Effect of P + Sr + RE Ternary Compound Modification on Microstructure of Eutectic Al-13wt%Si Alloy

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Abstract. Used Al-13wt%Si alloy was as raw material, the influence mechanism of Al-Sr, Al-P and Al-RE ternary compound modifier was studied by casting technology. The effects of P, Sr and RE modification on Al-13wt% Si were studied by metallographic microscope, scanning electron microscope and X-ray. The effects of the addition order and amount of modifier on the microstructure of Al-13wt% Si were investigated. The results show that compared with a single modifier, P + RE + Sr ternary composite modifier has more obvious modification effect on eutectic silicon in Al-13%Si alloy: the microstructure of different morphology can be obtained by using different amount and order of adding modifier. When the amount and order of modifier are 0.5wt%Sr, 0.7wt%P, 1.5wt%RE, the eutectic silicon with small size and uniform distribution can be obtained. Eutectic silicon consists of 70 μm, the slender lamella is refined to 5 μm.

Keywords. Compound metamorphism, metamorphic agent, Al-13wt%Si.

1. Introduction

Aluminum alloy is widely used in aerospace, aviation and transportation buildings because of its good conductivity, corrosion resistance and weldability [1]. Aluminum silicon alloy is widely used to manufacture key parts such as engine cylinder, piston rotor and so on because of its good castability, low cost, high output, low coefficient of thermal expansion and high specific strength [2, 3]. However, the Al Si alloy prepared by fusion casting usually exists in the form of flakes, and the distribution is very uneven, which affects its application effect. Modification is the most effective method to refine cast Al Si alloy [4, 5]. As early as the 1920s, researchers found that adding metamorphic elements such as Na, P, Sr, RE and Ba to the molten state can also refine the grains. The addition of metamorphic elements can move the eutectic point of the aluminum silicon phase diagram to the right, so as to inhibit the precipitation of primary silicon. At the same time, the addition of metamorphic elements can inhibit the grain growth of silicon, so as to achieve the purpose of grain refinement [6-8]. Li et al. [9] studied the effect of the addition of Sr on the modification treatment of Al Si alloy and found that the addition of Sr too high or too low is not conducive to the microstructure refinement of primary silicon. When the addition amount of modifier Sr is 0.04%, the refinement effect is the best. Stanislav K [10] studied the effect of Cerium on the microstructure refinement of aluminum silicon alloy and found that when the addition amount of cerium is less than 1%, the size of primary silicon will decrease with the increase of rare earth cerium. Due to the very limited solid solubility of Cerium in aluminum silicon alloy, serious overmodification will occur when the addition amount of cerium
Among the widely used methods for refining silicon grains of Al-Si alloy, the addition of modifier is the most commonly used technical means. However, a single modifier often has various deficiencies, resulting in the deterioration effect can not meet the ideal requirements. Therefore, researchers gradually shifted their research direction to the study of composite modifiers. Lai [11] studied the effect of compound modification of Na and Sr on eutectic Al-Si alloy, and the modification effect remained stable after remelting for 3 times at 740 ℃. Sun [12] studied the effect of compound modification of P and rare earth on the microstructure and properties of Al-Si alloy. It is found that P and rare earth do not interfere with the modification effect, but when the content of Si in Al-Si alloy exceeds 30%, the modification effect of primary silicon is not very obvious.

In this paper, a new ternary composite modifier is designed for casting Al-Si alloy. The process parameters such as pouring temperature, holding time, adding sequence of composite modifier and adding amount of modifier are changed. Eutectic silicon with uniform microstructure distribution and fine size is obtained, which provides a theoretical basis for the further application of eutectic Al-Si alloy.

2. Experimental

A certain proportion of Al-10wt%Si and Al-20wt%Si alloys are placed in a medium frequency induction furnace, raise it to 750 ℃ in nitrogen atmosphere, then add Al-8wt%Sr modifier for holding for 10min, raise the temperature to 840 ℃, add Al-3wt%P modifier for holding for 30min, add Al-10wt% RE modifier for holding for 30min, and pour it into the mold to prepare Al-13wt%Si metal ingot. In order to verify the influence of the addition sequence of the modifier on the modification effect, the addition sequence of the modifier can be changed at will. Then the cast samples were cut and polished. The metallographic observation was carried out by Zeiss large metallographic microscope, and the microstructure of eutectic Al-Si alloy was analyzed by XRD SEM and EDS.

