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# Modification effect of pure rare earth metal La on as-cast hypereutectic Al-17%Si alloys①

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**Abstract:** The modification effect of La addition on the microstructural characteristics of hypereutectic Al-17%Si alloys was studied. Microstructures were examined using conventional optical microscopy and electron probe X-ray microanalyzer. The morphology of Si crystal was evaluated by quantitative metallographical analysis. The results indicate that simultaneous modification to both primary and eutectic Si crystals is obtained by the addition of pure rare earth metal La in the hypereutectic Al-17%Si alloys while the optimal effect of La is obtained at a rather large scale. La begins to form intermetallic compound when its concentration exceeds approximately 1%, which appears as dark platelets in etched specimens. Electron probe X-ray microanalysis experiment shows that La-rich platelet could be represented as $Al_1Si_2La_2$ consisting of $LaSi_2$ and some unknown ternary $Al_xSi_yLa$ phase.

**Key words:** hypereutectic Al-Si alloy; casting; La; modification
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## 1 INTRODUCTION

Improved properties and lightweight are increasingly becoming the main goals of automotive and aerospace industries[1]. For the sake of achieving these characteristics, many efforts have been focused on aluminum alloys and their properties under severe conditions. Applying aluminum alloys to automotive parts such as pistons, cylinder liners, engine blocks and different parts of thermal motors, combinative improvement of the strength to mass ratio, wear resistance, heat resistance, and low heat expansion is an important goal[2]. Al-Si alloy is one type of potential candidate, which meets these demands. It is because that aluminum is extremely lightweight with excellent thermal and electrical conductivity characteristics and Si possesses low thermal expansion coefficient and outstanding wear resistance[3-6].

The microstructure of hypereutectic Al-Si alloys containing more than about 12% Si prepared by conventional casting routines normally consists of large plate-like acicular or lamellar eutectic Si phase with sharp sides and edges and very coarse primary Si phase, which are harmful to extrudability, machinability, strength and ductility because coarse Si phases (both eutectic and primary Si) lead to premature crack initiation and fracture in tension[7, 8]. To avoid these problems, structural modification must be done through elemental additions or/and processing alternatives to achieve fine Si phases with beneficial shapes.

It is well known that sodium and strontium are effective modifiers of the Al-Si eutectic, which have been put into commercial production of these alloys. However, it is difficult to control and maintain the modification effect of sodium because of the volatilization and oxidation loss, especially when longer holding time and higher temperature are required. Strontium does not confront this problem, but it is reported to result in micro- and macro-porosity in the cast Al-Si alloy[9]. Refinement of primary Si is usually achieved by the addition of phosphor to the melt. Some researchers also paid much attention to rare earth elements, which are reported also to be capable of modifying the Al-Si eutectic[7-12]. It has been proved that rare earth element is one kind of long effect refiners[9]. However, the modification effect of rare earth elements on primary Si morphology is still a rather controversial issue. Weiss and Loper[13] reported that Ce did not refine primary Si, but Ce had moderate effect on modifying eutectic Si. Kowata et al concluded that primary Si in a hypereutectic Al-20% Si alloy was refined with rare earth metals. Chang et al[7, 10] investigated the effects of mischmetal on Al-21%Si alloys and concluded that simultaneous refinement of both primary Si and eutectic Si morphology was achieved with the addition of rare earth (added as mischmetal) to hypereutectic Al-Si alloys.

However, many studies have been focused on the

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modifying effect of mischmetal on commercial alloys (i.e. A390). In order to make a better understanding of the role of rare earth element in Al-Si alloys, influential factors should be simplified. Therefore, the purpose of present investigation is to inspect the possibility of specific rare earth metal-lanthanum acting as a refiner of primary Si phase in pure hypereutectic Al-Si binary alloys and at the same time, to present some experimental proofs.

## 2 EXPERIMENTAL

The experimental alloys were prepared using high purity crystalline Si and high purity (99.9%) Al ingot except that Al-17Si binary alloy was made from industrially pure Al ingot. Rare earth metal was added as pure La to see its modification effect. Firstly, Al ingots were air heated and melt at approximately 700 ℃ in a clay/graphite crucible within a resistance heating furnace, then preheated Si crystals with the size from 1cm to 3 cm were added into the melt; secondly, temperature was rapidly increased to 850~900 ℃ and held for 30~60 min, puddling the melt once in a while; thirdly, the melt was degassed with hexachloroethane, cleared off dross, and standed for 8~10 min at approximately 750 ℃, then La was plunged and stirred into the melt, which was held for 30~40 min; at last, the melt was poured into metal mould at 690~730 ℃ after degassing again, clearing off dross, standing and temperature adjustment. Chemical composition of the prepared alloys is listed in Table 1.

