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Effect of phosphorus and heat treatment on microstructure of Al-25%Si alloy

Bo Dang, *Zeng-yun Jian, Jun-feng Xu, Fang-e Chang, and Man Zhu

Shaanxi Key Laboratory of Photoelectric Functional Materials and Devices, Xi'an Technological University, Xi'an 710021, China

Abstract: It is known that phosphorus can refine the primary silicon and heat treatment can spheroidize the eutectic silicon. This paper presents an optimal combination of heat treatment processes and P refinement on hypereutectic Al-Si alloy. The optimal P addition amount, and the solution and aging temperatures for Al-25%Si alloy were obtained through the orthogonal experiment, and their modification effects were discussed. The results show that P addition has the greatest modification effect, followed by aging temperature, and the modification effect of solution temperature is the least. The optimized modification parameters are: addition of 0.6% P, solution at 540 ºC and aging at 160 ºC . In addition, the cooling curve, superheating and hardness of the alloy were also analyzed.

Key words: Al-Si alloys; combination modification; microstructure; orthogonal experiment

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The hypereutectic Al-Si alloys play an important role in the fields of automotive and aerospace industries due to their excellent casting ability, low thermal expansion coefficient and high wear resistance [1-3]. The microstructure evolution of hypereutectic Al-Si alloy is mainly divided into two stages during solidification: the precipitation of primary silicon and subsequent eutectic transformation. The morphology and distribution of silicon affect the mechanical properties and application scope of the alloys. For hypereutectic Al-Si alloys, the coarse primary silicon may easily produce stress concentration, form the crack and accelerate the crack growth. To gain better mechanical properties, modification treatment and heat treatment are carried out for hypereutectic Al-Si alloys to change the morphology, size and distribution of silicon phase. Modification treatment can significantly improve the morphology and distribution of silicon [4-9]. Heat treatment aims at acquisitions of supersaturated solution, high density vacancies and spheroidization of eutectic Si.

Many researchers have focused on the improvement of modifiers to meet the requirements of environmental protection and industry applications. The common methods of modification are chemical treatment by modifiers [5-9], melt thermal treatment [10-12] and mechanical/electromagnetic stirring treatment [13-15]. Refinement by element addition has been widely applied in traditional casting Al-Si alloy due to simplicity and validity [4-9]. P is one of the most effective modifiers and refiners of primary Si particles and can be added into the melt as master alloys, such as Si-P [5], Cu-P [6], Al-P [7], Al-Si-P [8] and Al-Zr-P [9]. Adding P to Al-Si hypereutectic alloy can reduce the size of primary Si particles by the active nuclei sites [16]. Wu Yaping found the best modification effect can be achieved when Si-P master alloy is added into Al melt before the addition of silicon instead of directly adding into Al-24%Si alloy melt, because AlP can form after adding the Si-P into Al melt which can act as the nuclei of primary Si phases during the solidification process. The optimized modification parameters were modification temperature of 810 °C, addition level of 0.35% P, holding for 30+50 min (Si-P is added firstly to the Al melt, and silicon is added 30 min later, followed by 50 min holding) [5]. Jiang Q C, using the new Al-P-Ti-TiC-Y modifier, successfully modified primary silicon in Al-20%Si and Al-29%Si alloys. The results showed that the primary silicon sizes and the Brinell hardness values of Al-20%Si and Al-29%Si alloys are 20 and 35 μm, 96.1 and 129.0, respectively [17].

The good mechanical properties of Al-Si alloy are obtained generally after T6 heat treatment. From Ref. [18], the maximum hardness would be achieved after solution treatment at 813 K for 10 h and aging at 463 K for 10 h, indicating that the heat treatment plays an important role in improving the mechanical properties of Al-Si alloy. The optimum heat treatment process will give

***Zeng-yun Jian**

Male, born in 1962, Ph.D. Research interest: solidification processing of metal.

E-mail: jianzengyun@xatu.edu.cn

The first author Bo Dang is a doctoral candidate under his supervision.
E-mail: dangbo@xatu.edu.cn

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the best compromise between energy savings, time savings, and good mechanical properties [19].

