Materials Transactions, Vol. 44, No. 12 (2003) pp. 2611 to 2616

Influence of Sr and Mn Additions on Intermetallic Compound Morphologies in Al-Si-Cu-Fe Cast Alloys*

Peyman Ashtari[1], Hiroyasu Tezuka[2] and Tatsuo Sato[2]

[1]*Graduate student, Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Tokyo 152-8552, Japan*
[2]*Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Tokyo 152-8552, Japan*

The influence of Sr or Sr and Mn combined additions on the Fe-containing intermetallic compounds in Al-Si-Cu-Fe cast alloys has been investigated using Al-6.5%Si-3.5%Cu-1.0%Fe and Al-6.5%Si-3.5%Cu-1.0%Fe-0.3%Mn alloys (in mass%) with a similar composition to the 319 aluminum alloy. The results show that Sr successfully modifies the large, highly branched β-needle-like phase (β: Al_5FeSi) into the individual, less-branched and finer one. The combined addition of Mn and Sr results in modification of the needle-like β-phase as well as promotion of Chinese script and sludge morphology formation. The mechanism of the above morphological changes has been discussed in accordance with the mechanism of nucleation and growth of the β-needle-like phase during solidification.

(Received May 8, 2003; Accepted October 7, 2003)

Keywords: *aluminum-silicon alloys, strontium addition, intermetallic compounds, modification*

1. Introduction

Al-Si based cast alloys usually contain impurities or trace elements such as Fe, Mn, Cr that form preferentially high melting point and hard intermetallics with various morphologies. The needle-like iron containing phase (β-Al_5FeSi) is the most harmful one for the mechanical properties of Al-Si based cast alloys. This phase, like most other intermetallic particles, is brittle. Its morphology is plate-like, appearing as needles in the optical micrographs. These characteristics, brittleness and plate-like morphology, greatly affect to decrease the strength and ductility of the cast alloys. It is, therefore, important to avoid or at least to control the formation of this phase. Mn is widely used as an alloying addition to neutralize the effect of iron and modify the needle-like β-phase to less harmful morphologies. However, Mn is not always the best solution because it reacts with other elements existing in the melt and forms complex compounds. The major goal of this study is to find other effective elements to modify the β-phase. Some limited work has been done on this subject. Sigworth[1)] reported that the formation of Fe containing brittle phases were retarded in the Sr modified 319 alloy. Ouellet and Samuel[2)] reported that the Sr modification of the Mg added 319 alloys caused the segregation of both the $Al_5Mg_8Si_6Cu_2$ and Al_2Cu phases in the areas away from growing Al-Si eutectic regions. Samuel *et al.*[3)] reported that the Sr addition led to the dissolution of more than two-thirds of the β-needles and also to the modification of the Mg_2Si particles in the Mg added 319 alloy. In this study, the influence of Sr or Sr and Mn combined additions on the intermetallic compound morphologies in an Al-Si-Cu-Fe cast alloy has been studied. The Fe concentration was as high as 1 mass% to make clear the morphological changes of the Fe-containing intermetallic compounds.

2. Experimental Procedure

The alloys were melted in a graphite crucible by an electrical furnace with the composition of Al-6.5Si-3.5Cu-1.0Fe (in mass%). Two categories of melt; 0.3%Mn-added and Mn-free melt were treated with 0.015% Sr addition. The alloys were cast into cast-iron and graphite molds to give different cooling rates. The effect of Sr on the microstructures was studied using an optical microscope and SEM. An image analysis method was utilized to measure the size and volume fraction of needle-like particles and number of intermetallic compounds per unit area. The chemical composition of the compounds was determined by an EDX method with a FE-SEM.

3. Results and Discussion

3.1 Effect of Sr addition

Figure 1 and Fig. 2 show the microstructures of the Mn-free samples. These microstructures contain flake-like eutectic Si particles and coarse β-needle-like intermetallic compound in the Sr-free alloy (Fig. 1(a)). This figure also demonstrates that the β-phase has a complicatedly branched structure as indicated in the enlarged pictures as examples; however, in the Sr added samples (Fig. 1(b)) the eutectic Si is well refined and the β-phase has a modified and less-branched structure. This can be clearly observed in the SEM images of the deep-etched samples as shown in Fig. 2. SEM images also show that the β-phase observed as a needle-like shape has a plate-like structure actually in the three-dimensional shape. The image analysis results as shown in Fig. 3 clearly indicate that both the length and volume fraction of the β-phase decrease and that the number density of particles increases by the addition of 0.015%Sr. Thus, Sr is an effective element in modification and shortening the needle-like β intermetallic compound.