**Table 1** Chemical composition of experimental alloys (mass fraction, %)

| Alloy | Al | Si | La |
|---|---|---|---|
| Al-17Si | Bal. | 16.72 | - |
| Al-17Si-0.3La | Bal. | 16.94 | 0.36 |
| Al-17Si-1.0La | Bal. | 16.74 | 1.32 |
| Al-17Si-3.0La | Bal. | 16.51 | 3.15 |
| Al-17Si-6.0La | Bal. | 17.00 | 6.00 |

Optical samples were polished through standard routines and observed using optical microscopy (LEICA MEF4A/M) fitted with quantitative metallographical equipment at different magnifications to see the morphology of Si in the alloys with or without La addition. The quantitative metallography was carried out to estimate the morphology of Si phases (size distribution and shape factor). 0.5% HF water solution was used as etchant of polishing samples. Deep etched specimens were examined in the scanning electron microscope, and electron probe X-ray microanalyzer (EPMA-8705QH2) to identify and analyze La-rich compound.

## 3 RESULTS AND DISCUSSION

In the optical microstructures (Fig. 1) of the unmodified Al-17Si binary alloy, feathery and star-shaped primary Si crystals are evident instead of coarse hexagonal and platelet primary Si crystals usually present in hypereutectic Al-Si Alloys, while eutectic Si crystals are dispersed as strongly elongated needles throughout the remaining structure. It seems that the present experimental conditions are rather suitable to feathery and star-shaped morphologies formation. It suggests that the morphology of primary Si crystal is very sensitive to the cooling conditions. The appearance of this special five-pointed star-shaped morphology is unique because fivefold symmetry is impossible in cubic crystals (Si, for instance, has a diamond cubic crystal structure[13]). Weiss et al[13] reported several forms of star-shaped morphology of primary Si phase. However, only one form of star-shaped primary Si crystal, the fivefold symmetry as radial growth alone, is observed in our present study. Note that each branch of every five-pointed crystal is composed of many thin strip Si crystals instead of few coarse platelets in the case of Weiss. Above analysis implies that those coarse platelet branches of five-pointed primary Si crystals in Weiss's experiment may be deprived from the coalesce of those thin strip Si crystals within each branch in present study due to the decrease of cooling rate. It has been suggested that crystals nucleated at twinned decahedral nucleus tend to grow as star-shaped morphology at moderate cooling rate, that is, five Si crystals in twinned orientation stop to grow when they meet together, resulting in an assembly of their five-pointed star-shaped Si crystal[10, 14]. But the formation mechanism of star shaped morphology needs further investigations. Another common morphology of primary Si crystal is feathery morphology, which is present in all casting areas. It is noteworthy that the size of feathery Si crystal is within a wide range: some of the feathery Si crystals are large and some of them are so small that the feathers even can not be distinguished under some certain magnification (Fig. 1(b)); and some of the feathery Si crystals are connected with each other. It is also clearly observed that feathers at opposite side of each feathery Si crystal grow along different orientations, which are not symmetrical either.

The modification effects of La addition on the microstructure of Al-17Si alloy are shown in the optical micrographs exhibited in Fig. 2. 0.3% La (mass fraction) addition begins to take effect and act as modifier for both primary and eutectic Si