3. Results and Discussion

3.1. Effect of Modifier Addition Order on Microstructure of Eutectic Al-Si Alloy

3.1.1. Effect of P and Sr Addition Sequence on Modification Effect of Eutectic Al-Si Alloy. Figure 1 shows the effect of P and Sr addition sequence on the eutectic structure of Al-13wt% Si alloy. Among them, (a) is an unmodified eutectic Al-Si alloy, (b) is to add P first and then Sr, (c) is to add SR first and then P.

![Figure 1](image_url)

It can be seen from the figure that most eutectic silicon in eutectic Al-Si alloy without modifier exists in slender strip and block, and the addition order of P and Sr has a very significant impact on the Si phase in eutectic Al-Si alloy. It can be seen from figures (b) and (c) that whether P or Sr is added first, compared with the microstructure of eutectic Al-Si alloy without modifier, The size of eutectic silicon phase has been obviously refined, but the modification effect is obviously different with different modifier addition order. After adding P and then Sr, although the size of eutectic silicon is
refined, the modification effect is not complete, there is still a small amount of large block silicon, and the modification is uneven, and the size of eutectic silicon is still large. The modification effect is very good when Sr is added first and then P is added. The eutectic silicon is evenly distributed in the matrix, the long strip silicon is cut into fine needle shape, and the size of eutectic silicon is small.

At the same time, two modifiers P and Sr are added to the melt, which no longer play a role of modification alone, but play an interactive role. After adding P modifier first, P will react with Al in the melt to form AlP as a heterogeneous nucleation point. At this time, Sr salt modifier is added to the melt, and part of Sr will adhere to the surface of AlP to form Al-P-Sr compound. This compound can not be used as heterogeneous nucleation point to refine eutectic silicon particles. At the same time, because Sr is attached to the surface of AlP, it will consume some Sr salt modifier, which weakens the refining effect of Sr salt on eutectic silicon and inhibits its modification effect. On the contrary, if Sr is added to the alloy melt first, Sr can fully interact with eutectic silicon in the melt to refine and modify. Then, when P salt is added, the Sr salt in the melt is very limited and will not generate a large number of Al-P-Sr compounds. Therefore, AlP will not be consumed as the heterogeneous nucleation point of eutectic Al Si alloy, and both Sr and P will give full play to their modification effect. Therefore, the deterioration effect is better.

The scanning morphology of eutectic Al Si alloys prepared by two addition sequences is observed, as shown in figure 2 (a) is to add P first and then Sr, (b) is to add Sr first and then P. Through the same comparison in the figure, it is found that the size of eutectic silicon in figure 2 (a) is relatively large and presents a slender needle shape, and the morphology and size in figure 2 (b) is smaller and presents a small short rod shape with white heterogeneous nucleation points.

![Figure 2. The morphology of Al-13wt% Si with different modifier adding sequence](image)

Although the existence of bright white AlP heterogeneous nucleation points can be observed from the SEM of Al-13wt%Si, the heterogeneous nucleation points are easy to fall off during metallographic sample preparation, so the existence of heterogeneous nucleation points is not seen in the metallographic phase. In order to verify the existence of AlP heterogeneous nucleation points, we conducted XRD analysis on the samples prepared in different addition sequences, as shown in figure 3 (a) is to add P first and then Sr, (b) is to add Sr first and then P.

It can be seen that only the peaks of Al and Si appear in sample (a), and there is almost no heterogeneous nucleation point of AlP. This also indirectly shows that the addition of Sr will react with AlP nucleation points to form Al-P-Sr compounds. In sample (b), except for Al and Si phases, there are a large number of AlP peaks almost coincident with silicon, indicating that the addition of P salt can generate a large number of AlP heterogeneous nucleation points.
Figure 3. XRD patterns of Al-13%Si with different modifier addition sequence (a) adding P first then Sr (b) adding Sr first then P.