Unfortunately, so far, reports rarely mention the optimal combination of heat treatment processes with chemical treatment. Generally, refinement and heat treatment processes are investigated independently. Consequently, the interrelationship between them was not well known. For instance, whether the effect of refinement is negated once subjected to subsequent heat treatment, and how heat treatment influences the modified alloy, are questions not yet answered. Therefore, our aim is to study the influence of heat treatment on the microstructure and hardness of the P-modified Al-25%Si alloy.

1 Experimental procedure

The base alloy used in the experiment was hypereutectic Al-25%Si alloy prepared with commercial purity Al (99.9%) and Si (99.5%) using an electric resistantance heating furnace. (All alloy compositions are reported in wt.% unless indicated otherwise.) The base alloy was heated to 850 °C and degassed using solid hexachloroethane (C_2Cl_6). Subsequently, a nominal P addition amount (0.2, 0.4, and 0.6wt.%, as the Cu-13%P master alloys preheated at 300 °C) was added into the melt at 850 °C, wrapped in aluminum foil, then stirred and held for 30 min to ensure the homogeneity of composition. After the slagging off, the melt was poured at a series of temperatures (820 °C, 860 °C, 960 °C, 1060 °C) into a steel mold (30 mm in inner diameter and 100 mm in length, preheated to about 200 °C). A K-type thermocouple was inserted into the center of liquid in the steel mould to obtain the cooling curve during solidification, and relevant data was recorded by DX2008-3-4-3 Yokogawa Paperless Recorder.

The samples were then subjected to a T6 heat treatment. The solution treatment was carried out at 540 °C, 510 °C, and 480 °C, respectively, for 9 h followed by quenching immediately in water of 70–100 °C, and then artificial aging at 200 °C, 180 °C, and 160 °C, respectively, for 10 h followed by air cooling.

The optimal modification parameters of Cu-P and T6 treatment on Al-25%Si alloy were acquired through the orthogonal experiment. An orthogonal L_9 (3^3) test was designed. Three factors and three levels are determined, as shown in Table 1. Nine modification and heat treatment experiments were carried out.

Table 1: Factors and levels of experiments

Levels	Factors		
	A Addition amount of P (wt.%)	B Solution temperature (°C)	C Aging temperature (°C)
1	0.2	480	160
2	0.4	510	180
3	0.6	540	200

Evolution of the microstructure subjected to the heat treatment temperature was investigated. The samples were cut and mechanically polished followed by etching in 0.5% HF solution for 30 s to reveal the structure morphologies. The microstructures of the samples were examined using an optical microscope (OM; Olympus PMG). The mean diameter was used to describe the characteristics of primary silicon in the heat treated samples magnified at 100 times using Image ProPlus 6.0 software. Micro-hardness tests were performed using the Brinell method. The indentation was made on the well-polished surface of the specimens with a steel ball under a load of 250 kg for a period of 15 s. Indentation diameter was measured with a reading microscope, which reads the hardness value. The measurements were repeated ten times and the mean value was calculated.

2 Results and discussion

2.1 Cooling curves

The cooling curves of Al-25%Si alloy with different P concentrations were measured by a K-type thermocouple as shown in Fig. 1, where, representative cooling curves correspond to eutectic transformation of the alloy. The trend is that the eutectic transformation temperature was close to the equilibrium temperature with an increase in P addition amount from 0.2% to 0.6%. From Fig. 1, it can be seen that the undercooling is markedly reduced from 13.4 °C to 8.9 °C by increasing P from 0.2% to 0.6%. This is because the granular AlP in the melt may precipitate at the region with a higher P concentration, and they also often combine with primary Si, which results from the higher reaction temperature [8].