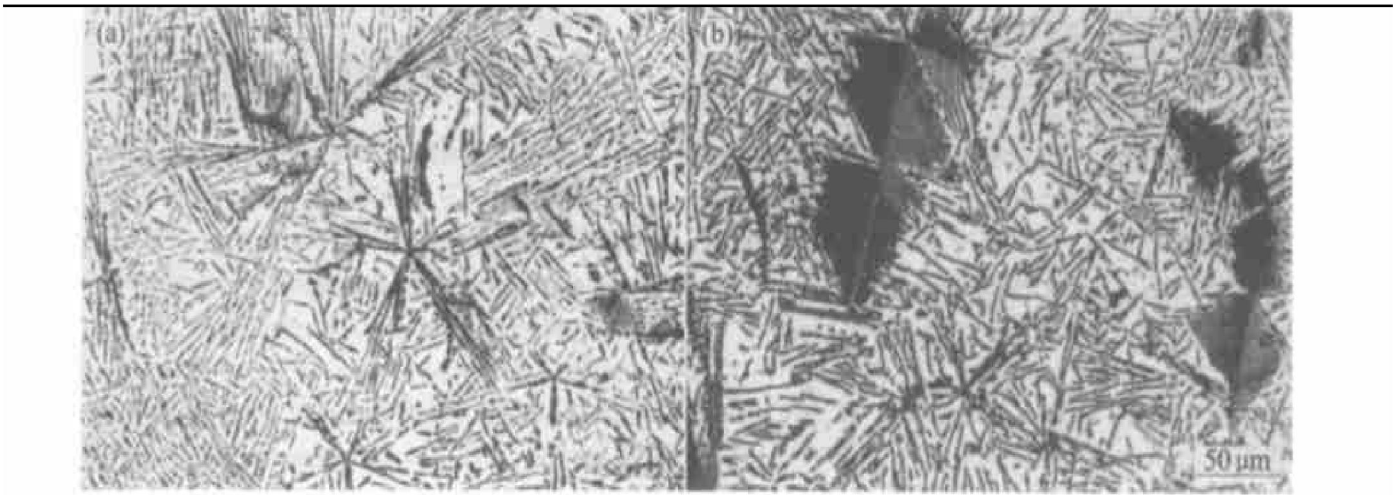


**Fig. 1** Optical micrographs of unmodified Al-17Si alloy
(a) —Star-shaped morphology of primary Si crystal, unetched;
(b) —Feathery morphology of primary Si crystal.

