Refinement of cast microstructure of hypereutectic Al-Si alloys through the addition of rare earth metals

JOONYEON CHANG, INGE MOON
Division of Metals, Korea Institute of Science & Technology, Seoul 136-791, Korea

CHONGSOOL CHOI
Department of Metallurgical Engineering, Yonsei University, Seoul 120-749, Korea
E-mail: presto@kistmail.kist.re.kr

Microstructural observation and thermal analysis of Al-21 wt % Si alloys with different rare earth metals were performed to examine the effect of rare earth metal on the refinement of primary silicon phase. Simultaneous refinement of both primary and eutectic silicon morphology is achieved with the addition of rare earth and its effect increases with the amount of rare earth addition and cooling rate. Depression of 12–17 °C in primary reaction temperature and 2–7 °C in eutectic temperature is measured with the addition of rare earth. Rare earth bearing compounds were not believed to act as a nucleation agent of primary silicon phase. Some rare earth bearing compounds determined to AlCe were around primary silicon in the matrix. The twin density of eutectic silicon remains same regardless of the addition of rare earth. The refinement of silicon in rare earth treated hypereutectic Al-Si alloys is supposed to be due to the suppression of the nucleation temperature of silicon phase. © *1998 Kluwer Academic Publishers*

1. Introduction

Alloys with silicon as the major alloying addition are one of the most effective ways to obtain good aluminum casting alloys mainly because of the high fluidity imparted by the presence of relatively large volumes of the Al-Si eutectic. Additional advantages of these castings are high resistance to corrosion, good weldability and the fact that silicon reduces the coefficient of thermal expansion. Commercial alloys are available with hypoeutectic, eutectic and, less commonly, hypereutectic compositions [1].

Binary Al-Si alloys close to the eutectic composition (11.7 wt % Si) exhibit, in the unmodified state, an acicular or a lamellar eutectic silicon which is in the form of large plates with sharp sides and edges. Al-Si alloys containing more than about 12% Si exhibit a hypereutectic microstructure normally consisting of a primary silicon phase in a eutectic matrix [2]. Cast eutectic alloys with coarse acicular silicon display low strength and ductility because of the coarse plate-like nature of the Si phase that leads to premature crack initiation and fracture in tension. Similarly, the primary silicon in normal hypereutectic alloys is usually very coarse and imparts poor properties to these alloys. Therefore, alloys with a predominantly eutectic structure must be modified to ensure adequate mechanical strength and ductility. It is widely recognized that the Group IA and IIA elements (Na, Mg, Ca, Sr) are effective modifiers of Al-Si eutectic; only sodium and strontium, however, have been used extensively in the commercial production of

these alloys [2]. Refinement of primary silicon is usually achieved by the addition of phosphor to the melt. The literature [3, 4] reports that rare earth (RE) metals are also capable of modifying the eutectic structure of cast aluminum-silicon alloys. Weiss and Loper [5] reported that cerium did not refine the primary silicon as phosphor, but that it was moderately effective in modifying the eutectic silicon. However, the role of RE metals as a modifying agent seems to be rather controversial. Recently, Kowata *et al*. [6] investigated the effect of RE addition on the refinement of primary silicon crystals in a hypereutectic Al-20% Si alloy and concluded that primary silicon crystals were refined with RE metals.

Many studies have been carried out in order to elucidate the mechanism of modification and many hypotheses have been formulated. However, the role of the modifying element is not yet clearly understood. Several models were suggested in the literature to illustrate and explain the mechanism of refinement (or modification, as it is sometimes termed) of the primary silicon crystals by the addition of phosphor [7, 8] and of the eutectic silicon by the addition of strontium [9].

The purpose of present study is to examine the potential of rare earth metals as a modifying agent for simultaneous refinement of both primary silicon and eutectic silicon and secondly to obtain further insight into the modification mechanism. Even though major application of Al-Si alloys is found in the casting, we are also interested in the wrought application of these

alloys. For this purpose, refinement of silicon crystals is essential, because fracture and decohesion of large silicon crystals occur during hot deformation [10].

2. Experimental

Starting with binary Al-21% Si alloy as a base alloy, 1 to 3 wt% of RE metals (added as misch metal) were added to the base alloy to see the effect of rare earth addition. Alloys were melted at 850 °C in a graphite crucible utilizing Al-23% Si mother alloy within a resistant heating furnace. The melt was covered with flux and degassed with chlorine. RE was added as a misch metal after complete melting of the alloy and held for 45 minutes. Wedge-shaped cast iron mold was used to study the effect of cooling rate as shown in Fig. 1. K-type thermocouples were put into the mold to record the cooling curves at four different positions. The chemical composition of the alloys studied and misch metal used are given in Tables I and II respectively.