Chemical compositions analyzed by the EDX are shown in Table 1 and exhibit that the stoichiometry of the β-phase corresponds to $(Al,Cu)_5FeSi$.

The mechanisms of the modification of the β-phase by Sr

*This Paper was Partly Presented at the Autumn Meeting of the Japan Institute of Light Metals held in Hitachi, Japan, on November 16-17, 2002

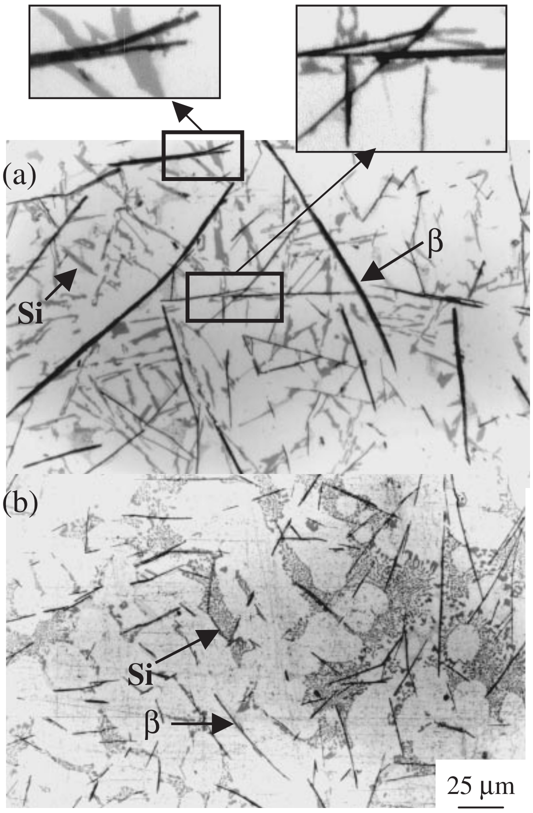

Fig. 1 Microstructures of the Al-Si-Cu-Fe alloys cast into an iron mold, showing the effect of Sr addition for (a) Sr free and (b) 0.015 mass% Sr. Branched structures of the β-phase are shown in the enlarged pictures in (a).

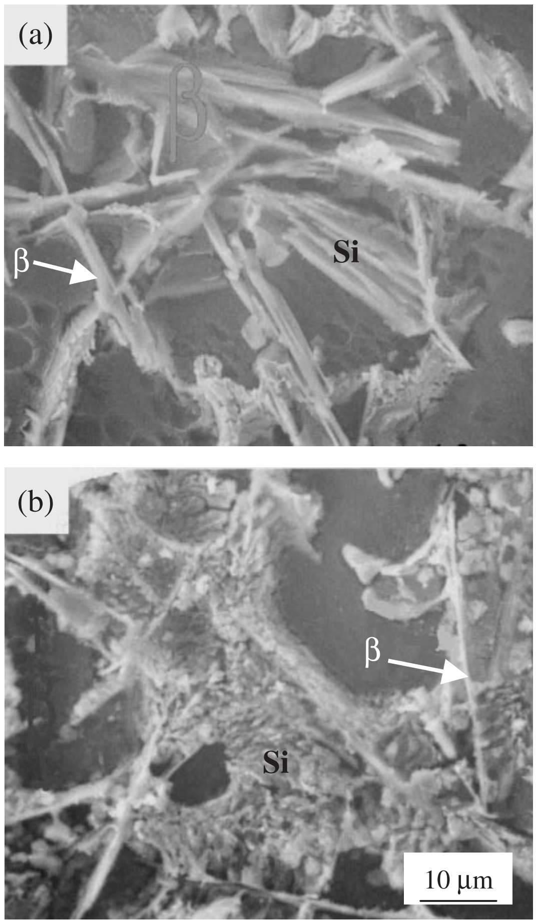

Fig. 2 SEM images showing the effect of Sr addition on the microstructure of iron mold cast alloys. (a) Sr free; (b) 0.015 mass% Sr.

can be explained with regards to (a) nucleation and (b) growth of the β-phase.

The number of the β-phase particles per unit area correlates with the nucleation mechanism. The increase in the number of the β-particles per unit area indicates that the nucleation process of the β-crystal is influenced by Sr addition. A change in the interfacial surface energy by addition of an impurity element (*e.g.* Sr) may affect the nucleation process. It can be suggested that Sr may reduce the interfacial surface energy between the α-Al and β phases, influencing the nucleation process of the β-phase. The same effect has been reported to occur for the nucleation of the eutectic Si by Mondolfo.[4] He reported that Na reduces the surface tension of the α-Al phase and thereby changes the interfacial surface energy between the α-Al and Si phases which may influence the nucleation of the Si phase.

