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Distributions of Sr and Fe and their influence on modification of hypoeutectic Al-Si alloy

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Abstract: The influence of cooling rate and Fe-containing phases on Sr-modification of Si phases in hypoeutectic Al-Si alloys, a problem with great industrial importance, was investigated. The microstructures of samples were examined using scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX). A new method of electron probe microanalysis (EPMA) map scanning was used to analyze the Sr distribution, which gave quantitative results covering more Si particles. EPMA map scanning, together with SEM with EDX, was also used in analyzing the distribution of Fe phases. Results show that Fe-containing phase was related to the unmodified Si particles in samples with partial modification failure and the plate-like Si phases in samples without modification failure. Such a relationship was further confirmed by the microstructure observation. In conclusion, a partial failure of Sr-modification can be caused by both slow cooling rate and Fe-containing phases.

Key words: Al-Si Alloys; cooling rate; modification theory; Sr segregation; Fe-contained phases

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Hypoeutectic Al-Si alloys are among the most important materials in modern industry [1]. Generally these alloys consist of two main parts: the primary dendrites of α-Al and between them the Al-Si eutectic, in which the brittle Si phases with various morphologies play a crucial role in the mechanical properties of the whole material. Some elements, such as Na, were found to be effective additives in Al-Si alloys as early as the 1920s [2], bringing significant improvement in mechanical properties, which was then proved as a result of the change in the morphology of Si phases, namely the modification of Si phases. Among the modifiers that have been found, Sr is widely used in modern industry.

The industrially important Sr-modification of Si phases in Al-Si alloys has been a focus of researchers for decades, with several important theories introduced to explain this phenomenon [3]. There is, however, still no commonly accepted understanding of the modification mechanism. Besides, complex factors are involved in the industrial production of casting Al-Si alloys, which bring many problems. One of them is the temperature of the molds, which has a great influence on the morphology of Si, and the final properties of the material. A relatively high mold temperature will sometimes lead to the loss of Sr modification effectiveness. Much attention has been paid on either the cooling rate [4, 5], or the addition of modifiers during the casting, while little has been paid on the simultaneous influence of them both. The failure of modification with a high mold temperature is a big problem, since it is a common situation in the process of die-casting manufacture. The solving of this problem will also deepen the understanding of Sr-modification.

The mold temperature will influence the cooling rate during the solidification, and probably the distribution of Sr, which it is suggested may segregate in Si phases [6]. This suggestion also corresponds to the the impurity-induced twinning theory [7], one of the most convincing explanations of the modification of Si, especially in conventional casting Al-Si alloys. The real distribution of Sr in Al-Si alloys, however, has remained unknown until recent years, due to the extremely low content of Sr.

Nogita et al [8] got the distribution of Sr in an Al-10Si-1Cu alloy with 250 ppm Sr addition using a μ-XRF (X-ray fluorescence) analysis. In recent years, researchers also used the fast developing EPMA (electron probe microanalysis) technique to analyze the distribution of Sr, and many important achievements have been made by Faraji et al [9], and Kim et al [10]. SIMS (secondary ion mass spectrometry) is an important surface analysis method, and the study by Simensen et al [11], using

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the NanoSIMS technique, was a good reference in this area, though applied to a different situation. In the atomic resolution, Timpel et al [12] and Li et al [13] succeeded in describing the segregation of Sr using APT (atom probe tomography) and TEM (transmission electron microscopy), and their work offered a strong support for the impurity-induced twinning theory.

Though great achievements were made by previous researchers, there were still some limitations in the results. For example, the study by Faraji [9] used line scanning mode of EPMA, and although map scanning analysis was carried out in some studies [8,10,12,13], only a small area was analyzed. The results achieved by those methods could only cover a range of no more than 10 μm, the size of one or two silicon particles, and cannot be used to compare different samples. The scales taken sometimes were limited by the methods used. Also, with the range of scanning enlarged, the interference of noise would be a serious problem due to the extremely low content of Sr, and might be a reason why researchers until now chose to limit the analysis range to a very small scale. To study the influence of cooling rate on the distribution of Sr, a new method should be introduced.

Besides, impurities are common in commercial alloys. For example, Fe exists universally in most commercial Al-Si alloys, and is known to be able to form several kinds of intermetallics with elements such as Al and Si. Shankar et al[14] made a detailed research on the relationship between Fe containing intermetallic and eutectic Si phases, and suggested an adhering relationship between the two kinds of phases. This theory is supported by the research of Zhang et al [15] and Li et al. [16], who observed the β-AlFeSi as the core of growth or nucleation site of Si particles.

