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Refinement and thermal analysis of hypereutectic Al-25%Si alloy①

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[Abstract] Refinement and thermal analysis of hypereutectic Al-25% Si alloy were investigated with scanning electron microscope (SEM) and differential scanning calorimeter (DSC). The results show that the average size of primary silicon in Al-25% Si alloy without and with phosphorus addition are 250 μm and 30 μm, respectively. But the primary and eutectic growth temperature is raised by about 17.3 ℃ and 4 ℃ respectively due to phosphorus addition. The primary nucleation temperatures are 745.0 ℃ and 762.0 ℃ for untreated and treated samples and in addition, the enthalpy changes of primary and eutectic transformation are - 261.0 J/g and - 397.3 J/g without phosphorus addition, - 294.2 J/g and - 386.1 J/g with phosphorus addition, respectively. Otherwise the mechanisms of refinement and thermal transformation of Al-25% Si alloy in solidifying process are also discussed.

[Key words] hypereutectic Al-Si alloys; refinement; differential scanning calorimeter; enthalpy
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1 INTRODUCTION

The hypereutectic Al-Si alloys exhibit a highly desirable combined properties, such as castability, high strength-to-weight ratio, low thermal expansion coefficient, high corrosion and abrasion resistances. So the hypereutectic Al-Si alloys have widespread usage in automotive applications, such as engine blocks, cylinders, brake parts, clutches, pumps and especially pistons[1~5]. However, small size and highly uniform distributed silicon particles in the alloy are essential for attainment of optimum properties. Refinement of primary silicon is usually achieved by the addition of phosphorus to the melt[6~9]. The two most common techniques to add phosphorus are usage of master alloys (such as P-Cu, and recently developed Ni-P and Fe-P) and special commercial fluxes[10].

So far, there is little information available on refinement of Al-Si alloys with high silicon content (> 24%, mass fraction) as well as thermal analysis. In this paper, the refinement and thermal analysis of these alloys without and with phosphorus addition are investigated.

2 EXPERIMENTAL

The hypereutectic Al-Si alloy with high silicon content (nominal composition of 25% Si, mass fraction) was prepared with medium frequency induction electric furnace from aluminum ingots and silicon lumps with the chemical composition presented in Table 1. The silicon content in the alloys obtained was 24.65% according to the chemical analysis results. Alloys weighing about 2 kg were melted in graphite clay crucible in electric resistance furnace. Phosphorus with amount of about 0.1% was added into the melt at about 860 ℃ in the form of fluxes containing phosphorus compounds and alkaline salts. The melt was poured into a permanent mould before phosphorus addition and at 20, 60, 90, 120, 180, 240, and 300 min after phosphorus addition to estimate the refinement effect. The microstructures of Al-25% Si alloy with and without phosphorus addition were examined by Scanning electron microscopy (SEM).

Table 1 Mass fraction of pure Al and Si(%)

Raw material	Al	Si	Fe	Cu	Ca	Impurities
Pure Al	Bal.	0.13	0.12	0.01	—	≤0.30
Pure Si	0.5	Bal.	0.2	—	0.2	≤1.0

Differential scanning calorimeter (NETZSCH DSC 404) was employed to determine the heat flow and enthalpy changes of Al-25% Si alloy without and with phosphorus addition. This involved heating the alloy at a rate of 20 ℃/min from ambient temperature to 1000 ℃, and cooling them at the same rate, under flowing argon gas with a flow rate of 80 mL/min.

3 RESULTS AND DISCUSSION

Fig. 1 shows the microstructures of Al-25% Si alloy with and without phosphorus addition. It can be seen that the alloy without phosphorus addition contains coarse, plate-like, non-uniformly distributed primary silicon and acicular eutectic silicon; however, after addition of phosphorus, the primary silicon becomes fine, blocky, and well-dispersed. The average

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size of primary silicon in Al-25% Si alloy without and with phosphorus addition is 250 μm and 30 μm (for sample at 20 min after phosphorus addition), respectively. After phosphorus is added into the melt in the form of fluxes, phosphorus compounds react with liquid aluminum to produce a fine dispersed aluminum phosphide (AlP) which has a crystal structure very similar to that of silicon (both AlP and Si are cubic crystal lattice, lattice constants of AlP and Si are very similar, 5.46 Å and 5.43 Å as well as the least interatomic distance are 2.56 Å and 2.44 Å respectively[11]) and in turn acts as nucleation sites for primary silicon[4, 8, 9]. Therefore, the enhanced nucleation that results from phosphorus addition yields a fine and usually well-dispersed primary silicon phase.