Other factors which possibly influence the nucleation behavior are the nucleation sites and the undercooling for the formation of the β and eutectic phases during solidification. Crosley and Mondolfo[5] found that in Al-Si alloys aluminum phosphide (AlP), which forms due to the presence of P in the melt as an impurity, acts as an effective nucleation site for the Si phase and presence of AlP coarsens the eutectic Si. AlP is also reported to have an important role in the nucleation of the undesirable iron-bearing phases in the 413 aluminum alloy by Sigworth.[6] Crosley and Mondolfo also found that the modifier element (Na or Sr) suppresses the formation of AlP, resulting in the decreased number of the nucleation sites for the eutectic Si. As a result, the addition of Na or Sr increases the undercooling for the nucleation of the Si phase on the α-Al phase. Yaneva *et al.*[7] reported that Sr refines the silicon particles and, to a certain degree, the iron-intermetallics as well, probably due to the undercooling at the solidification front caused by the Sr addition.

Table 1 Chemical compositions of intermetallics (mol%).

Phase	Al	Si	Fe	Cu	Mn
β-phase	67.9	13.1	12.5	3.8	2.7
Chinese script	68.1	5.8	13.3	5.4	7.6
Sludge	68.6	5.9	12.7	4.6	8.1

Therefore, the Sr addition should be important in influencing the β-phase nucleation by affecting nucleation sites and resultantly undercooling.

The length of the β-particles correlates with the growth mechanism. The decreased length and volume fraction of the β-phase in the Sr added alloys indicate that the growth of these particles is greatly suppressed by the Sr addition. This is particularly likely in the view of the well-known effect of Sr in modifying the growth of the eutectic silicon in Al-Si alloys.[8] Growth takes place in certain crystallographic lattice planes of the β and Si phases and adsorption of Sr on the lattice planes will suppress the growth. On the other hand, it has been reported by Samuel *et al.*[9] that the preferential

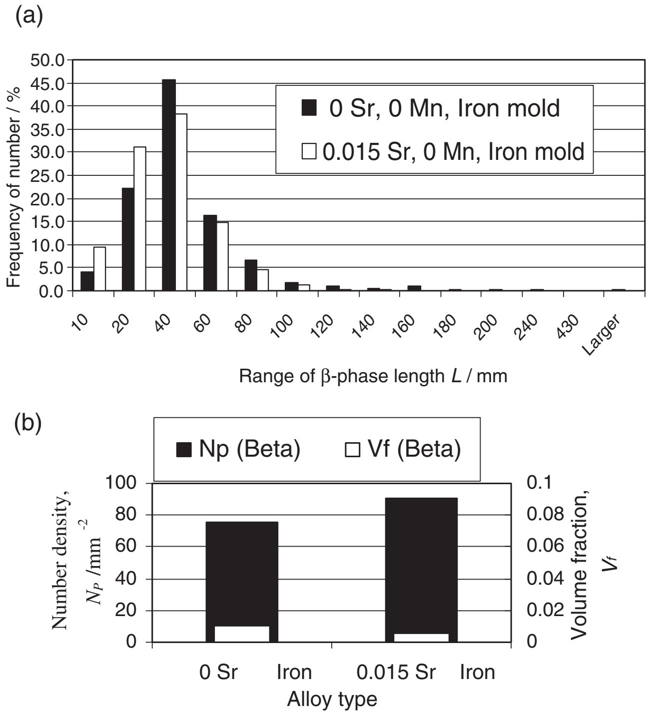

Fig. 3 Effects of Sr addition on the (a) length, (b) number density and volume fraction of the β-phase particles of iron mold cast alloys.