The Fe-containing phases in Al-Si alloys are suggested to be sensitive to the cooling rate [17] and would change in both shape and size with different mold temperatures. With a relatively low mold temperature, Fe-containing phases would refine the eutectic cells without any negative effects, as reported in Zhang's work [15]. With a slower cooling rate, however, Fe-containing phases would probably influence the modification of Si, and therefore should be studied.

In this research, several samples were designed and prepared to study the simultaneous influence of factors such as Sr-modifier, cooling rate and impurities such as Fe on the Si phase in Al-8Si alloy. A new method of line scanning mode of EPMA was used, and several other contrast experiments were designed.

1 Experimental procedure

Two groups of samples were designed in this experiment, slightly varied on the basis of hypoeutectic Al-8Si alloy. Samples of the first group were prepared using commercial pure aluminum and commercial Al-Si master alloy, with impurities in both of them; whereas those of the second group were prepared using high-purity aluminum (99.99%) and silicon (99.999%), in order to eliminate the possible interference of impurities such as Fe.

Each group consisted of 4 samples, solidified at 4 different cooling rates, which were achieved by keeping the mold at different temperatures: 873 K (600 ºC), 673 K (400 ºC), 473 K (200 ºC) and room temperature (*ca.* 300 K). This method simulated the conditions of actual production rather than making cooling rates extremely fast or slow. The mold, with a thickness of 20 mm, was made of medium-carbon steel, and can produce ingots weighing about 100 g.

The source of strontium was commercial Al-Sr master alloy. Master alloy of the same origin was added to both groups of samples. Only a small amount, approximately 0.5 g in an ingot of 100 g was used, thereby it would not make a significant impact on the high-purity samples of the second group.

Samples of each group went through similar processes of melting and solidification. Raw materials except the Al-Sr master alloy were put in an Al_2O_3 crucible, and heated to 1,053 K (780 ºC) in a box-type resistance furnace. The melt was kept at 1053 K (780 ºC) for at least 30 min, after which the Al-Sr master alloy was added. Then the temperature was held for another 10 min. The melt was poured at 963 K (690 ºC) after deslagging. Considering the burning loss of strontium is sensitive to the holding time, samples were made in turn rather than together. Several thermocouples were used to get an accurate temperature control.

There were some different details in the preparation of the two groups of samples. To remove the oxide inclusion contained in commercial alloys, refining was needed for the samples of the first group before the addition of Al-Sr master alloy, but this was unnecessary for those made from high-purity materials. In this experiment, refining was made by adding 0.3 g agent (commercial, mainly KCl-$MgCl_2$) into each sample and the melt was fully stirred and held for 10 min. After that the floating refining agent was skimmed as slag. Also, the silicon used in the second group, which was hard to melt and easy to burn, should be carefully prepared and loaded.

All the samples were taken from the lower part of the ingots, as shown in Fig. 1, and the observed plane was about 1 cm above the bottom. After machining, all the samples were electrolytically polished on the observed plane.

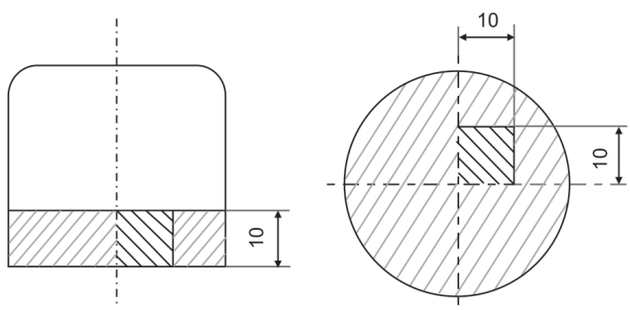

Fig. 1: Sketch of sampling location (unit: mm)

All the samples prepared were observed using a scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDX), and images at different magnifications were taken. Some of the samples were analyzed using electron probe microanalysis (EPMA) map scanning. Atomic emission spectroscopy (AES) was used to study the concentration of impurities in samples of both groups.

2 Results and discussion

Figure 2 shows the SEM microstructure of the first group samples, which were Sr-modified Al-8Si alloys made from commercial raw materials and solidified in molds of temperatures from 600 ºC to room temperature. Generally, these Sr-added samples have the modified Si phases and a higher cooling rate producing smaller grains and phases.