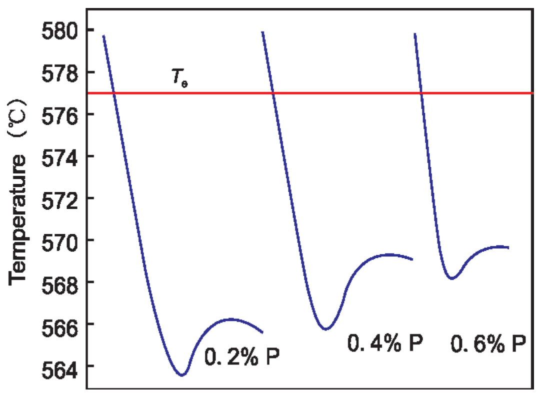

Fig. 1: Cooling curves for different P concentrations

2.2 Effect of superheating on Al-25%Si alloys

Figure 2 shows the microstructures of unmodified and modified Al-25%Si alloys with different pouring temperatures. It was noted that the primary silicon phases in unmodified Al-25%Si alloy exhibit coarse irregular plate and polygon, and the eutectic silicon phase is long needle-like in the matrix (Fig. 2a). The microstructures of the Al-25%Si alloy modified with 0.2% P at different pouring temperatures, as shown in Figs. 2b to 2d, indicate that when the Cu-P modifier was added into the melt, the morphologies of primary silicon were drastically changed to fine polyhedral shape with increasing P concentrations, and with

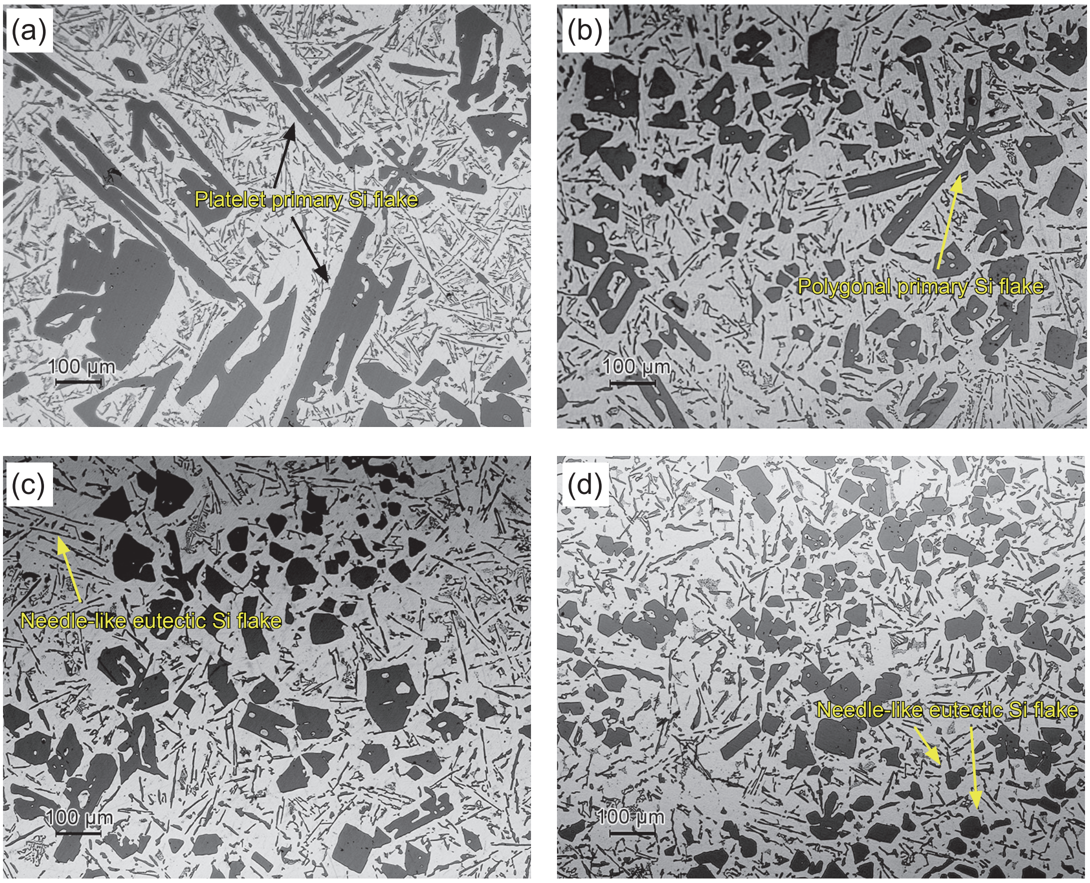

Fig. 2: Microstructures of unmodified Al-25%Si alloy pouring at 820 °C (a) and modified Al-25%Si alloys (0.2wt.% P) pouring at 860 °C (b), 960 °C (c) and 1,060 °C (d), respectively

increasing the temperature of melt, the size of primary silicon and eutectic silicon decreases gradually.

