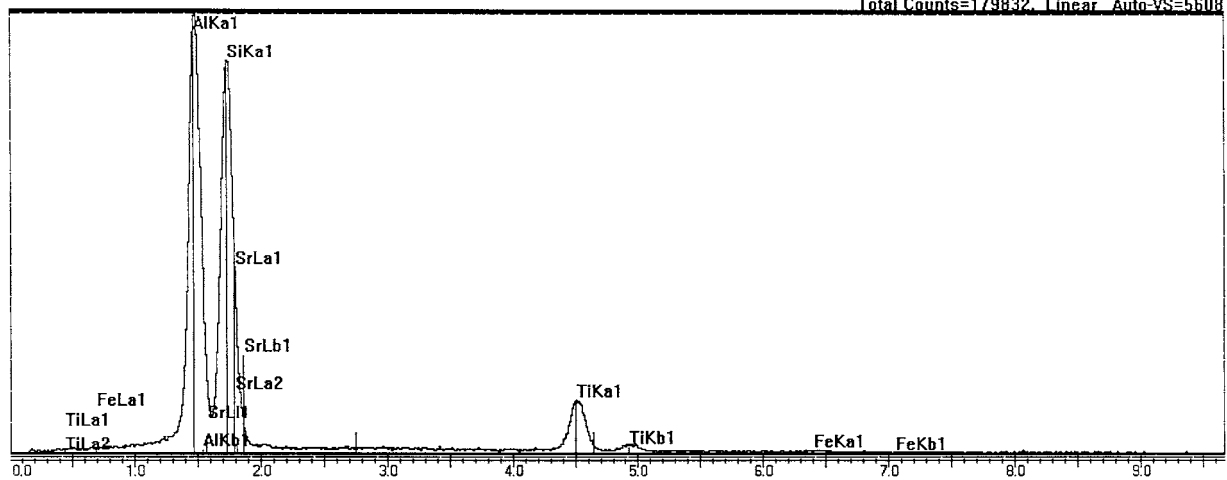
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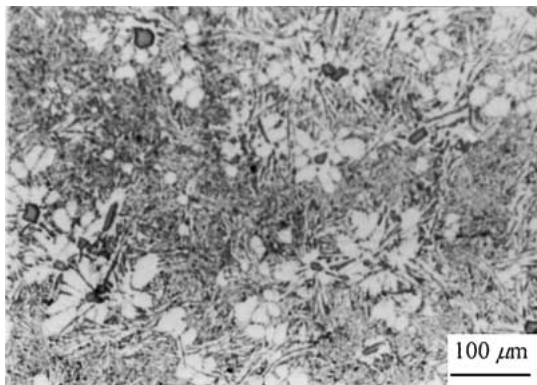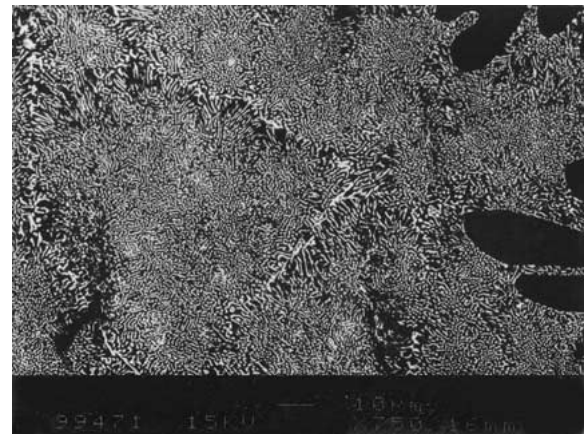*Figure 4* Energy-dispersive X-ray analysis of the fine particles shown in Fig. 3.

Figure 5 Microstructure in Al-13.0%Si alloy (modified by 0.03 mass% Sr) with 1.52 mass% addition of Al-5Ti-1B master alloy.

Fig. 8. For additions up to 0.82 mass%, the size of the eutectic cells remains virtually unchanged. At higher levels of addition, the eutectic cell size increases considerably. Fig. 7 also indicates that the eutectic cell size with 1.02 mass% addition of the Al-5Ti-1B mater alloy is larger than that with a 0.82 mass% addition. When the addition level reaches 1.2 mass%, it is difficult to evaluate the size of eutectic cells accurately due to the reappearance of the silicon flakes. This result implies that the effective Sr content in the melt may play a role in determining the eutectic cell size. This will be further studied.