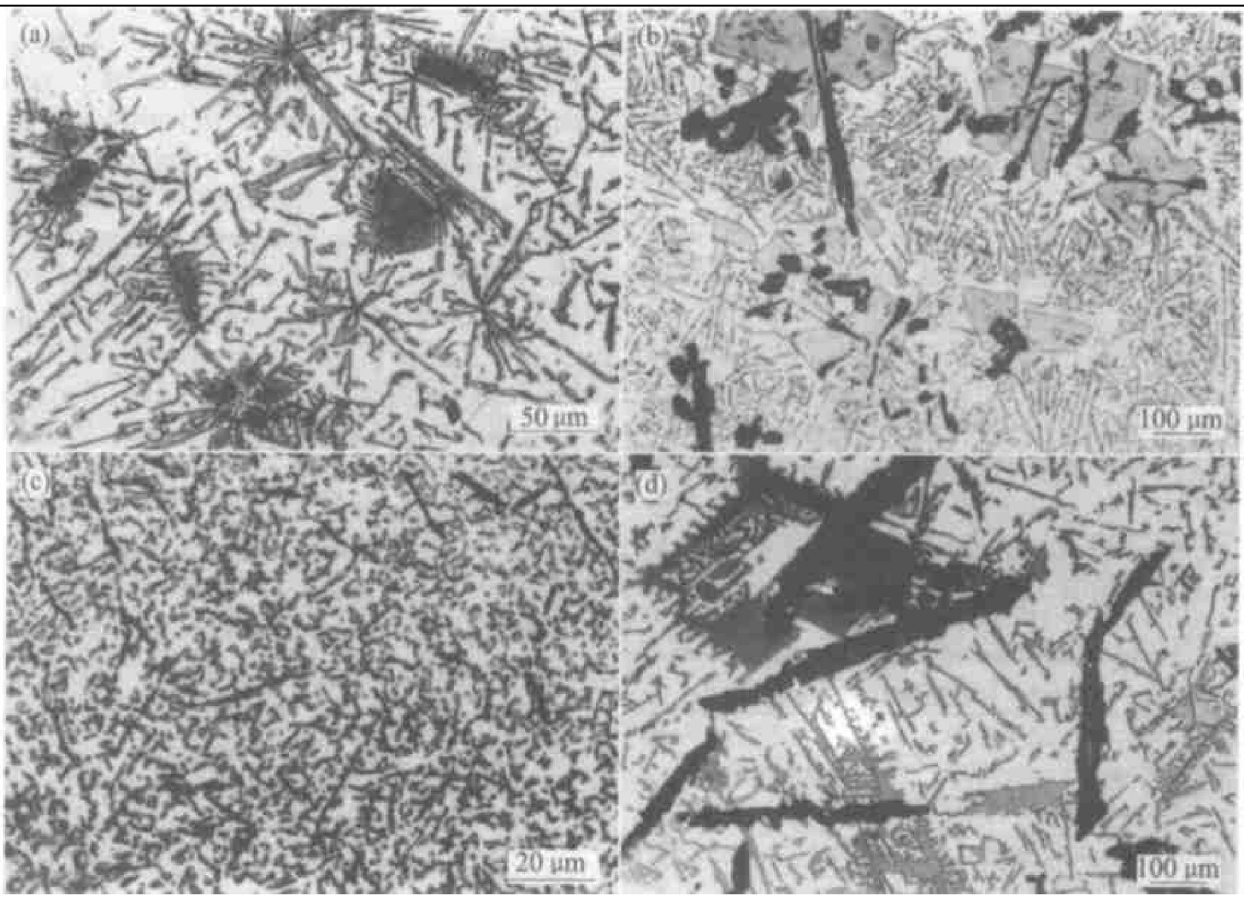


**Fig. 2** Microstructrures of Al-17Si-$x$La alloy with different additions of La (Dark phase is $Al_1Si_2La_2$)
(a) —Al-17Si-0.3La, etched, 0.5% HF; (b) —Al-17Si-1.3La, etched, 0.5% HF;
(c) —Al-17Si-3.3La, etched, 0.5% HF; (d) —Al-17Si-6.0La, etched, 0.5% HF.

crystals, which results in a smaller phase density and underdeveloped primary Si crystals compared to base alloy without La addition. However, the microstructural characteristics are similar to those of base alloy. It suggests that 0.3% La addition partially modifies Si crystals in Al-17Si alloy. Fig. 2 (b) indicates that La begins to form intermetallic compound, which appear as dark platelets or large particles, when its concentration exceeds about 1%. What is interesting is that the feathery and star-shaped morphologies of primary Si crystals are substituted by polygonal morphology that is absent in the microstructure of previous two alloys (La-free base alloy and 0.3% La-containing alloy). Furthermore, coarse polygonal Si crystals are always attached by coarse La-containing intermetallics. Remaining Si crystals are significantly modified by 1% La addition. Note that some of small primary Si particles are covered by La-containing intermetallics, as is more remarkable in alloy Al-17Si-6La (Fig. 2(d)). The relationship between polygonal Si crystals and coarse platelet-like La-containing intermetallics needs further confirmation and investigation. But it is obvious that coarse La-containing intermetallics are always staying with coarse Si crystal, while smaller La-containing intermetallic with smaller Si crystal. The optimal modification effect is obtained when about 3% La is added (Fig. 2(c)). Si crystals with large aspect ratios are drastically changed to fine equiaxed Si particles. It is impossible to differentiate between primary and eutectic Si crystals. Small needle-like La-containing phases, larger than Si particles though, distribute uniformly in all sections of the alloy with the addition of 3% La. Similar modification results are observed in Al-17Si-6La compared with Al-17Si-La, with microstructure consisting of polygonal, underdeveloped feathery and dendritic primary Si crystals, and modified needle-like eutectic Si crystals. The phenomenon of Si platelet covered by La-containing phase is more prevalent. The La-containing phase is larger. It implies that 6% La addition is excessive in modifying hypereutectic Al-17Si alloy.

Electron probe X-ray microanalysis experiment was carried out on the sample containing 6% La in which La-rich platelet is easy to confine electron probe on pure La-rich platelet for its large size. Concentration profile of La-rich platelet (Fig. 3) shows that La-rich platelet contains La, Al and Si atoms, which can be represented as a ternary $Al_1Si_2La_2$. It is different from the $Al_2Si_2RE$ reported by Chang et al[10]. Comparing X-ray diffraction patterns of Al-17Si and Al-17Si-6La alloys shown in Fig. 4, $LaSi_2$ phase is confirmed present in Al-17Si-6La alloy. However, there still have some unidentified peaks that do not conform to any of the peaks of Al-La or Al-Si or Si-La binary phases. Sharan et al[11, 15, 16] reported that mischmetal could easily form intermetallics with Al and Si. Therefore, it is suggested that these La-rich platelets are mixture of $LaSi_2$ and some unknown ternary $Al_x$ $Si_y$ La intermetallic compound. Obviously, this