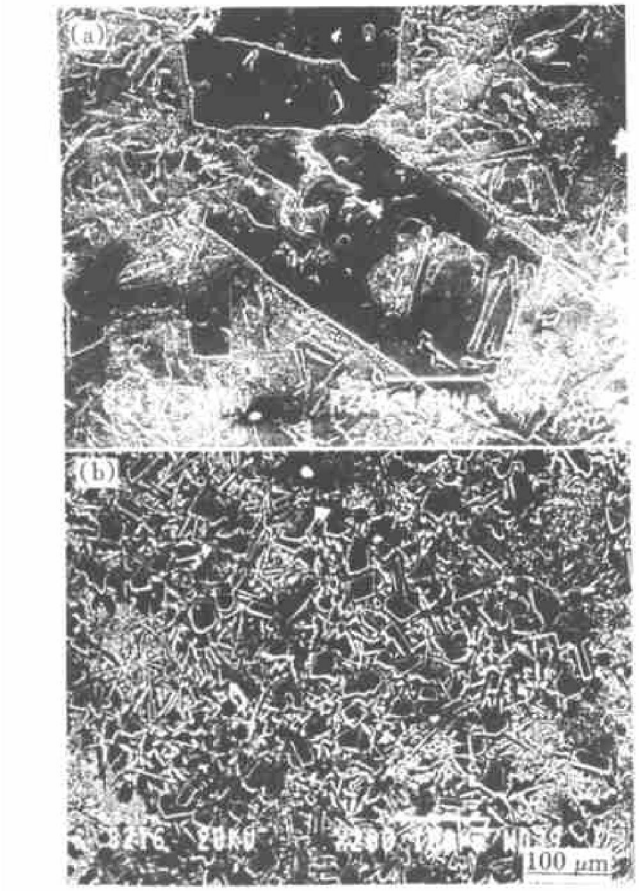

Fig. 1 Microstructures of Al-25% Si alloy
(a) —Without phosphorus addition;
(b) —With phosphorus addition

The average size of primary silicon after phosphorus addition as a function of holding time, is shown in Fig. 2. The result indicates that the average size reaches the minimum after holding for about 20 ~ 30 min, then increases gradually during the holding period. When holding for about 300 min (5 h), the average size is still below 70 μm. It can be seen that not only phosphorus has good refinement effect on primary silicon in Al-25% Si alloy, but also the duration of refinement effect is long-term.

DSC traces of Al-25% Si alloy without and with

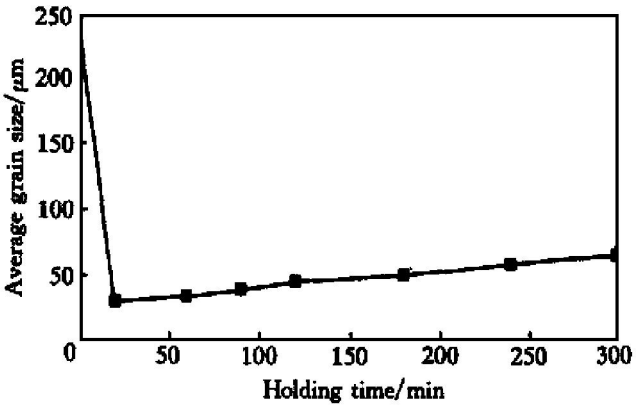

Fig. 2 Average grain size of primary Si in Al-25% Si alloy vs holding time after phosphorus addition

phosphorus addition are illustrated in Fig. 3. It is obvious that phosphorus addition results in the difference between DSC traces in cooling process (as shown in Fig. 3(a) and Fig. 3(b)); however, there is almost no difference in heating process, as shown in Fig. 3(c). And some solidification parameters of Al-25% Si alloy by DSC analysis are tabulated in Table 2. The enthalpy changes may be calculated by partial area method, namely, the area between baseline and DSC curve over the transformation temperature range represents the enthalpy change ΔH of the transformation, as shown in Fig. 3(a)[12]. It can be seen from Fig. 3(a) and (b) and Table 2 that the primary and eutectic growth temperature (here, refers to the beginning temperature of primary and eutectic transformation) is raised by about 17.3 ℃ and 4 ℃ due to phosphorus addition, respectively. Moreover, the primary and eutectic nucleation temperatures are 745.0 ℃ and 570.0 ℃ without phosphorus addition, 762.0 ℃ and 574.0 ℃ with phosphorus addition, respectively, according to the first derivative of DSC, as shown in Fig. 4.