The solidus and eutectic temperature of the alloy were measured from the typical cooling curve. Eutectic reaction temperature was confirmed again with DTA.
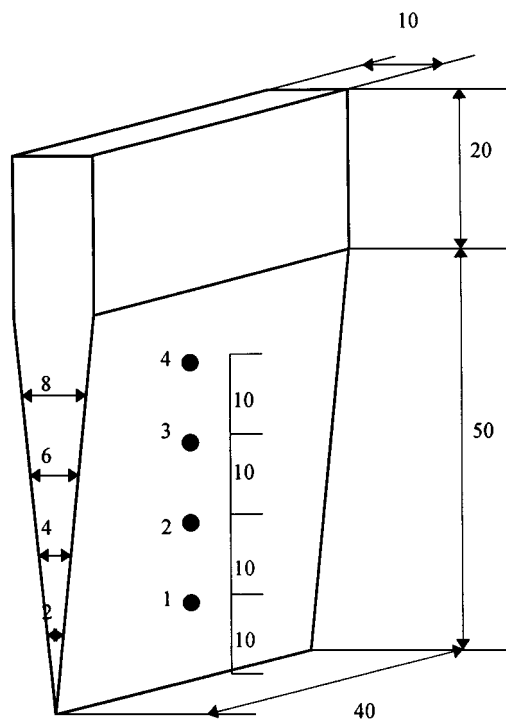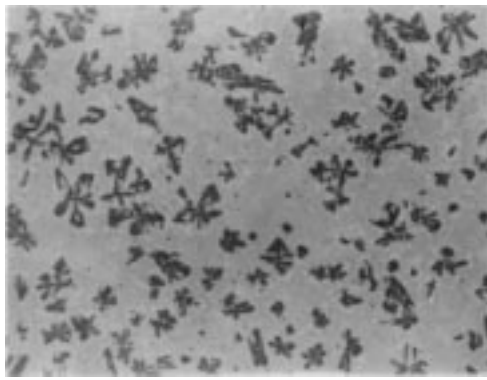
The cooling rates between primary reaction and eutectic reaction temperature were measured to be 130, 73, 45, 33 °C/s at positions 1 to 4, respectively, in the mold preheated to 200 °C. The microstructure of specimens was observed using optical microscopy (Olympus, AHMT-3) and transmission electron microscopy (TEM, Philips CM30). The Keller's reagent was used for the optical microscopy. For TEM analysis, discs of 60 μm in thickness were prepared from the specimens and final thinning was done by Ar ion beam milling (Technorg-Linda, IV3, Budapest, Hungary) with an ion beam energy of 10 keV, an incident beam angle of 3° and specimen current of 3 mA. Final perforation was carried out by applying 1 kV retarding potential on the specimen to ensure thin and large area. Deep etched samples were examined in the scanning electron microscope (SEM, Hitachi2400) and back scattered electron images were obtained in the energy probe micro analysis (EPMA, JEOL, JXA8600). Thermal analyses were made using a differential thermal analyzer (DTA, Sinku-Riko, TA7000) with a scanning rate of 2 °C/min. X-ray diffraction analysis was performed in order to check the change in twin density with addition of rare earth.
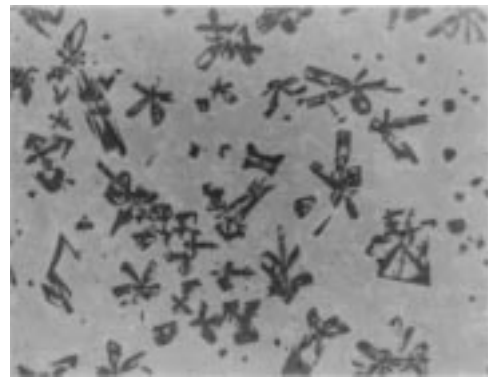
3. Results

Fig. 2 shows the optical microstructures of the untreated base alloy (Al-21% Si) at different positions of the mold. The primary silicon crystals of the untreated alloy show typical star-shaped morphology at all positions. The size of primary silicon crystals increases rapidly with the decrease in the cooling rate. When 3% of rare earth elements were added, the morphology of primary silicon crystal changes from star shape to fine polyhedral shape irrespective of cooling rates (the positions of the mold) as shown in Fig. 3, illustrating the powerful refining effect of RE addition.

Fig. 4 shows the effect of the amount of RE addition on the size and shape of primary silicon crystals under the same cooling rate of 45 °C/s. Addition of 1% RE appears to be enough to change the morphology of primary silicon crystal from star shape to polyhedral shape. The substantial refinement of silicon crystals is achieved with the addition of more than 2% RE. Fig. 5 summarizes the relationship between primary silicon size, amount of RE addition and cooling rate. It is worth noting from the figure that the refinement of silicon with RE addition is more effective at slower cooling rate. This implies that RE modification can be used for the refinement of silicon in heavy section.
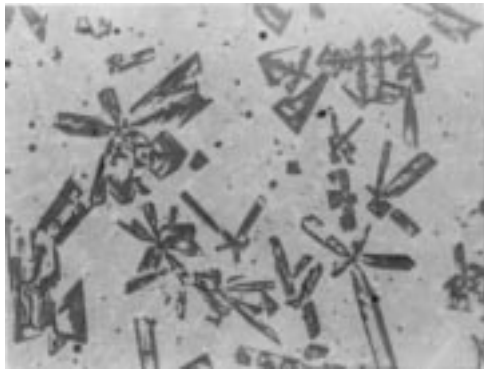
The scanning electron micrographs of a deep etched primary silicon and eutectic silicon in Al-21% Si-3% RE alloy are shown in Figs 6 and 7, respectively. The morphology of RE modified primary silicon shows typical polyhedral shape. It is clear that RE addition also causes the modification of eutectic silicon in hypereutectic Al-Si alloy, i.e. with the addition of RE the morphology of eutectic silicon changes from coarse acicular (plate like) to refined fibrous one. Therefore, it can be said that RE treatment is effective for the
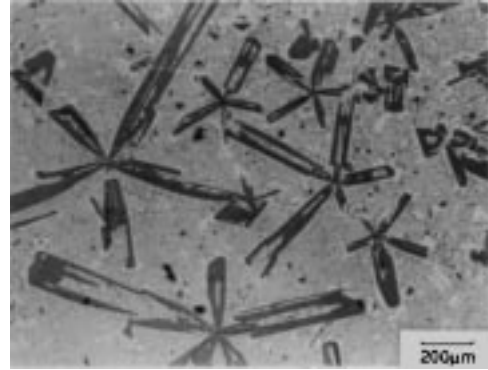

Figure 1 Dimension of wedge shape casting (in mm).