The changes in the dendritic α-Al phase, silicon phase and eutectic cells with the addition of Al-5Ti1B show similar trends, with 0.82 mass% addition level being associated with significant changes. The microstructural observations indicate that the effective Sr content in the melts decreases with addition of the Al-5Ti-1B master alloy. When the addition is below 0.82 mass%, the residual effective Sr in the melt is enough to produce a fully modified microstructure. With further increases in the level of addition, there is less effective Sr, and consequently the amount of dendritic α-Al reduces, the primary Si particles reappear and the eutectic silicon forms coarse flakes. When the addition is 1.52 mass%, the microstructure becomes fully unmodified again. So, it can be concluded that the addition of Al-5Ti-1B master alloy to the near-eutectic Al-Si alloys modified with Sr has no noticeable bene-

(a)
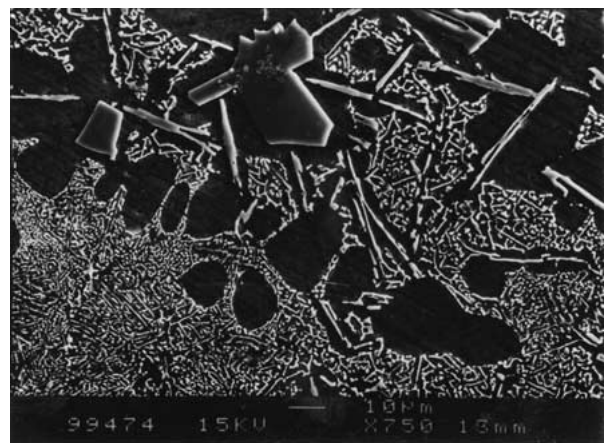
(b)

Figure 6 Eutectic structure in Al-13.0%Si alloy (modified by 0.03 mass% Sr) with (a) 0.82 mass% and (b) 1.20 mass% addition levels of Al-5Ti-1B master alloy.

fit in terms of the refinement of thedendritic α-Al and eutectic cells, and, when the addition is above a criticallevel (0.82 mass% in the present case) it impairs severely the modifying effect of Sr on eutectic silicon.

3.2. Poisoning effect of Al-5Ti-1B on Sr modification

The poisoning effect of the Al-5Ti-1B master alloy on the strontium modification is believed to be related to

(a)
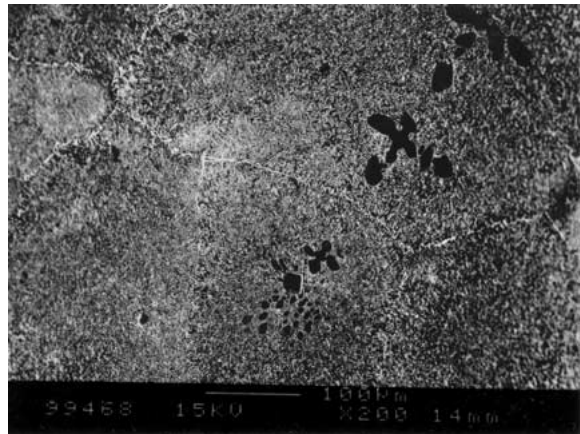
(b)

Figure 7 Eutectic cells in Al-13.0%Si alloys with (a) 0.82 mass% and (b) 1.02 mass% addition levels of Al-5Ti-1B master alloy, modified by 0.03mass%Sr.

(a)

(b)