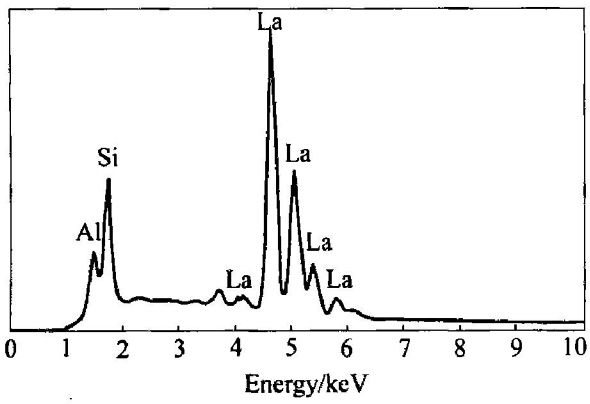


**Fig. 3** EDAX spectrum corresponding to La enrich intermetallic compound taken from Al-17Si-6.0La Alloy

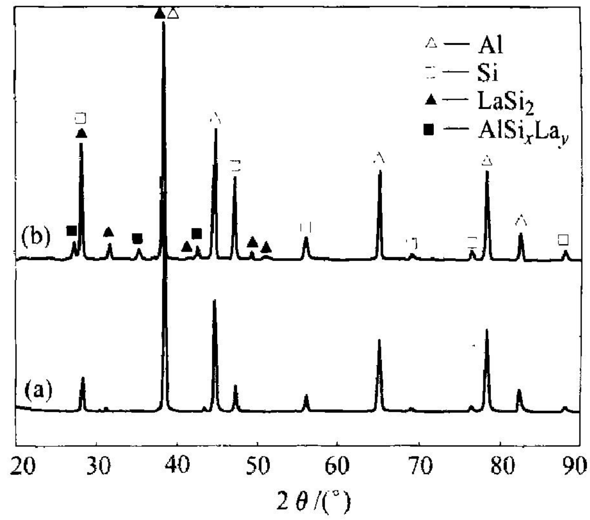


**Fig. 4** XRD patterns of Al-17Si (a) and Al-17Si-6La (b)

problem needs further investigation. Generally, it is possible to produce hypereutectic Al-Si alloy containing fine, polygonal Si crystals through suppressing their directional growth, either through poisoning the surface of Si nucleus in the melt, or through increasing their surface energy. It is well known that the content of rare earth element inside primary Si crystal is so small that it can be negligible. Thus, the former mechanism maybe the dominant one in modification. The average diffusion coefficient of La (less than 0.2%) at 973 K in eutectic Al-12.7% Si alloy was reported to be $(1.01 \pm 0.02) \times 10^{-5}$ $cm^2/s$. The average diffusion coefficient of another modification element Sr at the same condition is $(1.79 \pm 0.12) \times 10^{-5}$ $cm^2/s$. In our present study, the concentrations of La are far larger than 0.2%, so it is reasonable to conclude that the diffusion of La atom is rather slow. La atoms are rejected from the primary Si crystals, resulting in La enriched zone between two adjacent primary Si crystals. If the enriched La atoms enclose the growing Si crystals, the growth of some primary Si crystals would be stopped by the surrounding $Al_1Si_2La_2$, which make it difficult for external Si atoms to diffuse through intermetallics into internal Si crystal. Some other La atoms, which do not encapsulate Si crystals, form small needle-like $Al_1Si_2La_2$ intermetallics to inhibit the formation of large Si crystals. If the aggregation of La happens, very large $Al_1Si_2La_2$ intermetallics without any suppression effect to the growth of primary Si crystals appear and promote the formation of large Si crystal.

The quantitative metallography has been adopted to judge the modification effect of La on the experimental alloys. The results are exihibited in Fig. 5, which is reflected by equivalent diameter ($D_{equ}$) and aspect ratio ($R_{l/b}$) of the Si crystals.