TABLE I Chemical composition of the Al-Si alloys studied (wt %)

Alloy	Al	Si	RE
Base alloy	bal.	21.20	0
1RE	bal.	20.97	0.97
2RE	bal.	20.84	1.88
3RE	bal.	21.08	2.94

TABLE II Chemical composition of the misch metal used

Element	Ce	La	Nd	Pr	Fe	Pa
wt %	51.90	25.09	14.25	5.33	1.43	0.12

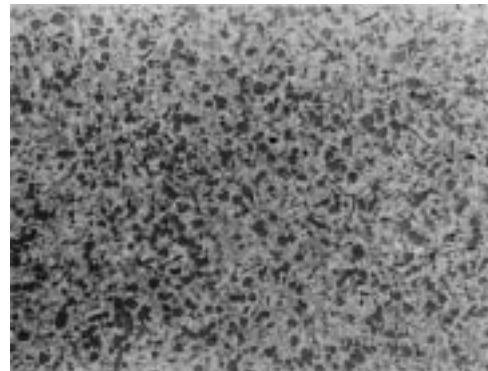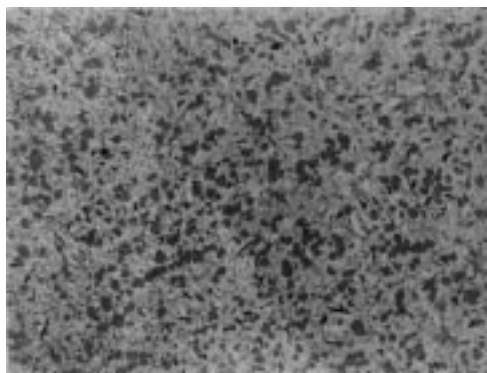*Figure 2* Optical micrographs of the unmodified base alloy (Al-21% Si) at different positions (cooling rate) of the mold: (a) 130 °C/s (b) 73 °C/s (c) 45 °C/s (d) 33 °C/s.
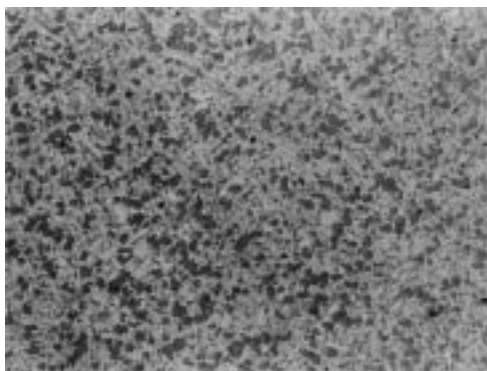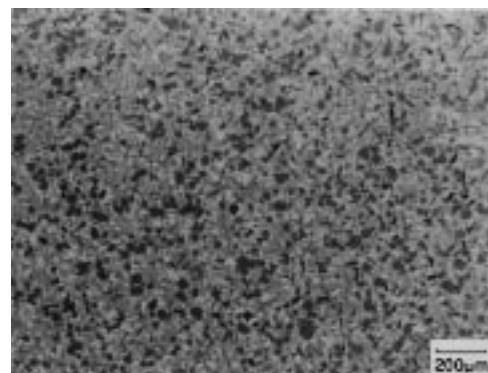

Figure 3 Optical micrographs of 3% RE added Al-21% Si alloy at different cooling rates: (a) 130 °C/s (b) 73 °C/s (c) 45 °C/s (d) 33 °C/s.
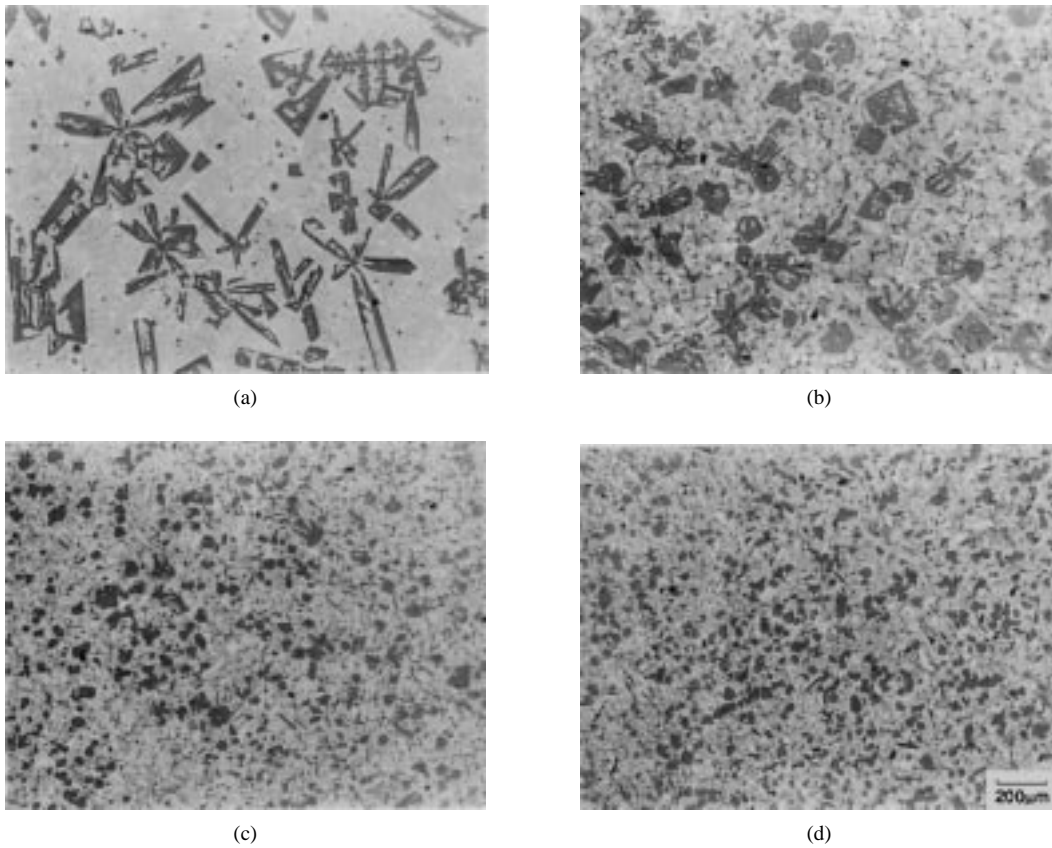
Figure 4 Change in primary Si size and shape with the addition of different amounts of RE under the same cooling rate of 45 °C/s: (a) 0% RE (b) 1% RE (c) 2% RE (d) 3% RE.
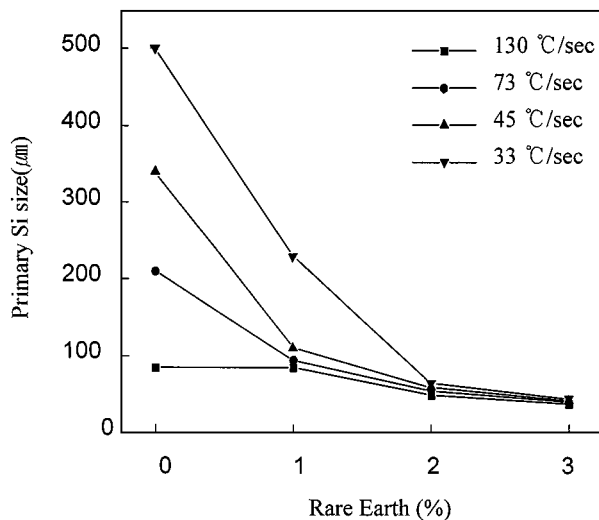

