

## Effect of AlP master alloy on grain refinement of primary silicon in eutectic Al-Si alloys

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**Abstract:** To obtain the finer primary silicon crystals, the proprietary Al-P master alloy was adopted to modify the eutectic Al-Si alloys and the most suitable modification process was made in the experiments. The SEM (Scanning Electron Microscope) and DSC (Differential Scanning Calorimeter) analysis indicate that the Al-P modifier has more advantages over Cu-P and Fe-P modifier in easily addition, no elemental alteration and less undercooling of primary silicon's solidification, which suggests the Al-P master alloy is an effective modifier of eutectic Al-Si alloys.

**Key words:** AlP master alloy; grain refinement; refining effect; Al-Si alloy

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### 1 Introduction

Al-Si alloys are widely used in automotive applications due to their excellent wear resistance, the high strength-to-weight ration and low thermal expansion coefficient. These properties are attributed to the high volume fraction of hard and fine Si particles embedded in an alloy matrix. However, the primary Si crystals become coarser with increasing Si content in excess of 3% [1,2], which results in deterioration in mechanical properties. It becomes significant to attain more small size and highly uniform distribution of Si particles in eutectic Al-Si alloys.

Phosphorus is an effective element to refine primary silicon grains of eutectic and hypereutectic Al-Si alloys. The techniques to add phosphorus to Al-Si alloys are usage of P-containing master alloys and commercial fluxes [3-6]. But a number of Al-Si alloys have a limited tolerance for copper and ferrous concentrations, which restricts CuP and FeP usage. NiP master alloy isn't used widely for its high price. Most fluxes contain red phosphorus as the active agent and other salts to prevent rapid oxidation or combustion of elemental phosphorus. However, the pollution and low degree of effectiveness restrict the application of the P-containing fluxes.

The phosphorus is an effective element lies in that

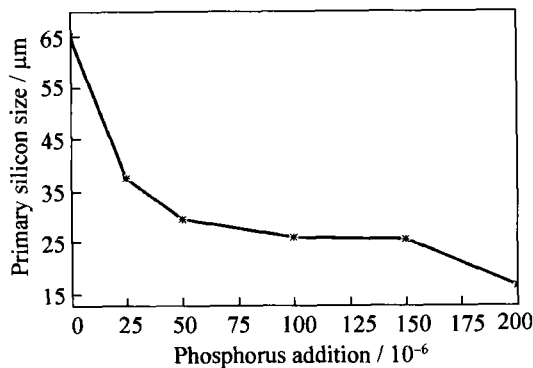
phosphorus reacts with liquid aluminum to produce a fine dispersion of aluminum phosphide (AlP) that has a crystal structure very similar to silicon, and a high melting point, and acts as effective heterogeneous nuclei for silicon. It can be thought that AlP master alloy is probably more effective than those aforementioned. This paper studies the refining effect of AlP master alloy with a proprietary route on eutectic Al-Si alloys.

### 2 Experimental

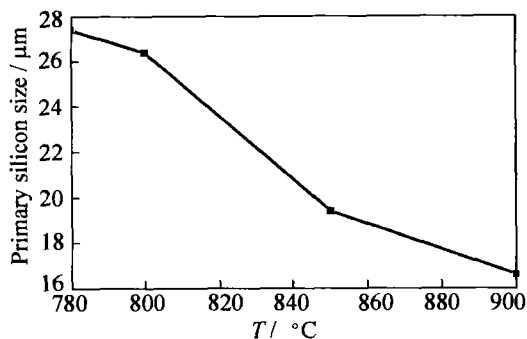
The Al-Si alloy BH135 studied in this paper was provided by China Bohai Piston Group. Specimens were prepared from BH135 base alloy, adding different levels of tableted Al-2.5%P (mass fraction) master alloy (Patent No. CN1317590A). For each trial, the base alloy was melted in a clay-graphite crucible in an electrical resistance furnace. The AlP master alloy, when added, was plunged and stirred into the melts which were held at 780, 800, 850, and 900°C for approximately 5 to 60 min. The melts were cast in standard tensile test mould and the samples were taken from the middle of the tensile test bar as cast conditions.

The primary silicon grain size was measured from photomicrographs with the aid of a graticule. Such measurements from at least 5 largest grains per field of vision and 5 fields of vision per sample were aver-

aged to obtain the results reported in **figure 1** and **2**. Microstructures were studied using optical and scanning electron microscope (SEM).