Figure 9 Acicular phase in the eutectic cell boundaries in Al-13.0%Si alloy modified by 0.03 mass%Sr (a) with 0.62 mass% and (b) with 1.02 mass% addition levels of Al-5Ti-1B master alloy.
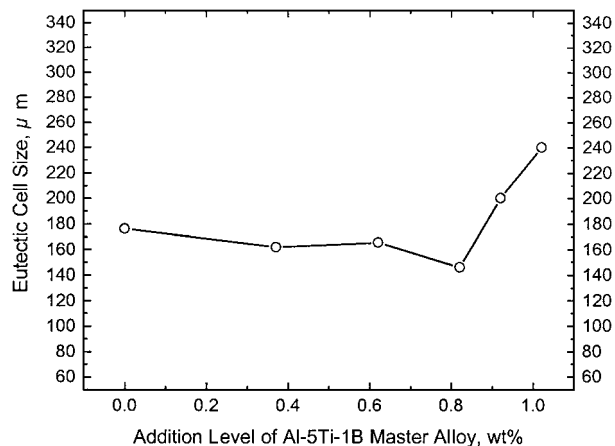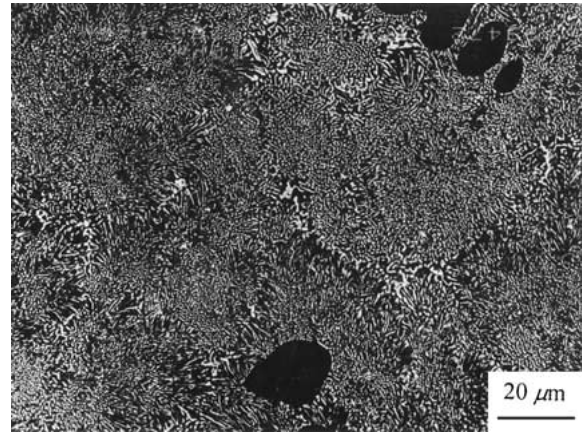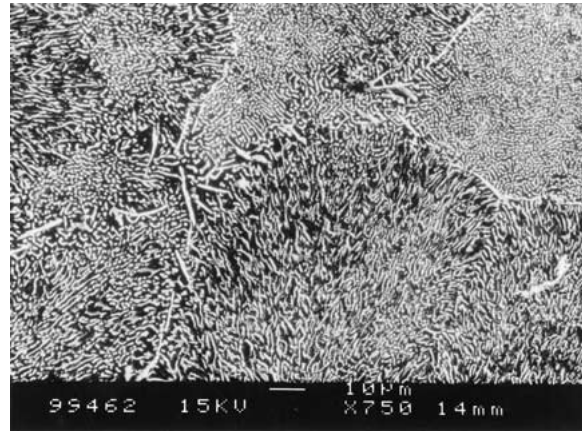

Figure 8 Variation of the eutectic cell size with Al-5Ti-1B addition levels in Al-13.0%Si alloy modified by 0.03 mass%Sr.

the reduction of the effective Sr content in the melts, which in turn changes the amount of dendritic α-Al phase and the morphology of silicon phase. This is further supported by observations of the amount and size of the accicular phases at the eutectic cell boundaries, as shown in Fig. 9. When the addition of Al-5Ti-1B is 0.62 mass%, a very fine needle-like phase is present at the boundaries of eutectic cells, as seen in Fig. 9a, which increases in size and amount as higher addition,

as shown in Fig. 9b. The energy-dispersive X-ray analysis of this acicular phase (shown in Fig. 10) indicates that it contains Al, Si, Fe and Sr. The increase in the quantity of the Fe phase containing Sr leads to a reduction in the effective Sr content in the melts. This is consistant with the observation of Shabestari and Gruzleski [37] that Sr in Al-Si alloys could result in a transition in a Fe-bearing phase from needle-like β-Al_5FeSi to Chinese script α-$Al_{15}Fe_3Si_2$ accompanied by a considerable decrease in the size and amount of Fe-bearing phase.