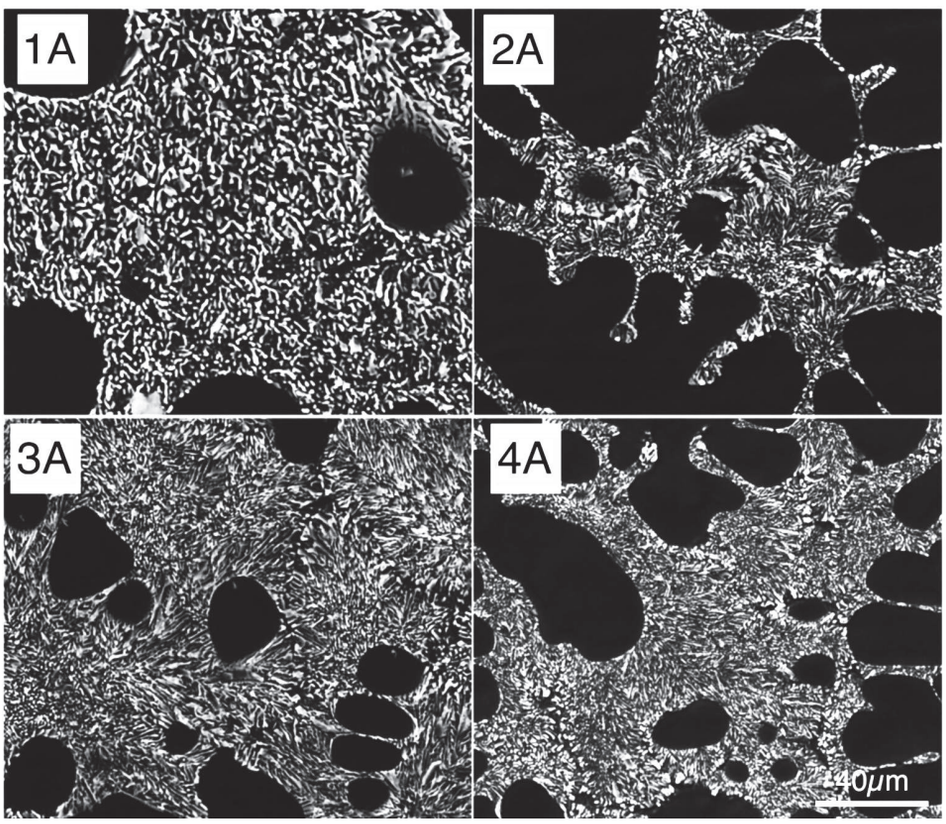

Fig. 2: SEM images of samples made of commercial pure raw materials: (1A) solidified in mold at 873 K (600 ºC); (2A) 673 K (400 ºC); (3A) 473 K (200 ºC); (4A) room temperature (*ca.* 300 K)

It is noteworthy that in the sample with the slowest cooling rate (sample 1A), the result of modification was obviously different from the others. As shown in Fig. 3, in sample 1A there are areas of modified and unmodified Si particles, and the unmodified parts irregularly spread among the modified ones.

Since an important difference between samples is that they were solidified at different cooling rates, it is possible that they have different levels of Sr segregation. EPMA was used to analyze the distribution of Sr, and similar to the result of Kim et al [10], it was found that Sr segregation strongly correlated to the distribution of Si particles. Figure 4 is an example of EPMA results.

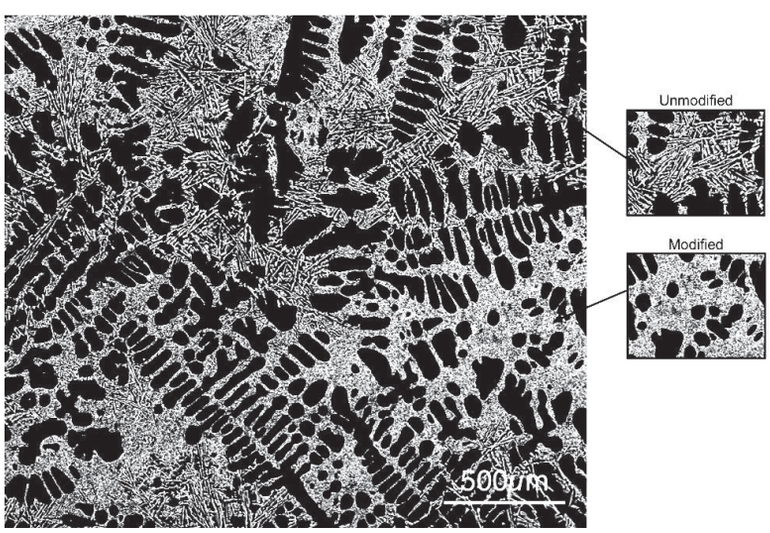

Fig. 3: SEM image of sample 1A (commercial, 873 K) with a lower magnification

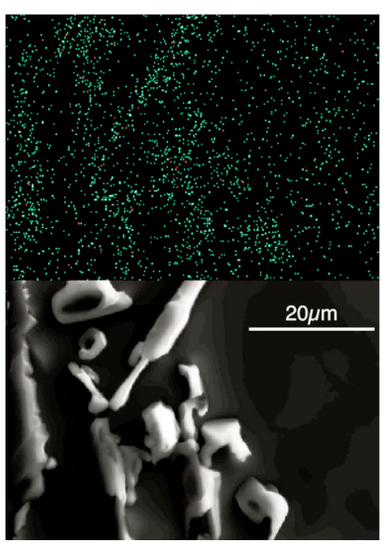

Fig. 4: EPMA image (Sr) of sample 1A (commercial, 873 K) and secondary electron image at same position