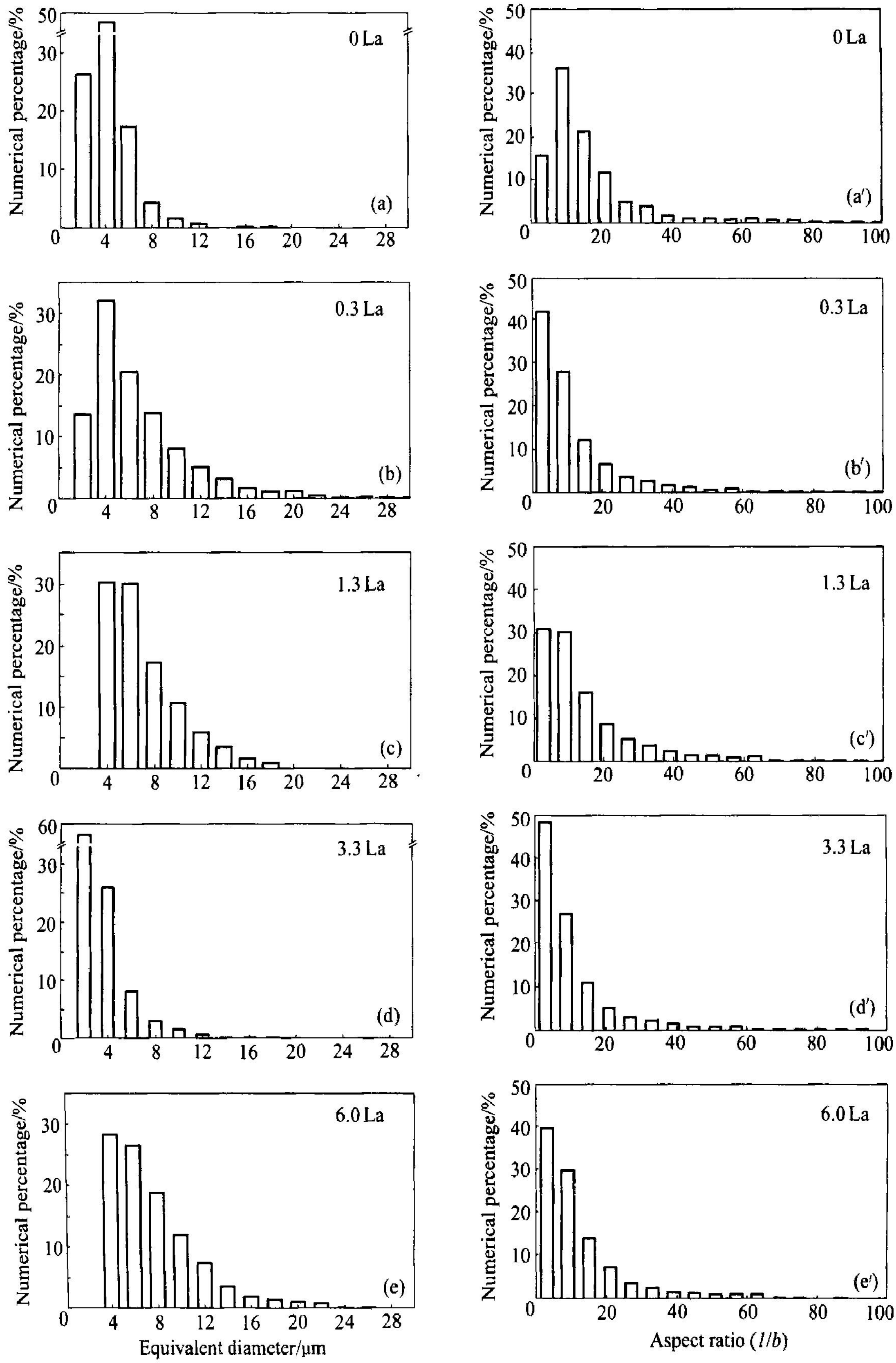


**Fig. 5** Histograms of equivalent diameter (a) ~ (e) and aspect ratios ((a′) ~ (e′)) of alloys with different concentrations of La