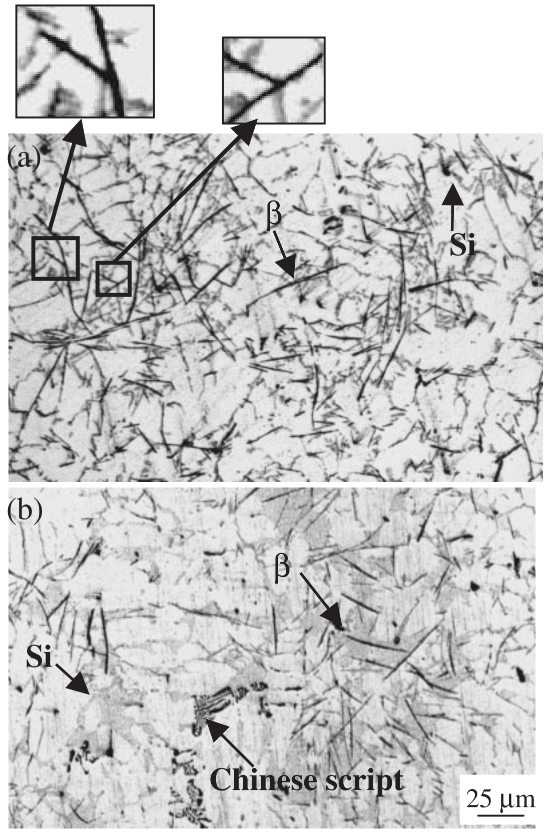

Fig. 4 Microstructures of the alloys cast into an iron mold, showing the effect of Sr and Mn (0.3 mass%) combined addition for (a) Sr and (b) 0.015 mass% Sr. Branched structures of the β-phase are shown in the enlarged pictures in (a).

nucleation of the β-needle-like phase from a "parent β-phase" (the firstly formed β-phase) results in branching and formation of a large β-phase (as can be seen in Fig. 1(a), and Fig. 2(a), the β-phase has several branching). It can be suggested that the Sr poisons the preferential nucleation sites on a parent β-phase and as a result, modification (less branching) of the β-phase can be expected.

Sr should have an affinity to Si and Al and preferably forms compounds with them. This will facilitate adsorption on the surface of crystals growing into the melt. A compound described by formulae Al_3SrSi_2 has been found to form near the eutectic Si by Igarashi,[10] which influences the Si growth. EDX analysis results clearly show that Sr segregates into both the Si and β-phases in the present samples (Table 2). However it is not simple to establish definitely the evidence of a compound or to describe how Sr is dispersed near the above phases. A comprehensive TEM study, for example, is necessary to make clear the above mentioned phenomenon.

3.2 Effect of Sr and Mn combined additions

Figure 4 shows the microstructures of the samples with Sr and Mn combined additions. The flake-like eutectic Si and the branched structure of the β-phase, as indicated in the enlarged pictures in Fig. 4(a) for the Sr free alloy (only Mn addition), is converted into a refined eutectic Si and a modified and less-branched β-phase structure (Fig. 4(b)) by Sr and Mn addition. It can be clearly seen in the SEM images of the deep-etched samples shown in Fig. 5. The image analysis results showing the above trends are given in Fig. 6. The length and volume fraction of the β-phase decreases and the number density of particles increases by the addition of 0.015% Sr. The quite important point in these alloys is the fact that the combination of Sr and Mn results in not only modifying the β-phase into more separated ones, but also, enhancing the formation of Chinese script type compounds as indicated in Fig. 6(b).

Table 2 Results of Sr analysis in each phase.

Phase	Sr (mol%)
β-phase	3.5
Si	11.0
Al	0.0
Al_2Cu	0.0

The chemical composition analysis by the EDX (Table 1) shows that the stoichiometry of the Chinese script and sludge is approximately the same and corresponds to $(Al,Cu)_{15}(Fe,Mn)_3Si$ which is called as the α-phase.

Mechanisms of the modification of the β-phase by Sr and Mn combined addition can be clarified from two points of view, including: (a) Changing the nucleation process and preventing growth of the β-phase in the same manner as mentioned above for the Sr-added alloys and (b) promotion of the Chinese script formation instead of the β-phase. For better understanding this mechanism of modification, solidification sequence of these alloys must be taken into account as follows.

Figure 7 shows the solidification routes depicted on the aluminum-rich corner of the Al-Si-Fe-Mn equilibrium phase diagram with certain amount of Mn equal to 0.3 mass%.[11)]