**Figure 1** Relationship between primary silicon size and addition level of phosphorus.



**Figure 2** Relationship between primary silicon size and treatment temperature.

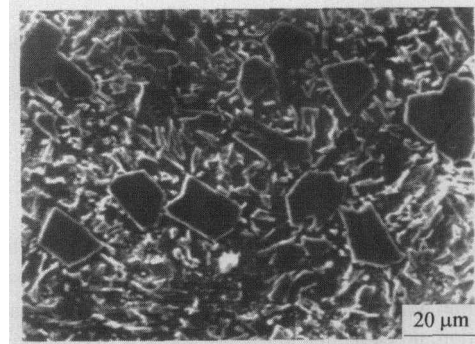
The change of phase and enthalpy during melt and solidification of the alloys was researched by differential scanning calorimeter (DSC).

### 3 Results and discussion

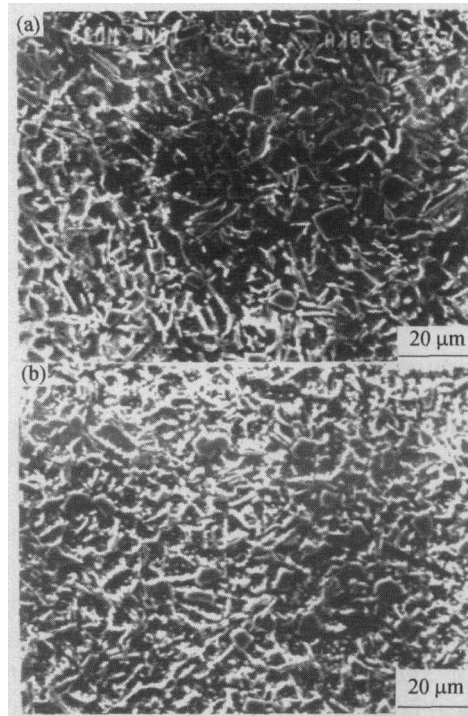
The microstructure of unmodified BH135 alloy is shown in **figure 3**. The primary silicon grains, about 65  $\mu\text{m}$ , exhibit a variety of complex shapes. The coarse and branched primary silicon is evident as the large particles while eutectic Si is dispersed as the finer particles throughout the remainder of the structure. Furthermore, the primary silicon grains are easy to coalesce under buoyancy forces during cooling of the upper part of the melt in the mould. This effect has been reported and discussed [7,8] for hypereutectic Al-Si alloys. While the primary silicon grains turn fine and polyhedral after adding AIP master alloy as shown in **figure 4**, which illustrates that AIP added into melts provides effective heterogeneous nuclei for nucleation of primary silicon and its effect is uniform throughout the melt.

Figure 4 shows the microstructures of specimens poured from the same melt with different contacting time, *i.e.* the time from the addition of master alloy to pouring. The two specimens have nearly equal size

and amount of primary Si per unit area. It suggests that AIP master alloy is less influenced by contacting time than other P-containing master alloys [4]. The AIP master alloy can refine primary silicon grains of eutectic Al-Si alloys with short contacting time and keep excellent refining effect in a long period.



**Figure 3** Microstructure of BH135 alloy as-cast at 900°C.



**Figure 4** Microstructure of BH135 alloy modified by 0.02% phosphorus treated at 800°C, (a) contacting time 5 min; (b) contacting time 60 min.

The more the amount of phosphorus from 0.0025% to 0.02% added into the melts, the finer is the primary silicon. **Figure 5** shows the transition of the morphology of primary silicon. The primary silicon grain size is relatively stable from 25  $\mu\text{m}$  to 30  $\mu\text{m}$  when the addition level of phosphorus from 0.005% to 0.015% (figure 1). The primary silicon becomes smaller (about 15  $\mu\text{m}$ ) when the addition level of P up to 0.02%. The refining effect is virtually similar to FeP and NiP, and better than CuP reported by other papers [4,5]. Figure 1 suggests that AIP nucleating particles of this master alloy directly become heterogeneous nuclei because the samples had almost the same cooling rate and su-

perheat, so the growth rate of crystal grains was almost the same, too. But it becomes important to keep high cooling rate of the melt. Otherwise, the AIP nucleating particles would agglomerate, which might

cause gravity segregation. The density of AIP ( $2850 \text{ kg/m}^3$ ) [9] is larger than that of eutectic Al-Si alloys (less than  $2400 \text{ kg/m}^3$ ) at  $800\text{--}900^\circ\text{C}$  [10].