The EPMA results, covering an area of several micrometers or a few Si particles, were able to prove the segregation of Sr, but had limited persuasiveness. Also, such results could not be used for comparison between the modified and unmodified parts in the slow-solidified sample, or among different samples. To solve this problem, a new mode of scanning was adopted by moving the samples instead of the detector during the scanning process, and Fig. 5 shows the results. For each sample, a squared area of the profile with a side about 200 μm long was analyzed, which contained a large number of particles, and by this method both the modified and unmodified areas of samples could be shown in one image.

As shown in Fig. 5, this method of scanning had obvious disadvantages compared with the previous one, with a serious amount of noise due to the low content of Sr, and the segregation of Sr could not be observed as clearly as in Fig. 4. If the two images (the EPMA image of Sr and the secondary electron image of the same position) of each sample were super-imposed, as shown in Fig. 6, the relationship between the distribution of Sr and Si phases became clear. In Fig. 6, the dark area shows the position of Si particles, while the translucent red part is the Al matrix, The dark area (Si) contains points of Sr signals that are more densely distributed than the translucent red area (Al), as shown in Fig. 6.

Since the results of EPMA were given in the form of bitmap images, with every point on the image corresponding to an analyzed area of the samples, the superimposed pictures could be used for statistical analysis. For instance, in either red or black part of sample 1A, the total number of points and the number of Sr points were calculated by classifying and counting points of different colors. In the Si part (dark), there were 166,431 points and 22,857 of them were Sr points. In the Al part (red), the numbers were 83,569 and 5,162 respectively. The statistical results of all the four samples are listed in Table 1. EPMA results were cut into 500 pixels × 500 pixels squares for further analysis; thus there were exactly 250,000 points in each image.