Figure 5 Relationship between primary Si size and amount of RE addition at different cooling rates.

simultaneous modification of both primary and eutectic silicon morphology of hypereutectic Al-Si alloys.

Fig. 8 shows the change of primary and eutectic reaction temperature of the Al-21% Si base alloy with the addition of RE at the cooling rate of 2 °C/min. Depression of 12–17 °C in primary reaction temperature and 2–7 °C in eutectic temperature is measured with the addition of RE. Fig. 9 shows the EPMA analysis of RE elements of a primary silicon. RE elements are not detected in the primary silicon but some particles (marked by an arrow in (c)) containing rare earth are

found around primary silicon in the matrix. Although these RE bearing particles were already reported in the previous works [4, 12], identification of the phase was not performed. Phase analysis was attempted combining energy dispersive spectroscopy (EDS) for chemical information and diffraction methods (selected area diffraction (SAD)) for crystallographic information in the TEM. Fig. 10 shows the morphology, X-ray energy spectrum and SAD patterns from the particle with three different beam directions. The EDS result indicates that the particle contains major elements of Al, Si and Ce with trace amounts of La, Nd. Three series of SAD patterns show good agreement with the indexed one with the direction normal to $(2\,0\,\bar{1})$, $(\bar{1}2\,0)$, $(1\bar{4}\,\bar{1})$ of an orthorhombic AlCe structure. Fig. 11 shows the transmission electron micrographs of the Al-21% Si-2% RE alloy. Traces of twins are observed within the eutectic silicon. But the number of twins does not seem to increase much with the addition of RE.