With regard to the role of P in the modified alloys, it is possible as a heterogeneous nucleation core for primary silicon in the melt. When P is added into the Al-Si melt, P and Al form AlP, whose melting point is above 1000 °C. It has a similar lattice parameter as does silicon, and belongs to diamond structure [20, 21]. So the effect of AlP is that it increases the number of crystal nucleus which promote the refinement of primary silicon. Meanwhile, the AlP particles cannot distribute uniformly in the Al melt due to their poor wettability, and they often float on the melt or adsorb on the inner walls of the vessels [8]. In addition, the size and morphologies of AlP particles depend on the reaction temperature and P content during the transformation process [22]. Therefore, Cu-P master alloy has a significant effect on primary silicon in hypereutectic Al-Si alloys modification, but not on eutectic silicon.

On the other hand, the small AlP particles will dissolve partly at high temperature, and the higher the temperature of melt, the higher the dissolve speed of small AlP particles. As a result, the size of small AlP particles decreases. In solidification of modified Al-Si alloy, some small AlP particles precipitate from the alloy melt before the primary silicon transformation. Therefore, the higher the pouring temperature, the smaller the AlP particle size in the melt. Since the small AlP particle can be used as a nucleation core of the primary silicon, the average size of primary silicon of modified alloy decreases with increasing pouring temperature. In addition, as the melt pouring temperature rises, the size of the silicon atomic cluster in the melt decreases gradually. This change is also one of the reasons why the primary silicon average size decreases with increasing pouring temperature.

2.3 Effect of processing parameters on Al-25%Si alloy

Pouring temperature of 1,060 °C was used to evaluate the optimized processing parameters for the microstructure and properties of Al-25%Si alloy. Results of the orthogonal test and the extreme difference analysis are listed in Table 2. *K* is the sum of the average size of primary Si at the same level of each factor, while *k* is the mean value corresponding to *K*. By comparing with values of different *k*, the optimal level of factors can be confirmed. The *R* value for each factor is produced by subtracting the minimum value from the corresponding maximum value among the k_1, k_2, and k_3 rows. The *R* value reflects the effects of factors on the result. The higher the *R* value, the greater the influence of the factor on the evaluation index [23-25].

Figure 3 shows the microstructures of Al-25%Si alloys modified under different conditions according to each horizontal column in the L_9 (3^3) orthogonal test in Table 2. It is shown that the morphology of primary Si is coarse platelet and star-

Table 2: Results and analysis of L_9 (3^3) orthogonal test

No.	Factors			
	A (wt.%)	B (°C)	C (°C)	Sizes of primary Si
1	0.2	480+9	160+10	29.3
2	0.2	510+9	180+10	31.5
3	0.2	540+9	200+10	33.2
4	0.4	480+9	180+10	32.1
5	0.4	510+9	200+10	28.5
6	0.4	540+9	160+10	26.1
7	0.6	480+9	200+10	25.4
8	0.6	510+9	160+10	23.6
9	0.6	540+9	180+10	22.8
K_1	94	86.8	80	
K_2	86.7	84.6	86.4	
K_3	72.8	82.1	87.1	
k_1	31.33	28.93	26.67	
k_2	28.9	28.2	28.8	
k_3	24.27	27.37	29.03	
R	7.06	1.56	2.36	

shape with sharp angle when the particles addition level is low regardless of different solution and aging temperatures. The distribution of primary Si is more uniform when the addition level is high despite of a lower or higher solution and aging temperature. Meanwhile, the sharp angle of primary silicon becomes passivation after heat treatment, and the size and amount of primary silicon decrease with the increase of solution temperature. The morphology of eutectic silicon transforms from distinct edges and long flake to tiny short rod-like.

Figure 4 reveals the relationship between evaluation index and levels. The influence of the factors on the size of primary silicon decreases in the order: A>C>B according to the R values. This indicates that the addition amount of P is the most important factor. The average size of primary silicon decreases distinctly from 31.33 μm to 24.27 μm with an increase of P content from 0.2% to 0.6%. It shows that the more the P addition amount, the higher the solution temperature and the lower the aging temperature, then the better the modification effect of P-Cu can be achieved. In this study, the solution temperature of 540 °C is close to the eutectic temperature of the alloy and without over burning. Therefore, 540 °C is a suitable solution temperature for the alloy.