The smaller $R_{l/b}$ is, the less sharpen the object is. Because some of the complex unmodified Si crystals are concave objects, special parameters should be chosen to represent the modification effect of La. The size of the Si crystals is determined using the parameter of equivalent diameter ($D_{equ}$). The morphological modification is characterized by the parameter of aspect ratio ($R_{l/b}$), which defines the length ($l$)-towidth ($b$) ratio. Above parameters have the following relationships with perimeter ($p$) and area ($a$) of the object:

$$D_{equ} = 2 \times \sqrt{a/\pi} \quad (1)$$

$$l = (p + \sqrt{p^2 - 16 \times a})/4 \quad (2)$$

$$b = (p - \sqrt{p^2 - 16 \times a})/4 \quad (3)$$

$$R = l/b \quad (4)$$

One thing should be pointed out is that the following Si crystals could not be counted: the distance between two adjacent Si platelets is too small to be differentiated and counted (feathery primary and lamellar eutectic Si crystals in Al-17Si and Al-17Si-0.3La alloys, Fig. 1(a) and Fig. 2(a)). Therefore, the proportions of both small $D_{equ}$ and small $R_{l/b}$ of these two alloys (especially of Al-17Si) appear larger. Big primary Si crystals are too large to be incorporated into one viewing field together with other small Si crystals (polygonal primary Si crystals in Al-17Si-1.3La and Al-17Si-6.0La alloys, Fig. 2(b) and Fig. 2(d).

The thin-needle morphology of Si crystals is greatly changed by the addition of La, which is confirmed by the notable increase of small aspect ratios of Si crystals (see Fig. 5($a'$)-($e'$)). For instance, the aspect ratios below 4 of La-free base alloy account for 6.5%, while the figure is 26% for Al-17Si-0.3La, 17% for Al-17Si-1.3La, 31% for Al-17Si-3.3La, 23% for Al-17Si-6.0La, respectively. It suggests the modification effect of La on Si crystals. Because the eutectic Si crystals in Al-17Si alloy are so thin (see Fig. 1(a)) that the proportion of their $D_{equ}$ below about 4 μm is relatively larger. The additions of 0.3% La, 1.3% La and 6% La result in the increase of the equivalent diameters of Si crystals. It can be concluded that the optimal modification effect is obtained by 3% La addition with the biggest proportion of small $D_{equ}$ (e.g. below 6 μm) and the biggest proportion of small $R_{l/b}$ (e.g. below 4 μm), as is in agreement with the conclusion resulting from the microstructural analysis. 0.3% La addition is not enough to modify Si crystals. The modification effects of 1.3% and 6% La additions are unsatisfactory for the local aggregation of La.

## 4 CONCLUSIONS

1) Cooling conditions have important influence on the microstructure of unmodified hypereutectic Al-Si alloy. In the optical microstructure of Al-17Si without La, feathery and star-shaped primary Si crystals with different sizes are observed instead of coarse hexagonal and platelet primary Si crystals, while eutectic Si crystals are dispersed as strongly elongated needles throughout the remaining structure.

2) Simultaneous modification to both primary and eutectic Si crystals is obtained by the addition of La to the hypereutectic Al-17Si alloys. However, the optimal amount of La required to achieve optimal modification effect is rather large (3.3%), in which the morphologies of eutectic and primary Si are totally changed to fine Si particles with smaller aspect ratios. The modification effects do not seem to be in direct proportion to the concentration of La. Addition of 0.3% La results in a partial modification effect. Very large polygonal primary Si crystals appear as the La addition level approaches 1.3% or 6.0%, therefore, the modification effect in either of these two alloys is far more satisfactory.

3) La begins to form intermetallic compound when its concentration exceeds approximately 1%, which appear as dark platelets or large particles. Electron probe X-ray microanalysis experiment showed that La-rich platelet could be represented as a ternary $Al_1Si_2La_2$, which contains $LaSi_2$ phase and some unknown ternary $Al_xSi_yLa$ phase. Note that large La enriched compounds are covering or attached onto primary Si crystals, while other relative small La enriched compounds separately distribute in the matrix.

4) If the enriched La atoms enclose growing Si crystals, the growth of some primary Si crystals would be suppressed by surrounding $Al_1Si_2La_2$ intermetallics, which make it difficult for external Si atoms to diffuse through intermetallics onto internal Si crystal. Some other La atoms, which do not encapsulate Si crystals, form small needle-like $Al_1Si_2La_2$ intermetallics to confine the growth of Si crystals within a small range. If severe aggregation of La happens, very large $Al_1Si_2La_2$ intermetallics without any suppression effect to the growth of primary Si crystal appear. This in turn, promotes the formation of large Si crystal.

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