It is assumed that the reduction in the effective Sr results from an interaction between the modifier and the dendrite refiner. TiB_2 particles from the master alloy are thought to be stable in an Al-Si melt [28, 30, 34, 38, 39], so an interaction between B and Sr is unlikely and no interaction between Ti_2B and Sr has been reported. So it is assumed that an interaction between strontium and titanium occurs, although a reaction has not been observed in this or other works. The change in the morphology of eutectic silicon, however, may provide indirect evidence for a reaction. The formation of coarseflakes of eutectic silicon in unmodified alloys was thought to be related to the phosphorus present in melts as AlP particles, acting as potential to act as the nucleation sites for the silicon phase [2, 40, 41]. In the case of very low phosphorus, the eutectic silicon
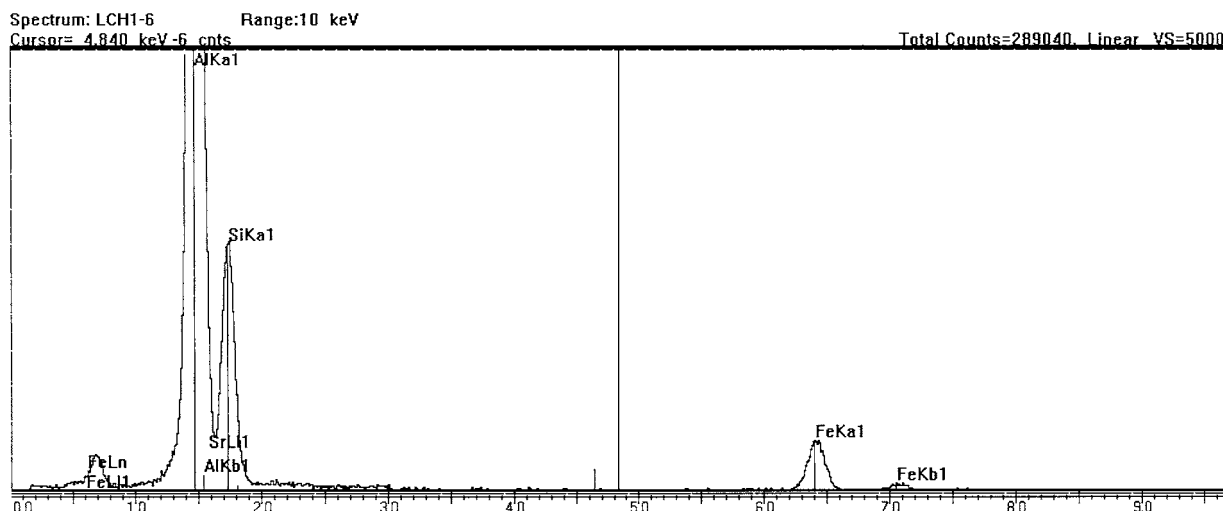
Figure 10 Energy-dispersive X-ray analysis of theacicular phase in Fig. 9b.

is present as fine lamellae or fibers, without or with Sr modification, respectively, as reported by Heusler and Schneider [2]. In the present study, before Al-5Ti-1B master alloy is introduced, there is enough time for strontium to remove the nucleation sites of the silicon crystals (AlP particles). If the result of the interaction between Ti and Sr was not capable of providing nucleation sites for the silicon phase, the eutectic silicon would be present as fine lamellae even with very low recovery of Sr in the melt, instead of the coarse acicular phase observed. One explanation may be that interaction between Ti and Sr may have occurred and that the reaction product has the potential to act as the nuclei for eutectic Si crystals. Consequently, the strontium is consumed and the residual effective Sr in the melt is decreased.

4. Conclusions
The following conclusions can be made.

(a) The addition of Al-5Ti-1B master alloy in near-eutectic Al-Si alloys modified with Sr has no noticeable positive influence on the refinement of the dendritic α-Al phase. The observation of a compound containing Al, Ti and Si provides supporting evidence for the hypothesis of Mohanty and Gruzleski.

(b) There are no considerable changes in the morphology and size of eutectic silicon and the size of eutectic cells when the addition of Al-5Ti-1B is less than 0.82 mass%. When the addition is more than 0.82 mass%, the deleterious influence of Al-5Ti-1B master alloy on the modification effect of Sr emerges and with further increase in addition a fully unmodified microstructure is produced.

(c) The addition of the Al-5Ti-1B master alloy poisons the modifying effect of strontium on eutectic silicon. It is supposed that the interaction between strontium and titanium consumes strontium and hence results in the reduction of the effective Sr in the melt.