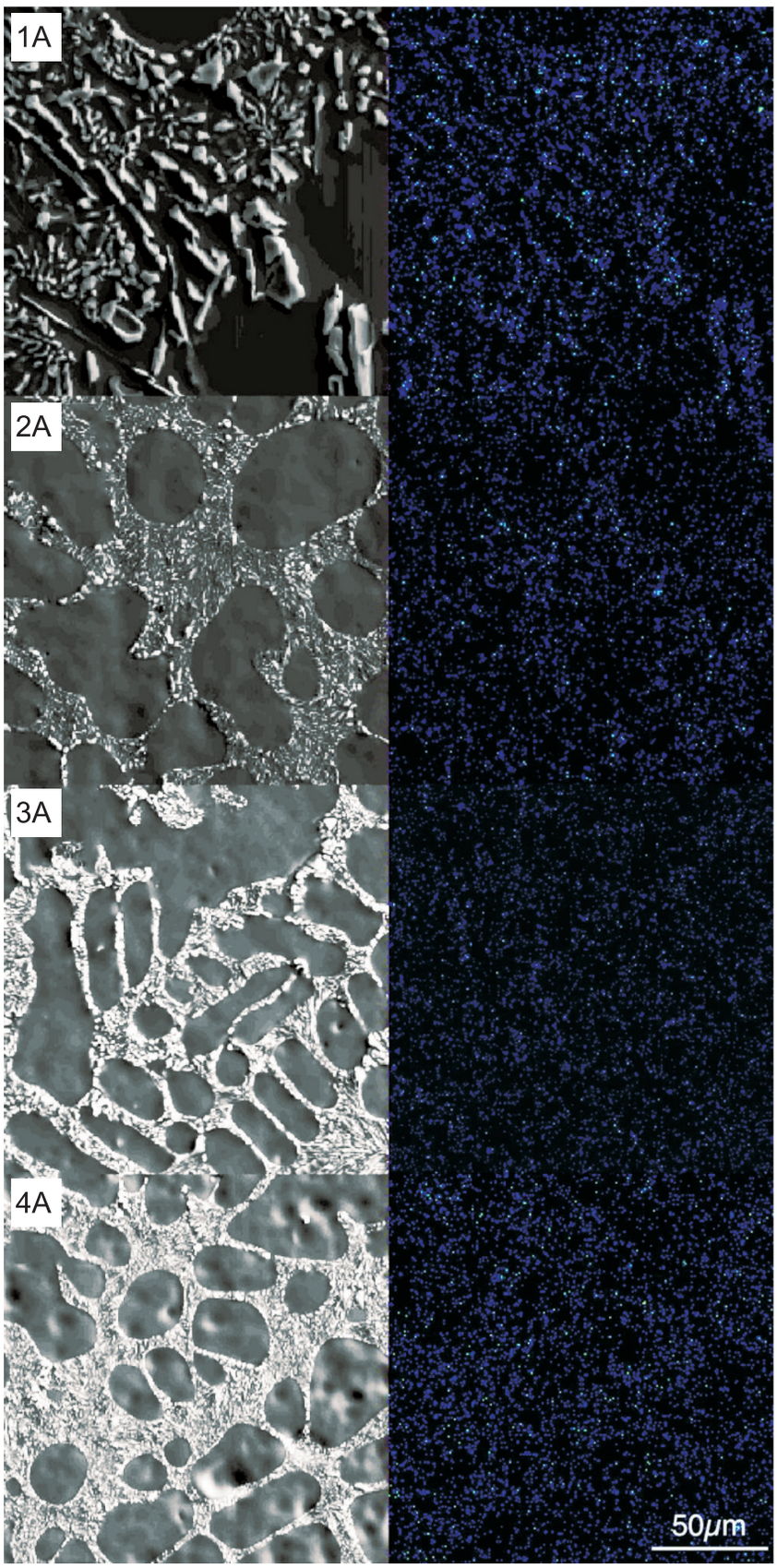

Fig. 5: EPMA images showing distribution of Sr in samples made of commercial pure raw materials with secondary electron images: (1A) solidified in mold at 873 K (600 ºC); (2A) 673 K (400 ºC); (3A) 473 K (200 ºC); (4A) room temperature (*ca.* 300 K)

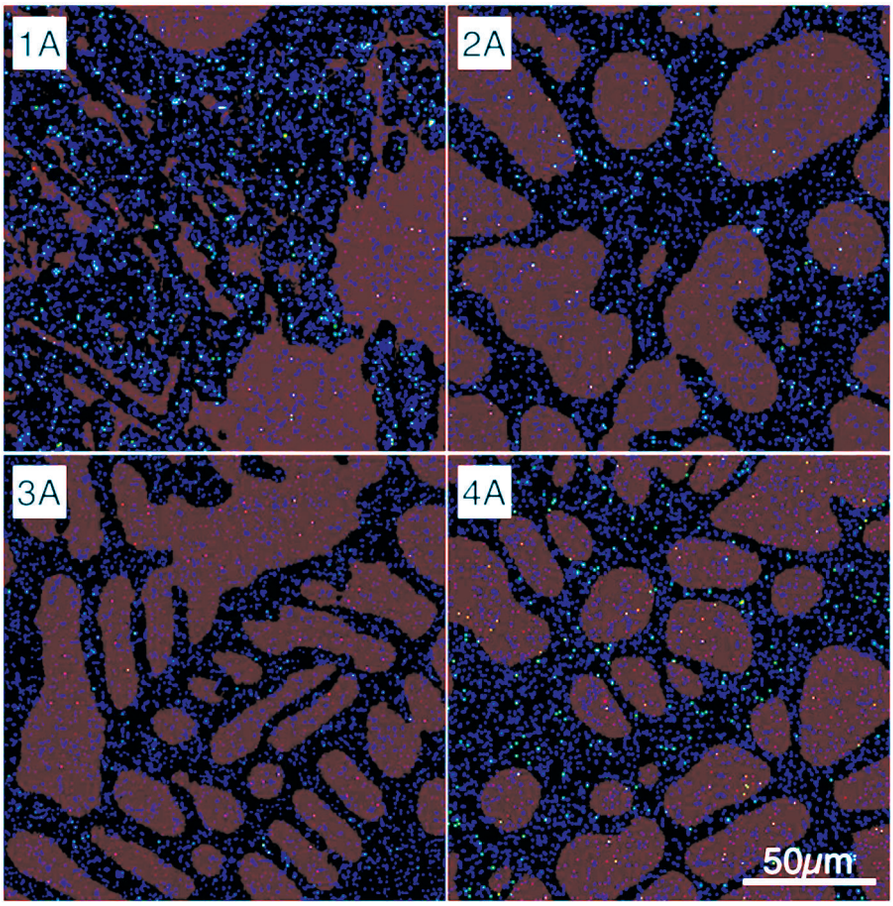

Fig. 6: Superimposed images (EPMA image and secondary electron image at same position) of samples in Fig. 5: (1A) solidified in mold at 873 K (600 °C); (2A) 673 K (400 °C); (3A) 473 K (200 °C); (4A) room temperature (*ca.* 300 K)

Table 1: Statistical results of images in Fig. 6

Sample	Si area			Al area		
	All points	Sr points	Sr ratio	All points	Sr points	Sr ratio
1A	166,431	22,857	13.73%	83,569	5,162	6.18%
2A	113,563	12,468	10.98%	136,437	8,496	6.23%
3A	112,166	10,807	9.63%	137,834	8,335	6.05%
4A	124,456	12,634	10.15%	125,544	7,715	6.15%

Results in Table 1 shows that Sr segregates in Si phases. Most previous studies used the line scanning method, or map scanning in a quite small area, possibly in order to avoid the noise caused by the low concentration of Sr. Those results usually covered only one or two Si particles, and their persuasiveness was relatively limited. In this work, statistical data was used to eliminate noise and the segregation of Sr was successfully proved in a relatively larger area covering more Si particles along with the Al matrix around them.