According to the research results of Xu C. L., et al. [26], when the primary silicon size is 20 μm, the tensile strength and elongation of Al-20%Si alloy could reach 300 MPa and 1.75%, respectively. Therefore, taking the production cost

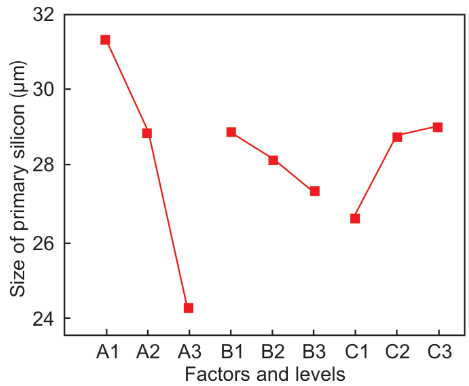

Fig. 4: Sizes of primary silicon with different factors and levels

and application requirements into consideration, the primary silicon size of Al-25%Si alloy should be less than 20 μm. The cost increases with an increase in the addition amount and heating temperature. Based on the above analysis, the optimal parameters are addition level of 0.6% P, solution temperature of 540 °C, and aging temperature of 160 °C. Figure 5 shows the microstructure of the Al-25%Si alloy modified under the optimized condition, which shows that the primary silicon size is about 19.7 μm.

2.4 Hardness tests

The Brinell hardnesses for the alloys both unmodified and modified using the optimized parameters are listed in Table 3.