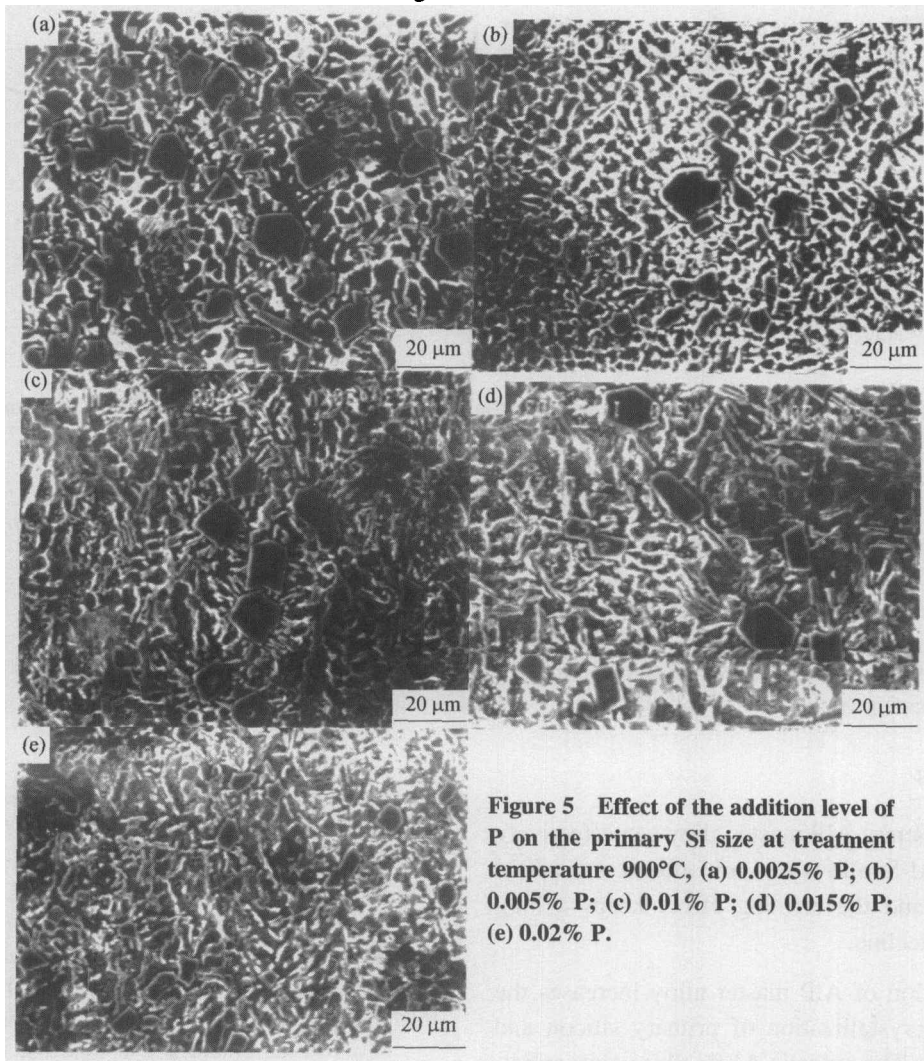


Figure 5 Effect of the addition level of P on the primary Si size at treatment temperature  $900^\circ\text{C}$ , (a) 0.0025% P; (b) 0.005% P; (c) 0.01% P; (d) 0.015% P; (e) 0.02% P.

Figure 2 shows the effect of temperature on the primary Si grain size. To determine the stability of AIP master alloy at high temperature in the Al-Si melt, AIP master alloy was added into the melt at  $900^\circ\text{C}$ , which is greatly above the treatment temperature in piston manufactures. It can be seen from the figure that the primary Si size becomes smaller and smaller from  $27.4 \mu\text{m}$  to  $15 \mu\text{m}$  with the adding temperature increasing from  $780^\circ\text{C}$  to  $900^\circ\text{C}$ . It can be explained that AIP master alloy is so chemically stable that it can act as effective refining agent below  $900^\circ\text{C}$  while the melting point of AIP is  $1060^\circ\text{C}$  [6]. Although the superheat of melt treated at  $900^\circ\text{C}$  is much larger than that at  $780^\circ\text{C}$ , the primary Si grain of the former is much smaller than that of the latter. It is perhaps partly determined by the effect of thermal-rate treatment concluded by X. Bian [11], which means that a melt is heated to  $300^\circ\text{C}$  above the normal pouring temperature and it is cooled rapidly to the pouring temperature before poured, the finer crystal grains can

be obtained in the structure after such treatment.