4. Discussion
4.1. Refinement of primary silicon
It is clearly demonstrated in Fig. 5 that the addition of 1% RE modifies the morphology of primary silicon crystals from coarse star shape to fine polyhedral shape, but an addition of more than 2% rare earth is required for the refinement of polyhedral silicon crystals. Several proposed mechanisms of refinement of the primary silicon crystals by the addition of phosphor can be summarized as follows. Widely accepted and
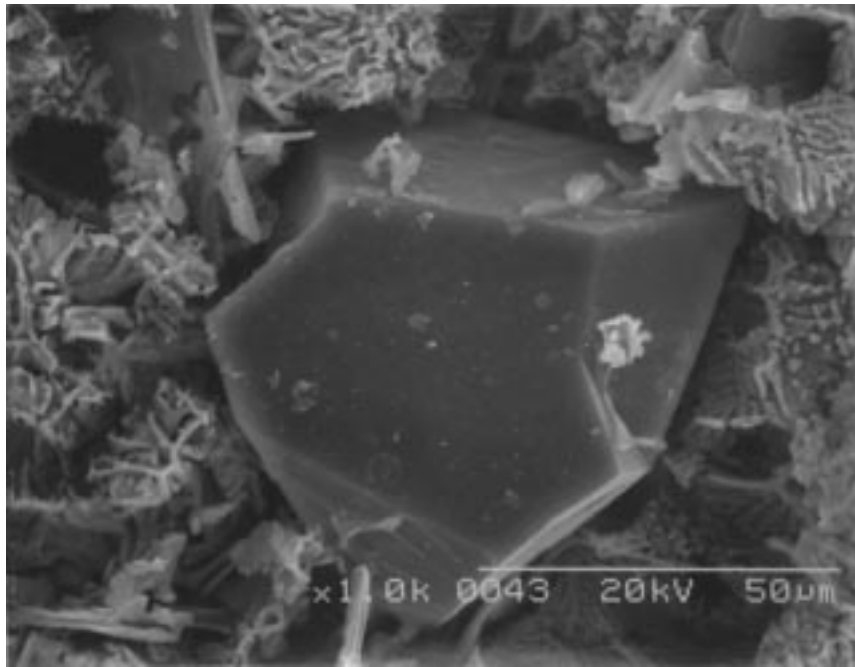
Figure 6 Scanning electron micrograph of the deep etched Al-21% Si-3% RE alloy. The RE modified primary Si shows typical polyhedral shape.
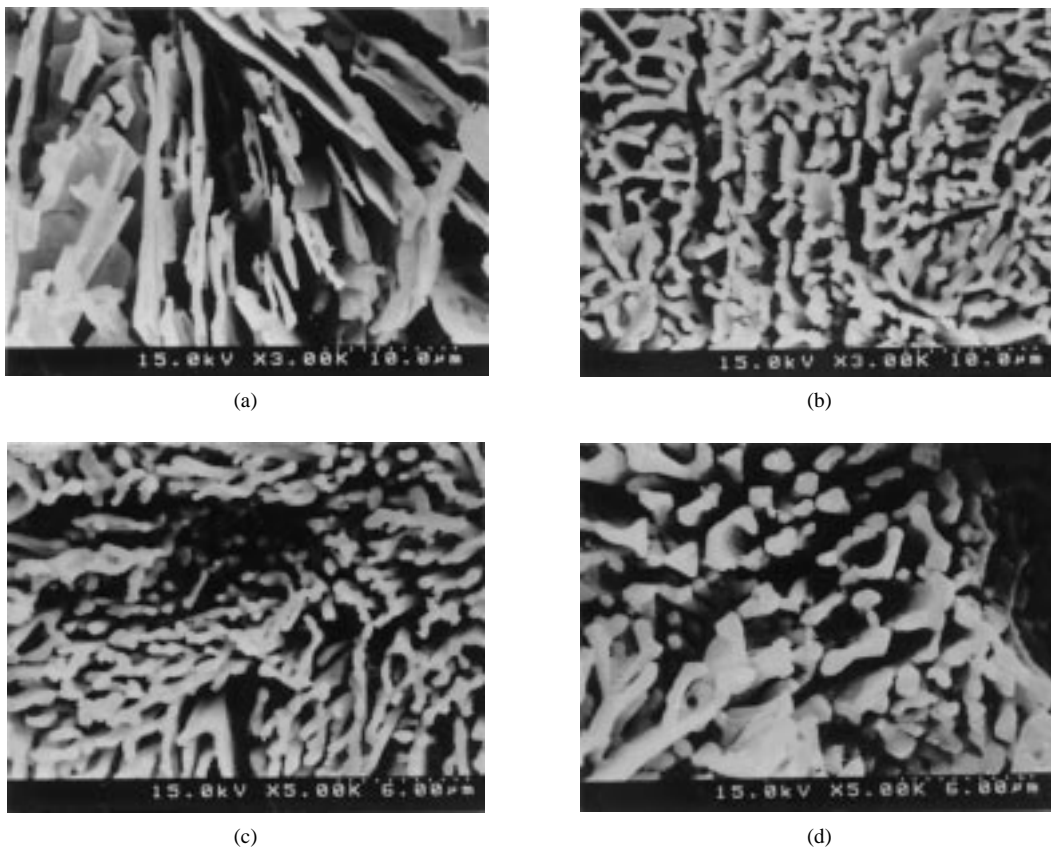

(a)

(b)

(c)

(d)

Figure 7 Scanning electron micrographs of the deep etched eutectic area of the Al-21% Si alloy modified with (a) 0% RE (b) 1% RE (c) 2% RE (d) 3% RE.

popular theory is based on the nucleation of Si crystal on AlP compound due to the phosphor addition. It has been proposed, and largely accepted on the basis of some evidence, that the compound AlP, having melting point higher than 982 °C, and a cubic structure with lattice constant of 5.45 Å, which is very similar to that of silicon ($a = 5.43$ Å), acts as a nucleating agent and thus refines the primary silicon crystals by inducing heterogeneous nucleation. Acceptance of this theory is largely based upon the facts that the presence of AlP in the melt prior to solidification has been found, and the recent work has shown, by microprobe analysis, the presence of AlP at the center of one primary silicon crystal [11].
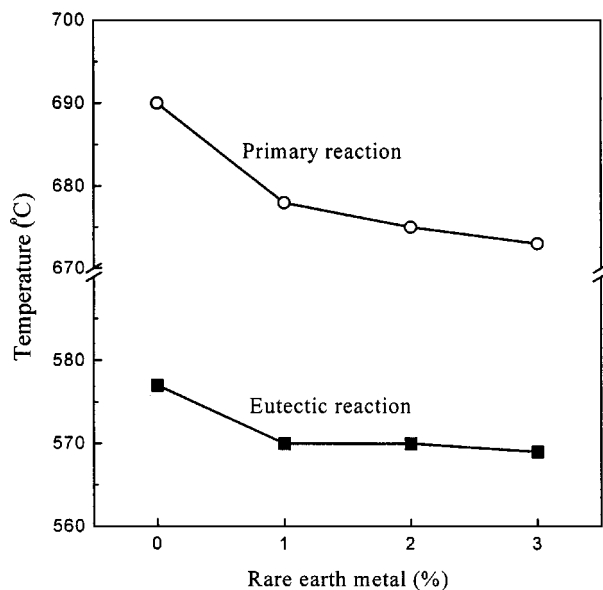
845 °C. Although it solidifies in the melt prior to the solidification of primary Si, the large misfit strain induced by the great difference in the lattice parameter and crystal structure may prevent an RE bearing compound from being an effective nucleation site of Si. Therefore, it is rather reasonable to think that RE metals can not provide a suitable nucleation site of Si, although some RE bearing compounds were observed around primary silicon in the Al matrix (Fig. 9).