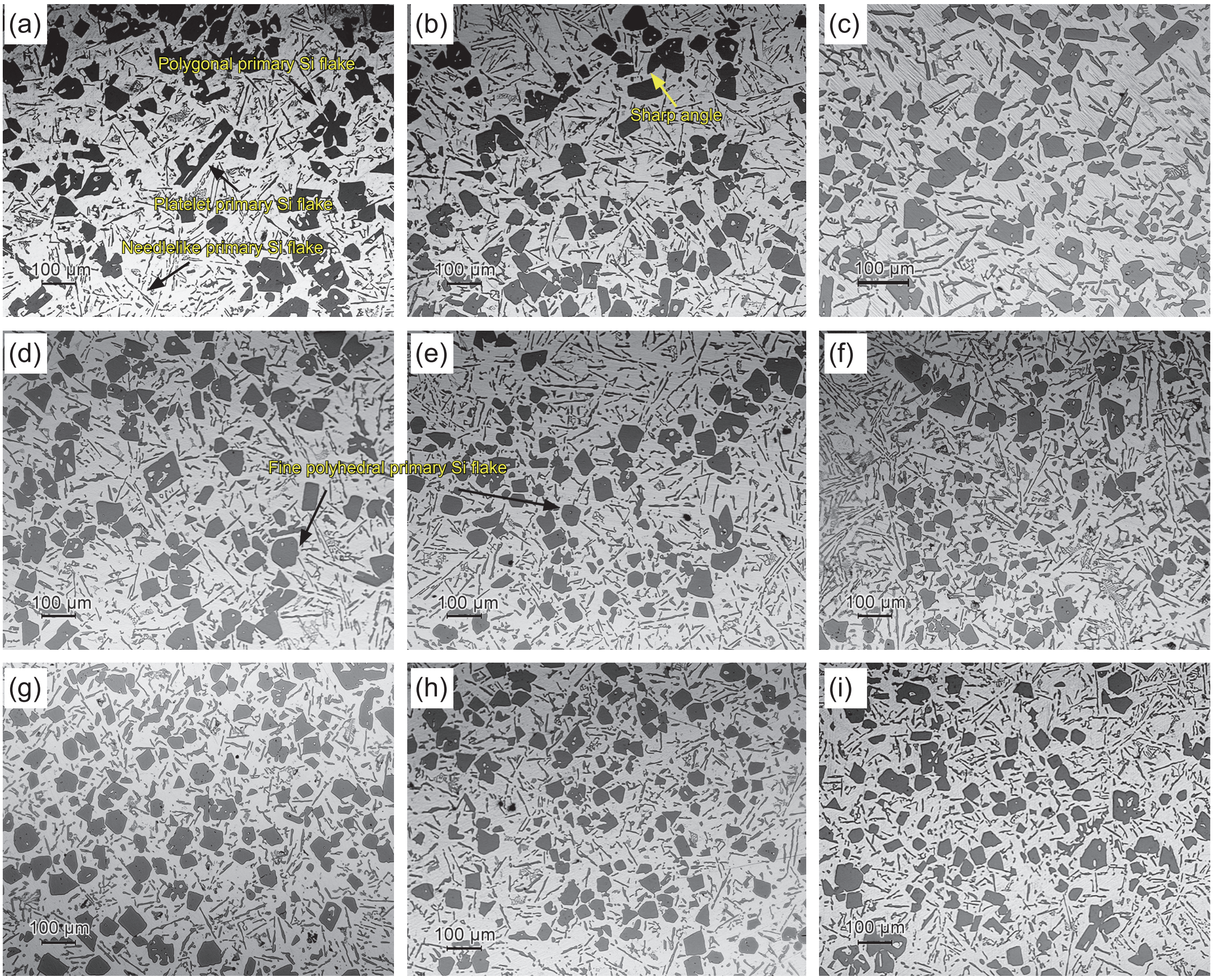

Fig. 3: Microstructures of modified Al-25%Si alloys under different conditions (P content, solution temperature and aging temperature): (a) 0.2%, 480 °C, 160 °C; (b) 0.2%, 510 °C, 180 °C; (c) 0.2%, 540 °C, 200 °C; (d) 0.4%, 480 °C, 180 °C; (e) 0.4%, 510 °C, 200 °C; (f) 0.4%, 540 °C, 160 °C; (g) 0.6%, 480 °C, 200 °C; (h) 0.6%, 510 °C, 160 °C; (i) 0.6%, 540 °C, 180 °C

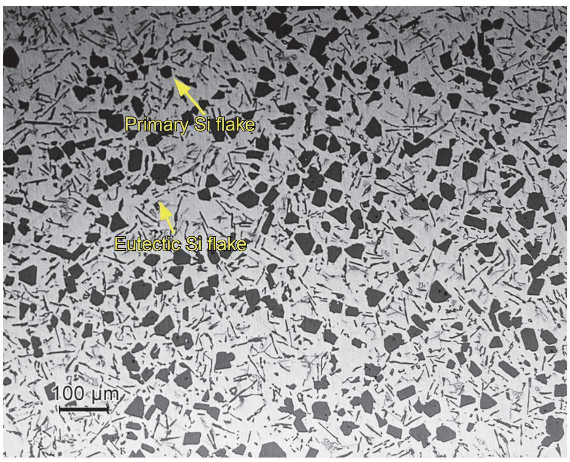

Fig. 5: Microstructure of Al-25%Si alloy under optimized processing parameters

Table 3: Brinell hardness of Al-25%Si alloys by optimized parameters

Unmodified	Modified
96.35	119.42

It can be found that the Brinell hardness of modified Al-25%Si samples is higher than that of unmodified by about 23.9%. The hardness of Al-Si alloys is affected by the size of primary silicon, and the heterogeneous nuclei of AlP particles can refine the primary Si, so it can dramatically improve the hardness of alloys. This can be confirmed by some previous studies [7, 17, 27], which show that the refinement of primary silicon contributes to the improvement of hardness of Al-Si alloys.

3 Conclusions

(1) Cu-P master alloy has a significant modification effect on primary silicon in hypereutectic Al-25%Si alloys, and there is no significant modification effect on eutectic silicon; eutectic silicon is spherodized after heat treatment.

(2) With the increasing of superheating temperature for modified melts, the dissolution speed of small AlP particles becomes quicker, and the average size of primary silicon of modified alloy decreases.

(3) Orthogonal test results show that the addition amount of P

is the most important factor for Al-25%Si alloys. The optimized processing parameters for the modified primary silicon in this study are the addition 0.6% P, solution at 540 °C, and aging at 160 °C.

(4) Under the optimized conditions, the average size of primary silicon decreases to about 19.7 μm; the Brinell hardness increases significantly by 23.9%.

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