Another advantage of this method is that the quantitative results can be used for the comparison of different samples. As shown in Table 1, there is no obvious evidence proving that a lower cooling rate might influence the segregation of Sr in Si, and then lead to the partial failure of modification. Further, the sample with the lowest cooling rate even had the highest concentration of Sr points in the Si area. Also, no obvious difference could be seen in Fig. 6 between the modified parts and the unmodified parts in Sample 1A (commercial, 873 K). Thus the possible difference of Sr segregation caused by different cooling rates could not explain the partial failure of modification in Sample 1A.

Since Fe is an important impurity element in Al-Si alloys and Fe-containing phases are possible nuclei for Si phases, EPMA was used to analyze the distribution of Fe in the 'border' area of the unmodified part and modified part of Sample 1A (commercial, 873 K). Figure 7 contains two pairs of the pictures, and both of them show the the distribution of Fe and the secondary electron image at the same position. A group of parallel lines of the same length were used to show the correspondence of positions in each pair. As shown in Fig. 7 the distribution of Fe is obviously related to the unmodified Si particles.

Shankar et al [14] systematically studied the relationship between Fe-containing phases and eutectic Si phases in Al-Si alloys. They suggested that Fe-containing phases would form on the surface of dendrites after the α-Al is solidified, and act as nuclei of the eutectic Si phases. Similar to the results of their work, the unmodified Si particles in the present study showed strong spatial relevance with Fe-containing particles and appeared on one side of these Fe phases. This theory was

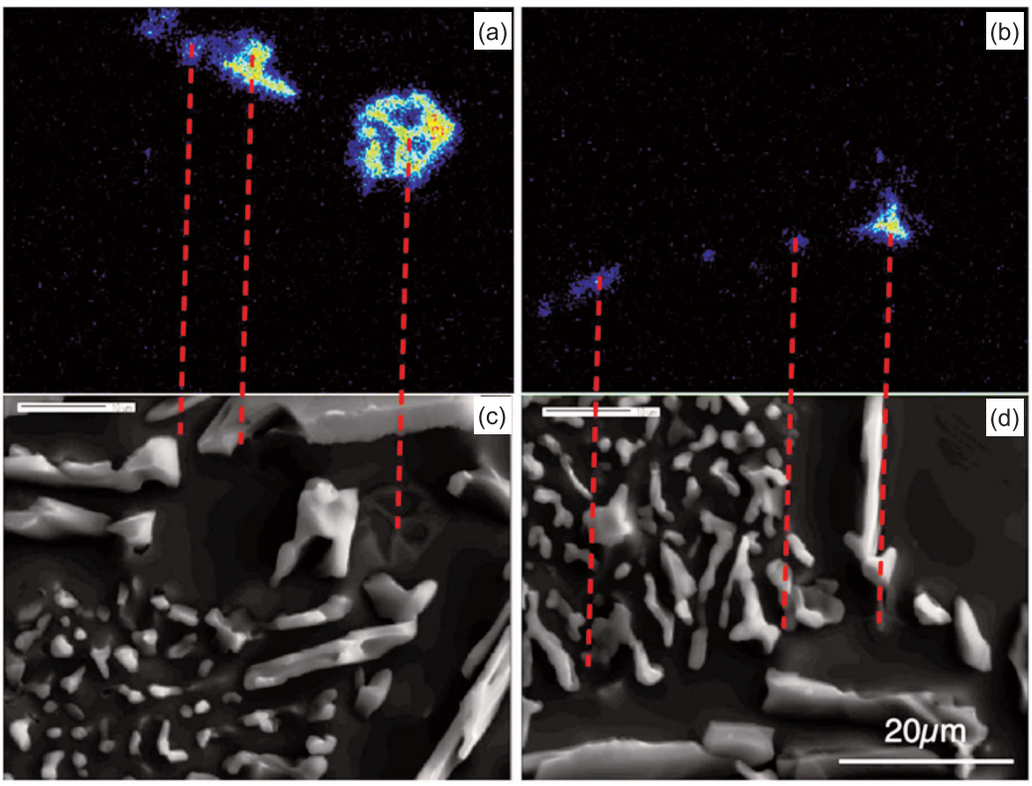

Fig. 7: EPMA results for Fe element in Sample 1A (commercial, 873 K) and secondary electron images at corresponding positions

supported by the research of Zhang et al [15] and Li et al [16]. There are some differences between the results of this study and those above. Since the solidification of Sample 1A was relatively slow, Fe-containing phases became larger, and the Fe element was more concentrated, different from the small and evenly distributed phases observed in previous studies. It is reasonable to suggest that, fewer and larger Fe-containing phases would form with a relatively low cooling rate, then Si phases would nucleate on them and grow into unmodified parts that distributed irregularly.