It can be seen from Table 2, the primary enthalpy changes (ΔH_p) of Al-25% Si alloy with and without phosphorus addition are − 294.2 J/g and − 261.0 J/g, while the eutectic enthalpy changes (ΔH_e) are − 386.1 J/g and − 397.3 J/g, respectively. The absolute value of ΔH_p for the alloy treated by phosphorus is higher than that for the alloy untreated, and it is inverse for ΔH_e. This elucidates that the amount of primary silicon in Al-25% Si alloy with phosphorus addition is more than that without phosphorus addition, and the amount of eutectic silicon is less.

$$r^* = \frac{\gamma_{SL}}{\Delta G_V} \tag{1}$$

$$\Delta G^*_{hom} = \frac{16\pi\gamma^3_{SL}}{3(\Delta G_V)^2} \tag{2}$$

$$\Delta G^*_{heter} = \frac{16\pi\gamma^3_{SL}}{3(\Delta G_V)^2} S(\theta) \tag{3}$$

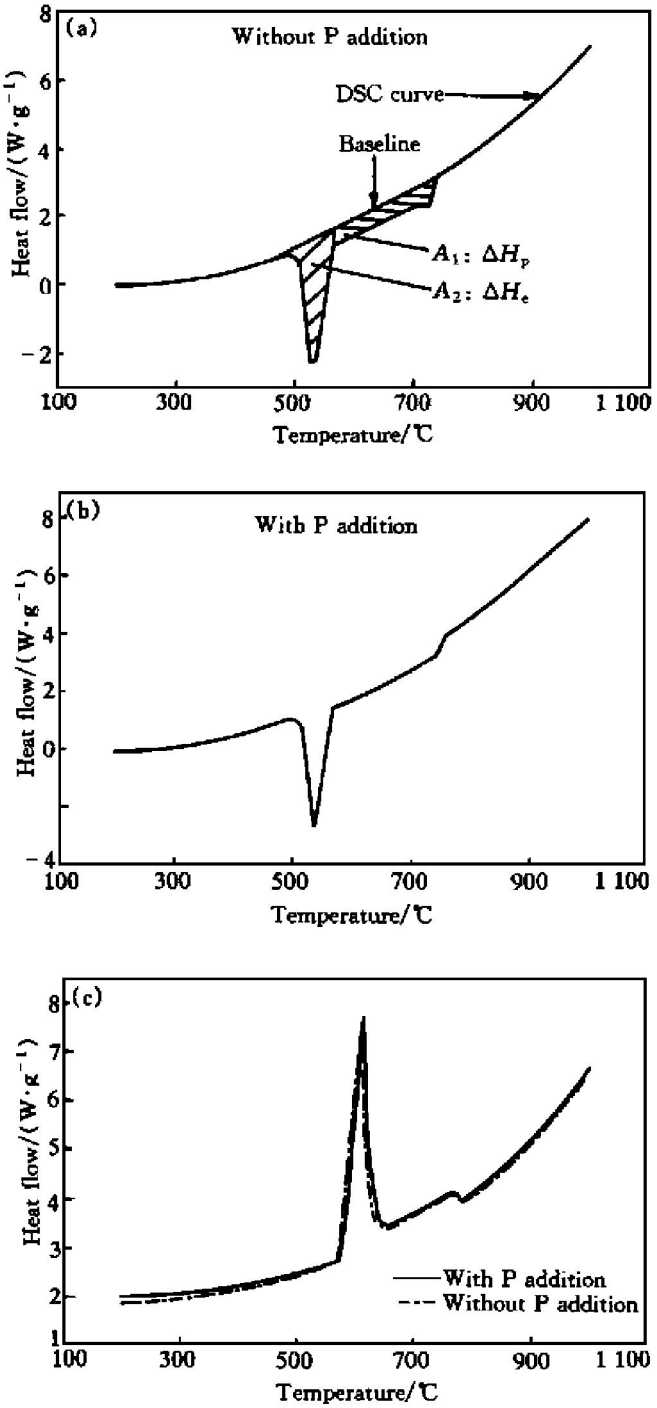

Fig. 3 DSC traces of Al-25% Si alloy
(a), (b) —Cooling process; (c) —Heating process

$$\Delta G_V = \frac{L_V \Delta T}{T_m} \tag{4}$$

where r^* is the critical nucleus radius for successful nucleation, which only depends on undercooling; ΔG^*_{hom} is the critical activation energy barrier against homogeneous nucleation; ΔG^*_{heter} is the critical activation energy barrier against heterogeneous nucleation; θ is the wetting angle between the solid and the substrate; γ_{SL} is the solid/liquid interfacial energy; L_V is the latent heat of fusion per unit volume; T_m is the solidification temperature; ΔT is the undercooling with respect to the solidification temperature[13].