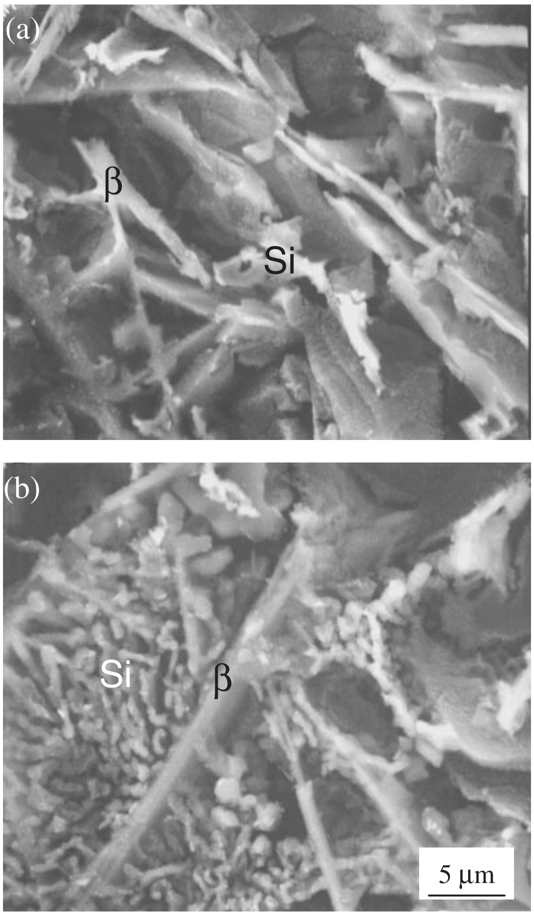

Fig. 5 SEM images showing the effect of Sr and Mn on the microstructures of iron mold cast alloys. (a) Sr free; (b) 0.015 mass% Sr.

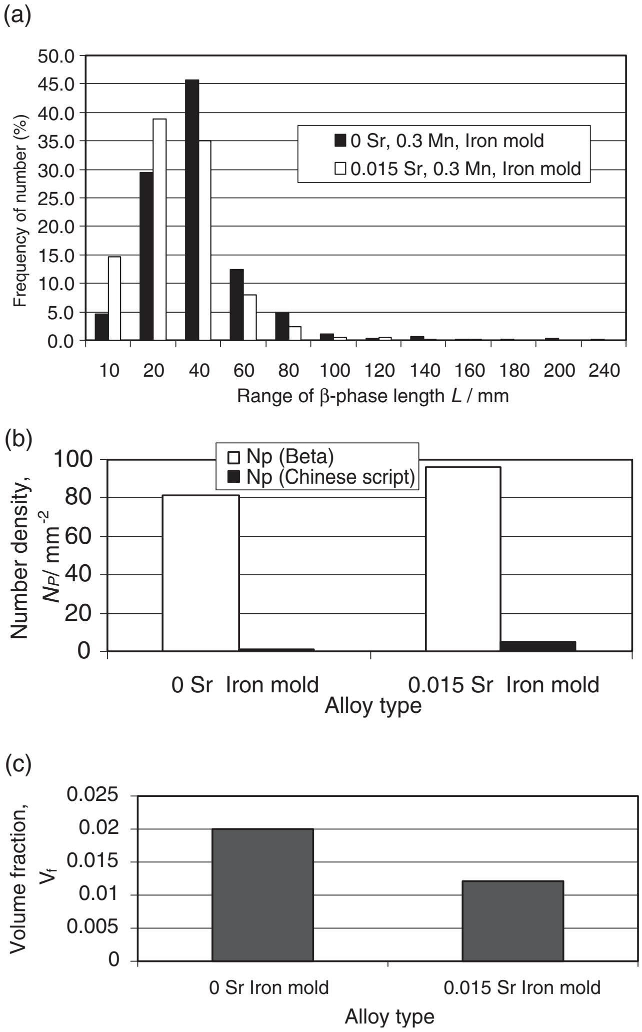

Fig. 6 Effects of Sr and Mn additions on the (a) length, (b) number density and (c) volume fraction of the β-phase of iron mold cast alloys.

The composition of the present sample is indicated in the phase diagram. The solidification process starts by the formation of Al dendrites and the interdendritic liquid becomes enriched in Fe and Si according to path (1). The solidification line penetrates the $Al_{15}(Mn,Fe)_3Si_2$ (Chinese script or sludge) surface and starts the second reaction, by which the latter phase crystallizes, path (2a) Some Mn is consumed, and the solidification line soon reaches the valley between the two iron bearing phases, $Al_{15}(Mn,Fe)_3Si_2$ and $(\beta)Al_5FeSi$, and during the following reaction these two phases crystallize together along with path (2b) until the eutectic composition, point (3) is reached.[11] From there on Al, Si and β-Al_5FeSi phases will crystallize together within the ternary eutectic reaction. The mechanism of preventing the β-phase formation may be suggested to take place by the effect of Sr to suppress the path (2b) reaction.

Sr and Mn combined addition has been found to be more effective than the Sr addition to modify the needle-like β-phase to shorter, more separated ones and changing the morphology to the Chinese script type. In this study, the amount of the iron impurity is very high (1.0 mass%). The addition of Sr and Mn causes a reduction of 34% in the size of the β-phase but the size of the β-phase is still larger to be expected as modified sufficiently. However, the present method will be much more effective to modify the β-phase in the case of lower iron contents such as 0.5 mass% Fe.