Sharan *et al.* [12] reported that the modification with RE could be explained using the critical growth temperature hypothesis of Kim [13]; nucleation of silicon is suppressed to the temperature of globular growth by the addition of rare earth, thus modifying the structure. This hypothesis may be applied to explain our experimental results because in the experiments the primary reaction temperature of the RE treated alloys were depressed by as much as 12 to 17 °C, which is in good agreement with the result of Kowata *et al.* [6].

Figure 8 Change of primary reaction and eutectic reaction temperature of the Al-21% Si alloy with the addition of RE. Depression of 12–17 °C in primary reaction temperature and 2–7 °C in eutectic reaction temperature was measured.

Basically, in order to provide an effective nucleation site of Si like AlP, the RE compound has to solidify at much higher temperature than Si as well as have similar crystal structure with Si. The RE bearing compound (mainly AlCe), however, shows orthorhombic structure with a lattice parameter $a = 9.269$, $b = 7.680$, $c = 5.761$ Å and the melting point is reported to be

4.2. Modification of eutectic silicon

It was shown in the experimental results that with the addition of RE the morphology of eutectic silicon changed from coarse acicular (plate like) to refined fibrous one (Fig. 7). Therefore, it can be said that RE treatment is also effective for simultaneous modification of both primary silicon and eutectic silicon morphology.

Many studies have been carried out to find out the mechanism by which the morphology of eutectic silicon
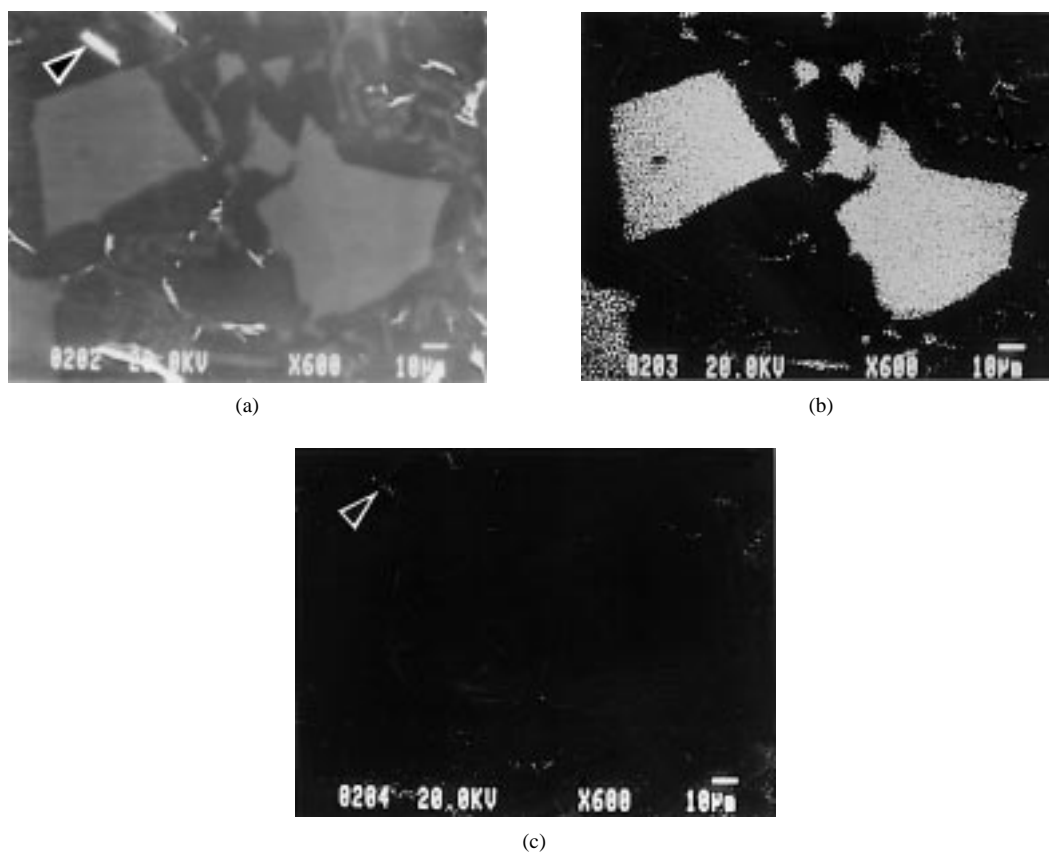

(a)

(b)

(c)