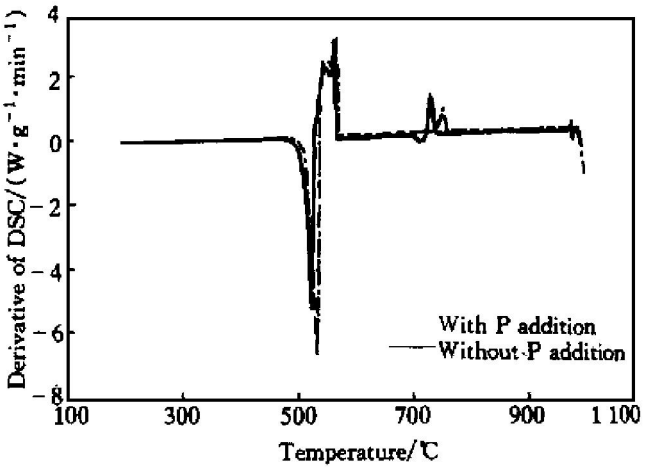

Fig. 4 First derivative of DSC of Al-25% Si alloy as function of temperature

In general, the primary silicon in hypereutectic alloys can not readily nucleate through the high melt point impurities in these alloys. According to the Eqns. (1), (2) and (4), the greater the degree of undercooling of the melt, the smaller the critical nucleus radius and the critical activation energy against homogeneous nucleation, and the more easily the melt nucleates. Thus, the nucleation and growth of primary silicon in Al-25% Si alloy melt without phosphorus addition may occur under greater degree of undercooling. After phosphorus addition, however, phosphorus reacts with liquid aluminium to produce a great amount of AlP particles in the melt. The size of many particles exceeds the critical nucleus radius and the diversity of the particle shape (shape factor $S(\theta)$) significantly depresses the critical activation energy, according to the Eqns. (1), (3), and (4). Thus, the critical activation energy as well as the degree of undercooling reduces, and many AlP particles can act as heterogeneous sites for the nucleation of primary silicon. Hence, the degree of undercooling is depressed by about 17.3 ℃. The depression degree of undercooling can be used as an indicator of degree of refine-

Table 2 Parameters of Al-25% Si alloy in cooling process by DSC analysis

	t_p/ ℃	t_e/ ℃	t_{ep}/ ℃	Δt_p/ ℃	Δt_e/ ℃	ΔH_p/ (J·g^{-1})	ΔH_e/ (J·g^{-1})
Without P addition	739.7	565.4	526.9	174.3	75.0	- 261.0	- 397.3
with P addition	757.0	569.4	536.5	187.6	69.4	- 294.2	- 386.1

t_p —primary growth temperature; t_e —eutectic growth temperature; t_{ep} —eutectic peak temperature; Δt_p —primary temperature range; Δt_e —eutectic temperature range; ΔH_p —primary enthalpy change; ΔH_e —eutectic enthalpy change

ment by phosphorus in practice. Furthermore, silicon concentration in the melt treated by phosphorus decreases more rapidly with precipitation of a good number of primary silicon particles, compared to the melt untreated. Therefore, eutectic transformation in the melt treated by phosphorus begins at a slight higher temperature.

4 CONCLUSIONS

1) The hypereutectic Al-25% Si alloy can be well refined by phosphorus addition, and the average size of primary silicon particles reaches 30 μm. The primary silicon without refinement is coarse, plate-like, and non-uniformly distributed. After refinement, the primary silicon is fine, blocky, and well-dispersed.

2) Due to phosphorus addition to Al-25% Si alloy melt, there is a raise of the primary and eutectic growth temperature, 17.3 ℃ and 4 ℃, respectively. The primary nucleation temperature of Al-25% Si alloy can be determined by the first derivative of DSC data, 762.0 ℃ for the alloy treated by phosphorus and 745.0 ℃ for the alloy untreated.

3) The absolute value of the primary enthalpy change of Al-25% Si alloy treated by phosphorus is higher than that of the alloy untreated, but it is inverse for the eutectic enthalpy change. This elucidates that the amount of primary silicon in Al-25% Si alloy with phosphorus addition is more than that without phosphorus addition, and the amount of eutectic silicon is less for the alloy with phosphorus addition.

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