However, the Fe element also acted as impurity in other samples made of commercial raw materials, in which those unmodified parts could not be found. Firstly, a higher cooling rate possibly would make it harder for large Fe-containing phase to form, as suggested by experiments and calculations of Seifeddine et al [17]. Fe-containing phase would therefore be more dispersed, and could be found occasionally when Sample 2A (commercial, 673 K), 3A (commercial, 473 K) and 4A (commercial, about 300 K) were observed using SEM. As shown in Fig. 8, plate-like Si phases could be observed around the Fe-containing phase, but there was not any area where such Si phases concentrated. Also, these Si phases in Fig. 8 were quite small, which had not grown into the large flake particles as those in Sample 1A. Fujiwara et al [18] reported that a relatively low undercooling is necessary for flake-shaped Si particles to grow, while the real reason for the difference between samples still needs further research.

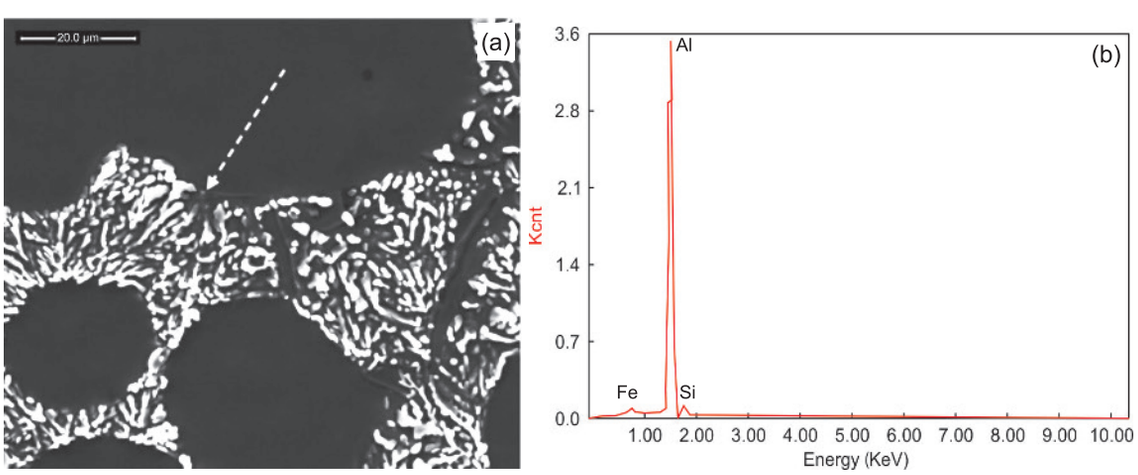

Fig. 8: SEM image of sample 4A (commercial, 300 K) (a) with EDX result at top of arrow (b)

To confirm the influence of an Fe-containing phase on the modification effect of Sr, a second group of samples made of high pure Al and Si were prepared. As shown in Fig. 9, all samples were fully modified with all Si particles in fibrous shape. No unmodified part could be found such as that in the first group samples.

AES was used to analyze the concentrations of several possible impurities in the samples of both groups. As shown in Table 2, the content of Fe made the main difference between the two groups, which were about 1,000 ppm in samples made of commercial raw materials while only one tenth of that in samples made of high pure Al and Si.