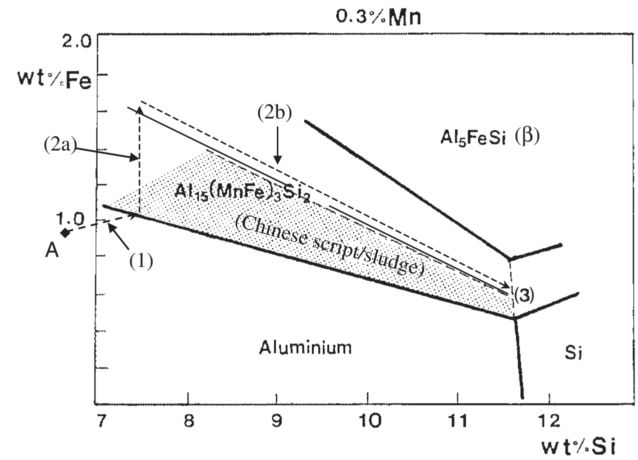

Fig. 7 Solidification routes down to the eutectic reaction shown by dotted lines with numbers (1), (2a), (2b) and the point (3) in the Al-Si-Fe-Mn equilibrium phase diagram.[11] The composition of the samples is indicated by the point A.

3.3 Effect of cooling rate

A comparison between the cooling rates obtained by an iron mold and a graphite mold is illustrated in Fig. 8. The

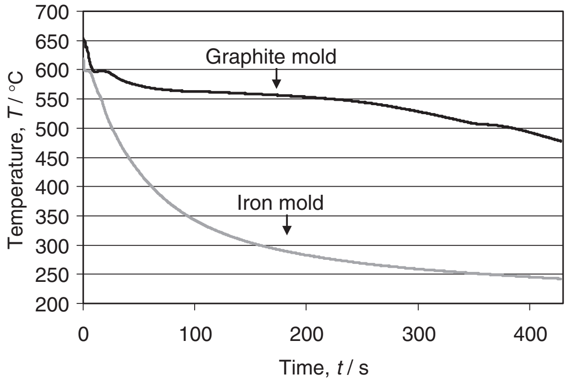

Fig. 8 Temperature-time cooling curves obtained from Sr and Mn added samples cast into an iron mold and a graphite mold.

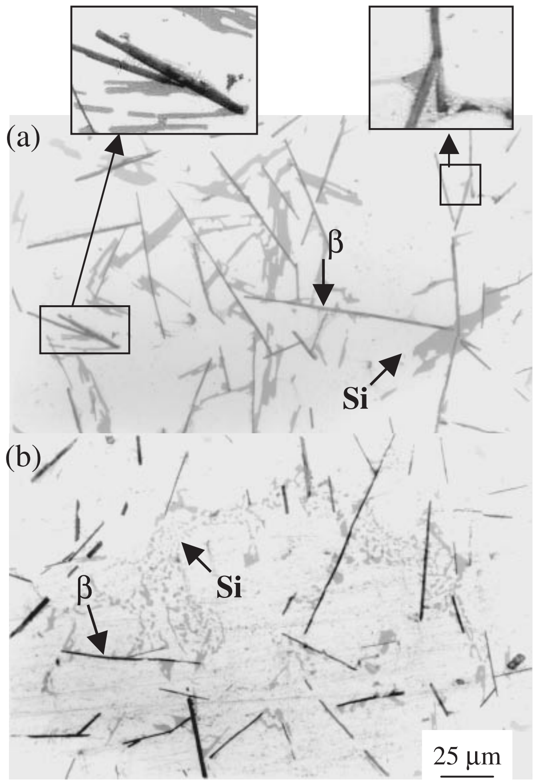

Fig. 9 Microstructures of the alloys cast into a graphite mold, showing the effect of Sr addition for (a) Sr-free and (b) 0.015 mass% Sr.