References
1. M. RAVI, U. T. S. PILLAI, B. C. PAI *et al.*, *Metall. Mater. Trans.* **27A**(5) (1996) 1283.
2. L. HEUSLER and W. SCHNEIDER, *AFS Trans.* **105** (1997) 915.
3. C. R. HO and B. CANTOR, *J. Mater. Sci.* **30** (1995) 1912.
4. D. L. ZHANG and B. CANTOR, *Metall. Trans.* **24A**(5) (1993) 1195.
5. S. C. FLOOD and J. D. HUNT, *Metal Science* **15** (1981) 287.
6. SHU-ZU LU and A. HELLAWELL, *JOM* **47** (1995) 38.
7. J. M. DOWLING, J. M. CORBETT and H. W. KERR, *J. Mater. Sci.* **22** (1987) 4504.
8. SHU-ZU LU and A. HELLAWELL, *J. Crystal Growth* **73** (1985) 316.
9. M. SHAMSUZZOHA and L. M. HOGEN, *ibid.* **73** (1985) 735.
10. SHU-ZU LU and A. HELLAWELL, *Light Metals* TMS Annual Meeting (Warrendale, Pennsylvania) (1995) 989.
11. *Idem., Metall. Trans.* **18A** (1987) 1721.
12. M. SHAMSUZZOHA, L. M. HOGEN and J. T. BERRY, *AFS Trans.* **101** (1993) 999.
13. M. SHAMSUZZOHA and L. M. HOGEN, *Philisophical Magazine* A **54**(4) (1986) 459.
14. A. PACZ, U. S. Patent No. 1,387,900, 13 Feb., 1920; British Patent No. 158,827, 26 Jan., 1921.
15. M. O. PEKGULERYUZ and J. E. GRUZLESKI, *AFS Trans.* **96** (1988) 55.
16. H. BEUMLER, B. WIETING and R. DASGUPTA, *ibid.* **96** (1988) 1.
17. B. CLOSSET and S. KITAOKA, *ibid.* **95** (1987) 233.
18. N. HANDIAK, J. E. GRUZLESKI and D. ARGO, *ibid.* **95** (1987) 31.
19. G. CHAI and L. BACKRUD, *ibid.* **100** (1992) 847.
20. T. J. HURLEY and R. G. ATKINSON, *ibid.* **93** (1985) 291.
21. B. KULUNK and D. J. ZULIANJ, *JOM* **10** (1996) 60.
22. BIAN XIUFANG, LIU XIANGFA, WANG XIANE *et al.*, *Acta Metall Sinica* **33**(6) (1997) 609.
23. M. M. HAQUE, *J. Mater. Processing Tech.* **55** (1995) 193.
24. G. K. SIGWORTH, *AFS Trans.* **91** (1983) 7.
25. B. CLOSSET and J. E. GRUZLESKI, *ibid.* **89** (1981) 801.
26. *Idem., Metall. Trans.* **13A** (1982) 945.
27. LIAO HENGCHENG, FANG XINXIAN and SUN GUOXIONG, *Special Casting and Nonferrous Alloy* **20**(3) (1999) 49.
28. G. K. SIGWORTH and M. M. GUZOWSKI, *AFS Trans.* **93** (1985) 907.
29. H. T. LU, L. C. WANG and S. K. KUNG, *Journal of Chinese Foundryman's Association* **29** (1981) 10.
30. T. SRITHARAN and H. LI, *J. Mater. Sci. Tech.* **63**(1–3) (1997) 585.
31. S. A. KORI, B. S. MURTY and M. CHAKRABORTY, *Indian Foundry Journal* **45**(1) (1999) 7.
32. H. C. LIAO, Ph.D. thesis, Southeast University, Aug. 2000
33. HENGCHENG LIAO, YI DING and GUOXIONG SUN, *Acta Metallurgica Sinica* **38**(3) (2002) 245.
34. P. S. MOHANTY and J. E. GRUZLESKI, *Acta Mater.* **44**(9) (1996) 3749.

35. S U N W E I C H E N G , Z H A N G S H O U R O N G and H O U A I Q I N G , in "Behaviors of RE Elements in Aluminum Alloys" (Weapon Industry Press, Beijing, 1993) p. 165.
36. L . M . H O G A N and H . S O N G , *Acta Metall.* **35**(3) (1987) 677.
37. S . G . S H A B E S T A R I and J . E . G R U Z L E S K I , *AFS Trans.* **103** (1995) 285.
38. D . G . M c C A R T N E Y , *Intl. Mater. Reviews* **34**(5) (1989) 247.
39. D . A P E L I A N and J . A . C H E N G , *AFS Trans.* **94** (1986) 797.
40. J . Y . C H A N G , G . H . K I M , I . G . M O O N *et al.*, *Scripta Materialia* **39**(3) (1998) 307.
41. G . W . B O O N E , R . F . C A R V E R and R . G . S E E S E , *Modern Casting* **38** (1998) 52.