3.1.2. Effect of P and RE Addition Sequence on Modification Effect of Eutectic Al Si Alloy. Figure 4 shows the effect of P and RE addition sequence on the eutectic structure of Al-13wt%Si alloy. Among them, (a) is an unmodified eutectic Al Si alloy, (b) is to add RE first and then P, (c) is to add P first and then RE. Compared with (a) and (b), it can be found that the modification effect of adding RE first and then P is not obvious. Compared with the unmodified eutectic Al Si alloy, the size of eutectic silicon has almost no change. It exists in the form of thick flakes, with large size and uneven distribution. The refining effect of eutectic Al Si alloy modified by P and then RE is very obvious, and the grains are fine particles and evenly distributed. This is because after P is added to the melt of Al-13%wt Si alloy, RE is added on this basis after P fully becomes refined grains. RE will enrich at the crystal plane of refined eutectic silicon, inhibit the diffusion of atoms, limit the further growth of grains, further refine the microstructure of eutectic silicon, and make the modification effect more obvious.

Figure 4. Influence of modifier addition order on the modification effect of Al-13wt%Si alloy (a) unspoiled (b) add RE first then add P (c) add P first then add RE.

The scanning morphology of eutectic Al Si alloys prepared by two addition sequences is observed, as shown in figure 5 (a) is to add RE first and then P, (b) is to add P first and then RE. It can be seen from the figure that when RE modifier is added first, there will be obvious component segregation, one part of the structure presents slender needle structure, while the other part has a large amount of primary silicon due to component segregation. RE will react with Al and Si to form rare earth compounds with complex structure, poor modification effect and uneven distribution. Then the sample with rare earth has uniform size distribution and good modification effect.
Figure 5. The morphology and EDS of Al-13wt%Si with different modifier adding sequence (a) adding RE first then P (b) adding P first then RE.

For Al-13wt% Si added with RE and then P, take 3 points for energy spectrum analysis, as shown in figure 6. The percentage of each element is shown in table 1.

It can be found from the comparison of three points that the phase composition of Al, Si and re at each point is very different, indicating that re will form very complex compounds with Al and Si, and the formed Al RE compounds cause component segregation. Therefore, the modification effect of adding RE first and then P is not good. Based on the above analysis, in the process of composite modification, Sr, P and RE should be added to the melt successively in order to obtain the best modification effect.

Figure 6. Energy spectrum analysis of Al-13wt%Si different acquisition points with RE added first and P added later.
Table 1. Element percentage of collection point.

| Element | Collection point |
|---------|------------------|
|        | 11   | 12   | 13   |
| Al     | 34.1 | 35.1 | 47.1 |
| Si     | 63.7 | 63.5 | 51.4 |
| Ce     | 0.6  | 0.2  | 1.1  |
| Sm     | 0.4  | 0.3  | 0.1  |
| Pm     | —    | 0.6  | —    |
| P      | 0.5  | 0.2  | 0.2  |

3.2. Effect of Modifier Addition

The microstructure refinement of eutectic Al Si alloy mainly depends on the addition of modifier, and the amount of modifier is a very important factor affecting the modification effect. When the amount of modifier is too small, the microstructure can not achieve the effect of complete modification, and incomplete modification will occur. When too much modifier is added, there will be over metamorphism. Too much modifier will be enriched in the tissue, rich metamorphic phase will appear, worsen the tissue and affect the metamorphic effect of the tissue. Therefore, selecting an appropriate amount of modifier can effectively play a metamorphic effect without over metamorphic phase. The key problem of modification is to obtain uniform refinement of eutectic Al Si alloy. Therefore, in order to explore the effect of the amount of composite modifier on the microstructure refinement of eutectic Al Si alloy. In this section, the orthogonal experiment is used to reduce the number of experiments, analyze the influence of each factor level, and obtain the optimal addition amount of composite modifier.

According to the type of modifier and the addition amount of modifier, three kinds of modifier and three addition amounts are determined by using the 4-factor 3-level orthogonal table, i.e. L9 (34), as shown in table 2. The experimental scheme is determined according to the test factors and level numbers, as shown in table 3.