From DSC profiles (figure 6) of BH135 alloy with and without refinement by AIP master alloy during cooling, it can be seen that they have similar solidification process containing the crystallization of primary Si and the eutectic reaction. However, by comparing the thermodynamic parameters listed in table 1, it is evident that the transformation temperatures with refinement are higher than those without refinement except for the latent heat of crystallization. The solidification temperature with refinement ( $600.5^\circ\text{C}$ ) is  $6.4^\circ\text{C}$  above that without refinement, and the eutectic reaction peak ( $541.5^\circ\text{C}$ ) of the former is  $12.3^\circ\text{C}$  more than that of the latter. The latent heat of primary Si crystallization is  $32.7 \text{ J/g}$  and  $34.1 \text{ J/g}$ , respectively. These differences suggest that AIP compounds act successfully as heterogeneous nuclei, which make the primary Si grains grow easier than that without modification. Therefore, the solidification temperature of

primary Si modified is higher than unmodified. Moreover, the heat given off by modified primary Si grains is more than unmodified ones since the former solidifies at higher temperature, *i.e.*, the latent heat of crystallization of the modified primary Si is higher

than the unmodified. So it needs less undercooling for primary and eutectic Si to crystallize after adding AIP master alloy. It's perhaps the thermodynamic causes for AIP master alloy to modify eutectic Al-Si alloy effectively.

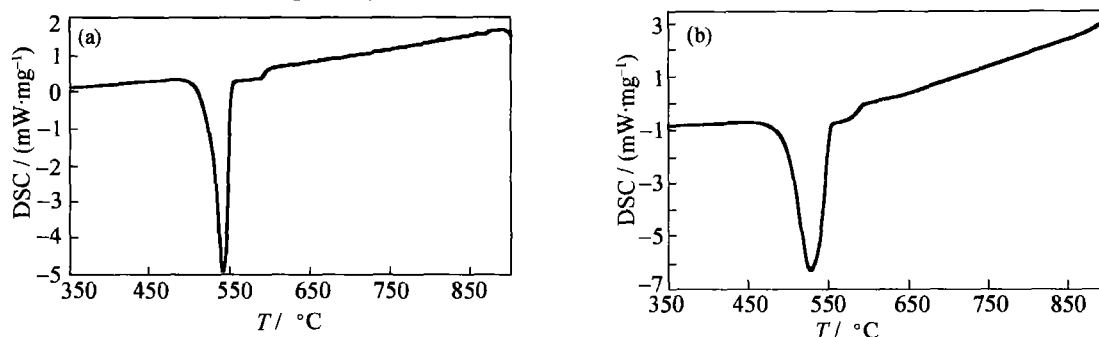


Figure 6 DSC results of BH135 alloy during cooling from 900°C to 350°C, (a) BH135 alloy with the addition of 0.02% P; (b) BH135 alloy.

Table 1 Parameters of temperature from DSC profiles in figure 6(a) and (b)

Specimens	Temperature / (°C)				Latent heat / (J·g <sup>-1</sup> )	
	1	2	3	4	5	6
a	489.2	541.5	554.5	600.5	364.1	34.1
b	477.3	529.2	552.4	594.1	455.2	32.7

Note: point 1—ending temperature of solidification; point 2—peak temperature; point 3—ending temperature of primary grains reaction; point 4—starting temperature of solidification; 5—general latent heat of crystallization; 6—latent heat of primary silicon crystallization.

#### 4 Conclusions

(1) The proprietary AIP master alloy can effectively refine eutectic Al-Si alloys in 5 min after it was added in the melting and the refining effect keeps a long period without decline.

(2) The addition of AIP master alloy increases the temperature of crystallization of primary silicon and eutectic reaction. The eutectic Al-Si alloys start solidification with less undercooling.

(3) AIP master alloy can keep good refining effect from 780-900°C with little addition level of 0.02% P. This master alloy can be well and easily used without elemental alteration in piston-manufacturing industry.

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