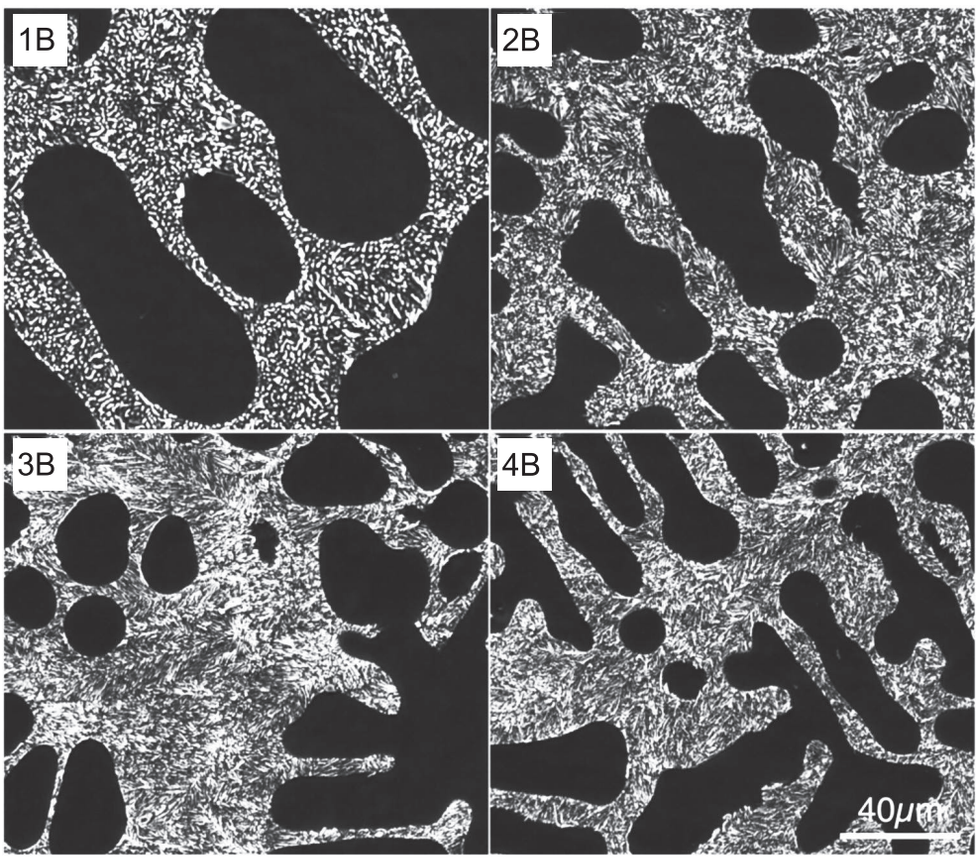

Fig. 9: SEM images of samples made of high pure raw materials: (1B) solidified in mold of 873 K (600 °C); (2B) 673 K (400 °C); (3B) 473 K (200 °C); (4B) room temperature (*ca.* 300 K)

Table 2: Contents of impurity elements in samples of both groups

Sample		Element content (wt.%)			
		Fe	Mg	Ca	Ti
Commercial	1A	0.1257	0.0009	0.0007	0.0045
	2A	0.1228	0.0006	0.0007	0.0045
	3A	0.1281	0.0002	0.0006	0.0042
High pure	4A	0.1172	0.0001	0.0006	0.0041
	1B	0.0100	0.0000	0.0003	0.0010
	2B	0.0109	0.0000	0.0005	0.0010
	3B	0.0115	0.0000	0.0004	0.0010
	4B	0.0116	0.0000	0.0007	0.0010

The confrontation between the two groups of samples confirmed the suggestion that Fe-containing phases are an important factor that lead to the failure of modification of Sr in Al-Si alloys. Taking the Fe-containing phases and the cooling rate as variants, the Sr-modification of eutectic Si are suggested to have 3 different situations. In samples containing Fe, a relatively low cooling rate will make the Fe-containing phases larger and less dispersed, on the basis of which Si nucleate and continue to grow into large flake-shaped phases that distribute irregularly even with the presence of Sr. With a higher cooling rate, the Fe-containing phases are supposed to be smaller and more dispersed, but also act as nuclei of plate-shaped Si phases, which are, however, unable to grow up. While in samples free of Fe, the Sr would modify Si phases ideally.

Considering that Fe is universally contained in commercial Al alloys, it is almost impossible to remove those Fe-containing phases in the production. Thus the control of cooling rate, especially the mold temperature in manufacture is of great significance. To pay attention on Fe-containing phases is necessary for further research on Sr-modification.

3 Conclusion

In summary, a trace concentration of Sr can significantly change the morphology of eutectic Si phases in Al-Si alloys. However, samples made of commercial raw materials solidified in a low cooling rate will suffer a partial failure of modification, with the unmodified parts spread between the modified ones without any

obvious regularity.

It is proved that Sr is segregated in the Si phases of Al-Si alloys, and this is not only observed on a small scale, but also confirmed by statistics in a larger scale of about 200 μm, covering a large amount of Si particles. However, the segregation situation will not be influenced by the different cooling rates.

In samples that modification partly fails, Fe-containing phases are relative to the unmodified Si phase in position. While in other samples, Fe-containing phases also appear with plate-like Si phase, which are smaller and dispersed. In comparison, sample made of high purity Al and Si contains no unmodified part even with a slow cooling rate during solidification. Thus Fe-containing phases that universally exist in commercial alloys are an important reason for the partial failure of modification. Fe element thus acts as an important factor in the simultaneous influence of cooling rate and Sr-modifier in Al-Si alloys.

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