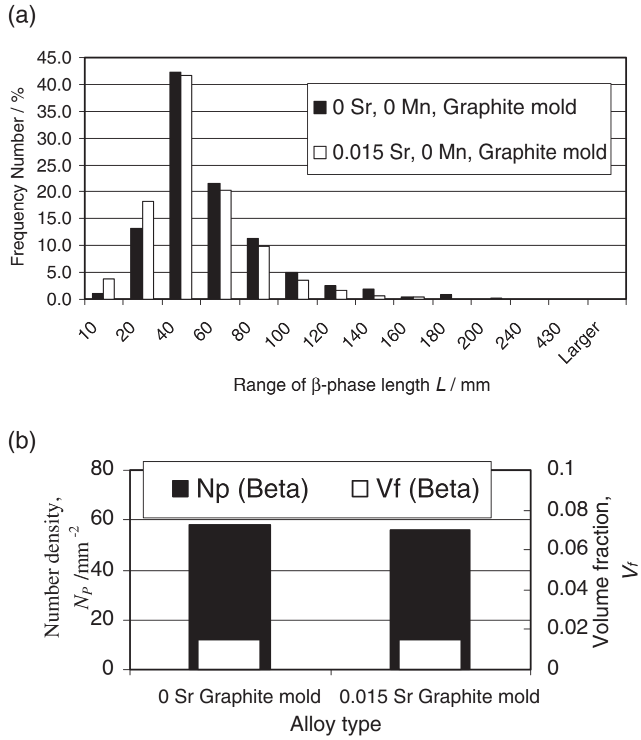

Fig. 10 Effects of Sr addition on the (a) length and (b) number density and volume fraction of the β-phase particles of graphite mold cast alloys.

cooling rates at the beginning before solidification are 17.4 and 6.3°C/s for the iron and graphite molds respectively. The average cooling rates from beginning to the eutectics temperature (~570°C) are 4.2 and 1.4°C/s for the iron and graphite molds respectively.

Figure 9 shows the microstructures of the Sr-added alloys cast into a graphite mold. These microstructures contain flake Si particles and the coarse, branched needle-like β-phase in the Sr-free alloy which is changed into a refined Si and a modified and less branched β-phase in the 0.015%Sr added alloy. These microstructures, which are solidified at a lower cooling rate, are coarser than the microstructures of the alloys solidified at a higher cooling rate (compare the Fig. (1a) and Fig. (9(a)) and the β-phase modification effect happens at lower extend compared with the alloys solidified at higher cooling rate (compare the Fig. (1b) and Fig. 9(b)). The above trends can be clearly noticed in the image analysis results. Figure 10(a) shows that the length of the β-phase slightly decreases by addition of Sr, however higher cooling rate solidification exerted by an iron mold decreases the length of the β-phase dramatically compared to the values obtained during the lower cooling rate solidification exerted by a graphite mold (compare Fig. (10(a) and Fig. (3(a)). Thus, the cooling rate is an important factor to control the size of the β-phase. Figure 10(b) shows that the number density and volume fraction of the β-phase changes slightly by addition of Sr during a low cooling rate solidification.

Figure 11 shows the microstructures of the Sr and Mn added alloys cast into a graphite mold. In these alloys both the Chinese script and sludge type morphologies are also formed in addition to the needle-like β-phase in the Sr-free alloy and the β-phase almost disappears by the addition of Sr. Figure 12 shows that a dramatic change in the β-phase number density and volume fraction occurs in the graphite mold cast alloy and the amount of sludge phase increases. The presence of higher amount of Chinese script or sludge in these alloys suggests that Sr and Mn stabilize the $Al_{15}(Mn,Fe)_3Si_2$ phase, thus suppressing the β-Al_5FeSi phase formation with the same mechanism as mentioned above in section 3.2.

On the other hand, higher cooling rate results in the solidification of a higher number density and volume fraction of the β-phase; however, the lower cooling rate caused crystallization of a higher amount of sludge phase (see Fig. 6(b) and Fig. 12(a)). It suggests that the kinetics of the nucleation and growth of intermetallic compounds plays an important role to determine the finally solidified structure in

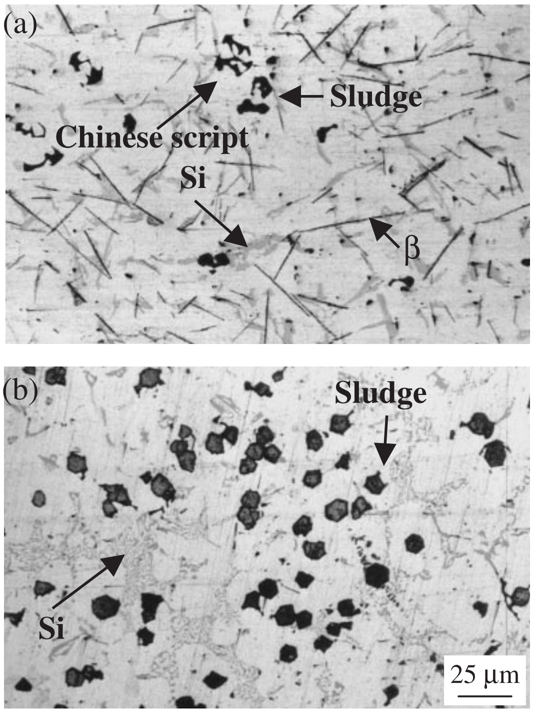

Fig. 11 Microstructures of the alloys cast into a graphite mold, showing the effect of Sr and Mn (0.3 mass%) combined addition for (a) Sr-free and (b) 0.015 mass% Sr.