Table 2. Factors and levels of orthogonal test.

| Level | Element(wt%) | A(P) | B(RE) | C(Sr) |
|-------|--------------|------|-------|-------|
|       |              | 0.5  | 0.5   | 0.5   |
| 1     |              | 0.7  | 1     | 1     |
| 2     |              | 0.9  | 1.5   | 1.5   |
| 3     |              |      |       |       |

Table 3. Arrange of orthogonal test.

| Group number | Factor | A(P) | B(RE) | C(Sr) |
|--------------|--------|------|-------|-------|
| 1            | 1(0.5) | 1(0.5) | 1(0.5) |
| 2            | 1(0.5) | 2(1)  | 2(1)  |
| 3            | 1(0.5) | 3(1.5) | 3(1.5) |
| 4            | 2(0.7) | 1(0.5) | 2(1)  |
| 5            | 2(0.7) | 2(1)  | 3(1.5) |
| 6            | 2(0.7) | 3(1.5) | 1(0.5) |
| 7            | 3(0.9) | 1(0.5) | 3(1.5) |
| 8            | 3(0.9) | 2(1)  | 1(0.5) |
| 9            | 3(0.9) | 3(1.5) | 2(1)  |
The microstructure of the above 9 groups of experimental samples is observed, as shown in figure 7.

Compared with the unmodified eutectic Al Si alloy (figure 2 (a)), the size of eutectic silicon is refined to varying degrees, but the modification effects of nine groups are significantly different, indicating that the addition amount of composite modifier has an obvious influence on the modification effect of eutectic Al Si alloy. It can be seen from figure 7 (a) (b) (d) that although the composite modifier has an impact on the size of eutectic Al Si alloy, the morphology change of eutectic silicon is not particularly obvious, and it is still dominated by strip eutectic silicon. Figure 7 (c) (g) although the modification effect is obvious, eutectic silicon mostly exists in long rod or short needle shape, there is obvious segregation, and the distribution of eutectic silicon is not uniform. (e) (H) excessive metamorphism occurs due to the excessive addition of compound metamorphism dose. Among the nine groups of samples, the modification of (f) (I) is the most thorough, the eutectic silicon structure is refined into rod structure, the size is very small and the distribution is very uniform. Considering the addition amount of (f) (I) two groups of modifier, group (f) achieved the same modification effect under the condition of less addition amount of modifier. Therefore, based on the principle of cost saving, the best process of compound modification is selected as (f).

![Figure 7](image-url)

Figure 7. The microstructure of orthogonal test samples.

Scanning transmission observation was carried out on Al-13wt% Si after ternary composite modification, and its surrounding morphology is shown in Figure 8(a) TEM image of Al-13wt% Si eutectic alloy, (b) saed pattern of Al-13wt% Si eutectic alloy. A large number of longitudinal twins were formed in Al-13wt% Si after composite modification and cooling rate interaction. The existence of twins can also be seen from the saed diagram in Figure 8 (b). Because Si has low stacking fault
energy on the (111) surface, twin plane defects appear on the (111) surface. According to the concave edge mechanism of twins, the addition of composite modifier will generate a large number of twins and stacking faults on the (111) crystal surface. The addition of composite modifier improves the density of twins. At the same time, the modifier is easy to be adsorbed on the Si surface, which inhibits the longitudinal growth of Si, changes the original growth mode, and grows into rod or needle along the axial twin direction.

![Figure 8](image)

**Figure 8.** Microstructure of the Al-13%Si eutectic alloy by composite modification (a) TEM image of the Al-13%Si eutectic alloy (b) SAED pattern of the Al-13%Si eutectic alloy.

4. Conclusion
The effect of the interaction of P + Sr + RE composite modifier and rapid cooling on eutectic silicon in Al-13wt%Si was studied, the optimum process parameters were determined, and the following conclusions were drawn:

1. The correct adding order of ternary composite modifier is determined: Sr, P, re, and the optimal adding amount of modifier is 0.5% Sr, 0.7% P, 1.5% RE.
2. It is found that compared with a single modifier, P + RE + Sr ternary composite modifier has more obvious modification effect on eutectic silicon in Al-13wt% Si alloy: the size of eutectic silicon is smaller, and the microstructure of eutectic silicon is 70 μm, the slender lamella is refined to 5 μm.

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