Figure 9 EPMA analysis of RE modified primary Si: (a) backscattered electron image, (b) distribution of Si and (c) distribution of Ce. RE elements were not detected within the primary Si but rare earth rich particles (bright particles in (a)) were observed in the matrix around primary Si marked by an arrow.
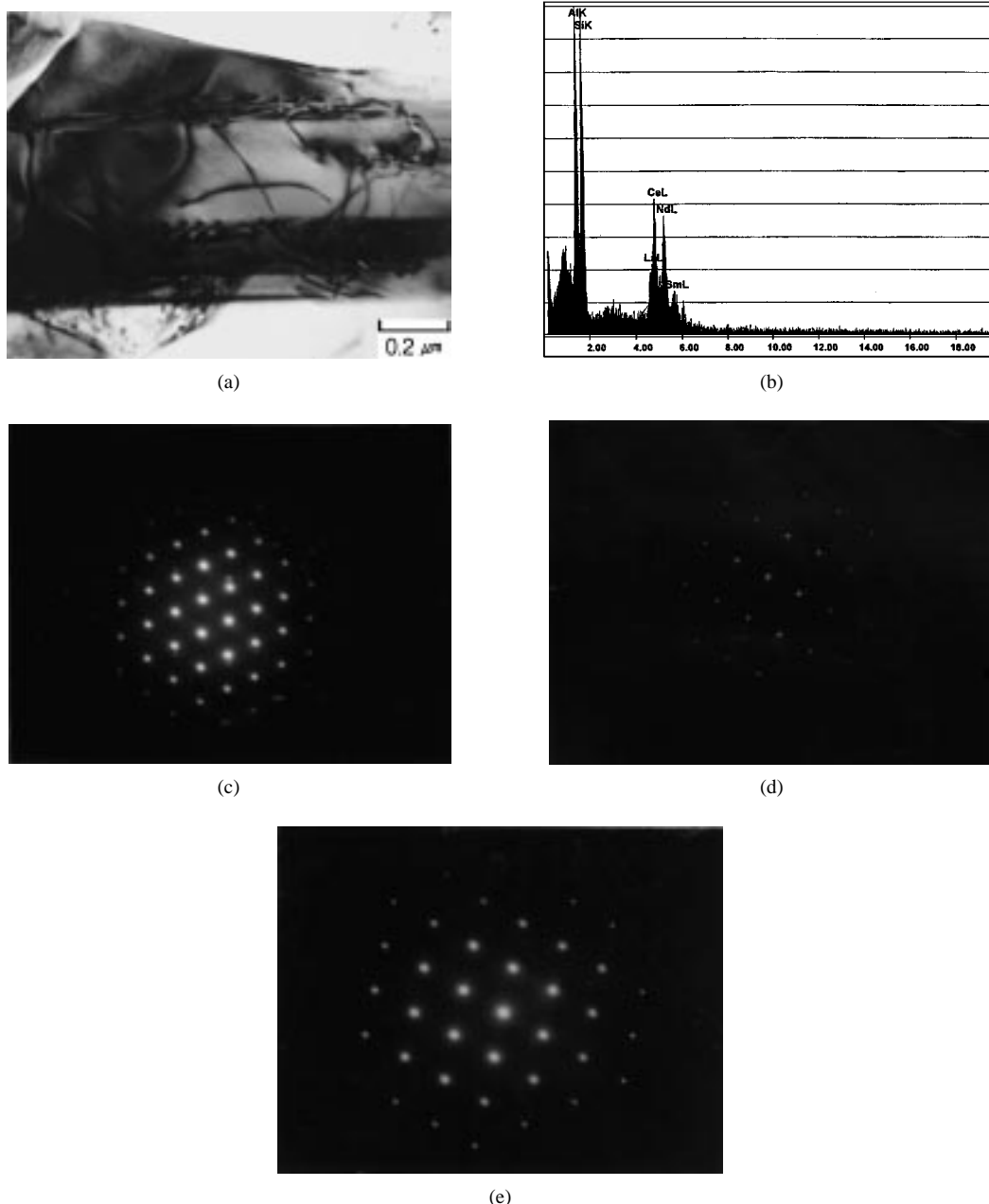
(a)

(b)

(c)

(d)

(e)

Figure 10 Bright field image, EDS spectrum and SAD patterns of the RE bearing particle, AlCe. Diffraction patterns can be indexed with the beam direction normal to $(2\,0\,\bar{1})$ for (c), $(\bar{1}2\,0)$ for (d) and $(14\,\bar{1})$ for (e).

is modified. Controversy still remains although most theories involve possible effects of modifying agent on the nucleation and/or growth of eutectic silicon during solidification [1, 7, 9].

One explanation for the modification of eutectic silicon by sodium is based on the concept that sodium may depress the eutectic temperature by as much as 12 °C and a finer microstructure is therefore to be expected because the rate of nucleation will be greater in the undercooled condition. Depression of the eutectic temperature implies that sodium reduces the potency of nucleating sites for the eutectic silicon [1]. One characteristic feature of eutectic modification is the depression of eutectic reaction temperature caused by the addition of modifying agent [14]. Many researchers believe that a modifier keeps nuclei from growing to stable nuclei until the temperature reaches the proper undercooled temperature. Many reasons have been given to explain

the modificaiton of the eutectic structure which accompanies the lowering of the eutectic arrest temperature, such as a decrease in the diffusion rate with a decrease in temperature, or limited growth due to the poisoning of the growth steps of silicon by the modifier [15]. Several theories have been proposed to account for the possible effect of sodium on the growth of silicon. For example, it has been suggested that sodium segregates at the periphery of growing silicon plates and prevents, or poisons further growth [1]. It can be concluded that a modifier should prevent nucleation of eutectic silicon phase and poison growth steps to achieve the proper modification.