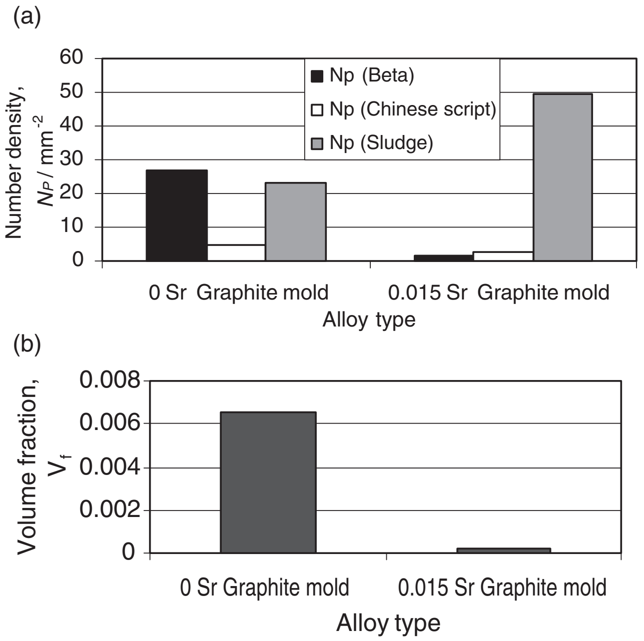

Fig. 12 Effect of Sr and Mn additions on the (a) number density and (b) volume fraction of the β-phase particles of graphite mold cast alloys.

the case of Sr and Mn combined additions. In this case the sludge type phase will be the stable one in the equilibrium condition because slower cooling rate produces higher amount of the sludge type phase.

4. Conclusions

The present investigation has revealed that Sr is a very effective element to change the size, amount and morphology of the intermetallic compounds. The phenomenon has been observed in both Sr or Sr and Mn additions. The conclusions drawn from the present study are summarized as follows:

(1) The reduction in size and volume fraction, modification and increase in the number of particles per unit area of the β-needle-like phase (β-Al_5FeSi) occurs under a fast cooling rate solidification in an iron mold by Sr addition. In the absence of Mn, no Chinese script or sludge forms.

(2) The same effect but in lower extend is observed under a slow cooling rate solidification by the addition of Sr. Also there will be no Chinese script or sludge formation in the absence of Mn in the alloys.

(3) In the high cooling rate condition, Sr and Mn additions cause the modification, reduction of the size and volume fraction, increase in the number of particles per unit area and transforming some needle-like β-phase to Chinese script.

(4) In the low cooling rate condition, Sr and Mn additions cause the elimination of most of the needle-like β-phase and high amount of sludge and some Chinese script appear instead.

(5) The Sr and Mn combined addition, together with higher cooling rate is found to be the most effective method to modify the intermetallic compounds to shorter and separated ones. The highest reduction of the length is 34%.

Acknowledgements

P. Ashtari gratefully acknowledges the financial support from Ministry of Education, Science, Culture and Sports, Japan, as "Honors scholarship for privately financed international students". Also, we would like to thank the technical support of the laboratory members for conducting experiments.

REFERENCES

1) G. K. Sigworth: Mod. Cast. **77** (1987) 23-25.
2) P. Ouellet and F. H. Samuel: J. Mater. Sci. **34** (1999) 4671-4697.
3) F. H. Samuel, P. Ouellet, A.M. Samuel and H.W. Doty: Metall. Trans. A **29A** (1998) 2871-2884.
4) L. F. Mondolfo: *Aluminum Alloys: Structure and properties*, (Butterworths, London, 1978) pp. 678.
5) P. B. Crosely and L. F. Mondolfo: Mod. Cast. **49** (1966) 89-100.
6) G. K. Sigworth, S. Shivkumar and D. Apelian: AFS Trans. **79** (1989) 811-824.
7) S. Yaneva, N. Stoichev, Z. Kamenova and S. Budurov: Z. Metall. **75** (1984) 395-398.
8) Lu, Shu-Zu and A. Hellawel: Metall. Trans. A **18A** (1987) 1721-1733.
9) A. M. Samuel, F. H. Samuel and H. W. Doty: J. Mater. Sci. **31** (1996) 5529-5539.
10) Y. Igarashi: Collected abstracts of the 139th JFS meeting (2001), pp. 57.
11) L. Backerud, G. Chai and J. Tamminen: *Solidification Characteristics of Aluminum Alloys, Vol. 2*, (AFS/Skanaluminium, 1990) pp. 84.