It was clearly shown in our experiment that the eutectic reaction temperature was depressed as much as 2–7 °C with the addition of RE. Thus, nucleation occurs in the undercooled condition. Normally, crystal growth in diamond cubic systems, such as silicon, tends to be
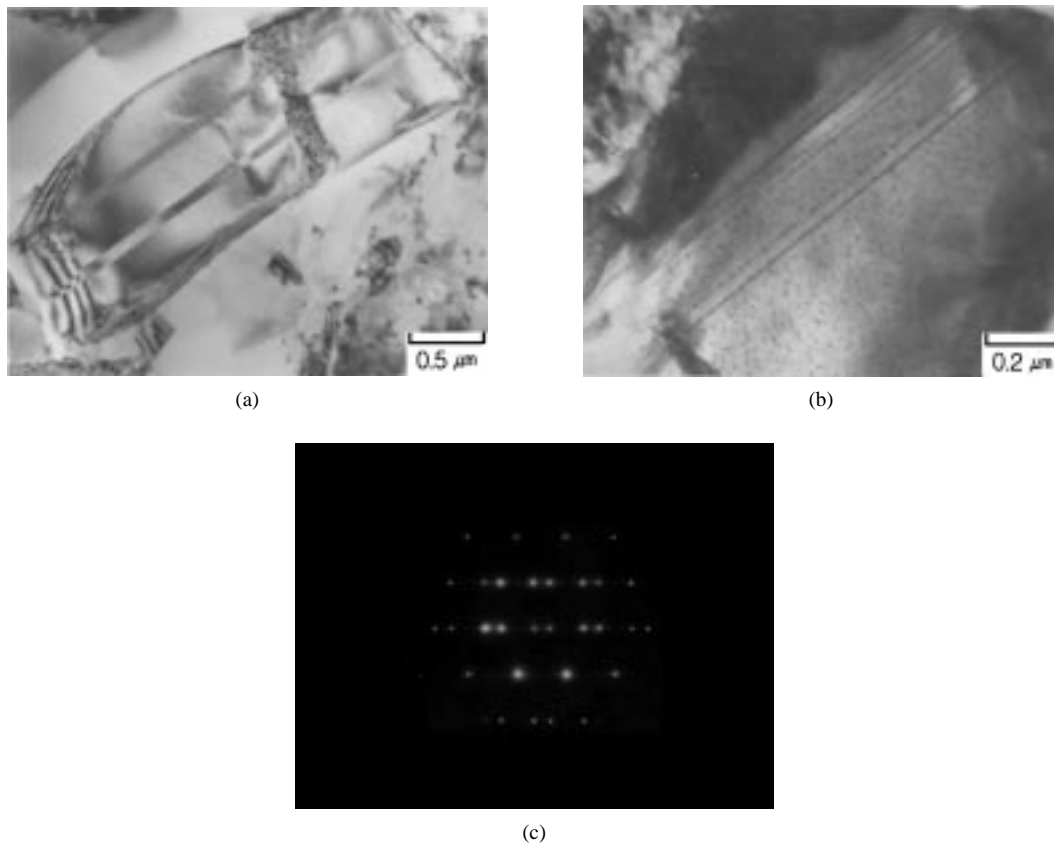
(a)

(b)

(c)

Figure 11 Transmission electron micrographs of the eutectic Si area of Al-21% Si alloy showing twinning.

highly anisotropic leading to the plate or flake form. The individual silicon flakes grow as flat platelets with plate surfaces parallel to internal (1 1 1) twin planes and it is established that this behavior conforms with the so-called twin plane re-entrant edge (TPRE) growth mechanism, in which the grooves between the (1 1 1) twin planes act as preferred sites for the attachment of silicon atoms. However, it is not clear whether the growth step was poisoned or not in our experiment with the addition of RE. Ye *et al*. [14], however, insisted (from the result that high lanthanide levels have been detected at the silicon and aluminum interface in the eutectic, which appears to support the adsorption of modifiers on the growth front) that lanthanides be adsorbed onto the fast growing (1 1 1) faces and effectively poison the growth steps, preventing the (1 1 1) faces from developing. Twin density is known to be much greater in modified eutectic silicon and this is thought to produce numerous alternative growth directions thereby leading to the desirable fibrous form of the silicon [1, 2]. In this experiment, twins were observed in eutectic silicon regardless of the addition of RE. However, the twin density of modified alloy did not seem to increase much compared to the unmodified one. It is more obvious with the help of X-ray diffraction result. If twinning is promoted by the poisoning effect of RE like the effect of sodium and strontium, the relative intensity of (1 1 1) peak is expected to be stronger because the extra intensity caused by twinning is added to the original (1 1 1) peak [16]. Thus, the overall change in twin density can be evaluated by measuring the relative intensity of each peak and comparing them with the standard diffraction

TABLE III Comparison of the relative intensity of {1 1 1} peak based on the intensity of {3 1 1} peak

Alloy	Intensity ratio (I_{111}/I_{311})
0RE	4.76
1RE	3.52
2RE	3.49
3RE	3.23
Ideal Si phase	3.33

from JCPDS card. Table III summarizes the relative intensity of {1 1 1} peak at each alloy compared to the intensity of {3 1 1} peak. The relative intensity of {1 1 1} peak does not show any increase with the addition of RE. Therefore, it is believed that RE does not increase the twin density.

Conclusively, the change in silicon morphology caused by the addition of RE is clearly different from the accepted mechanisms in that RE does not act as a nucleating agent in primary silicon and does not increase the twin density in eutectic silicon. From the above results, the refinement of primary silicon and modification of eutectic silicon in RE treated hypereutectic Al-Si alloys is supposed to be due to the suppression of the nucleation temperature of silicon phase and limited growth due to the decrease in diffusion rate with the decrease in growth temperature.

5. Conclusions

1. Simultaneous refinement of both primary silicon and eutectic silicon morphology is achieved with the

addition of rare earth (added as mischmetal) to hyper-eutectic Al-Si alloys.

2. The refining effect increases with the amount of rare earth addition and cooling rate within the range of the present study.

3. In the EPMA analysis no rare earth element is observed in the primary silicon crystal, although rare earth bearing particles determined to AlCe are observed around primary silicon in the matrix.

4. Unlike other modifier such as sodium and strontium, rare earth addition does not increase the twin density of the eutectic silicon.

5. The refinement of eutectic silicon in RE treated hypereutectic Al-Si alloys is supposed to be due to the suppression of the nucleation temperature of eutectic silicon phase and limited growth due to the decrease in diffusion rate with the decrease in growth temperature.

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