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Modification mechanism of hypereutectic Al-Si alloy with P-Na addition①

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Abstract: Effect of P-Na united modification on Al-22%Si-1.0%Cu-0.5%Mg-0.5%Mn alloy was studied. The results show that the refining effect of P-Na addition on primary silicon is superior to that of P and the former could modify eutectic silicon at the same time. Effects of P-Na modification on crystallization and microstructure of hypereutectic Al-Si alloys were studied with Electron-Scanning Microscope, Electron-Probe and X-ray diffractometer. The modification mechanism represents that on one hand, the primary silicon is refined by AlP as heterogeneous nucleus; on the other hand, when Na is added at the same time, P atoms are difficult to diffuse in the melt, and then enrichs on the growing faces of silicon phase. Moreover, a SiP compound was also discovered in Si crystals, which prevents the growth of silicon phase and refines the primary silicon.

Key words: hypereutectic Al-Si alloys; modification mechanism; grain refinement; modification
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1 INTRODUCTION

As a structural material having many merits such as high friction resistance, high heat resistance and low expansion coefficient[1-3], hypereutectic Al-Si alloy has been attracting attention of many researchers. However, for the hypereutectic Al-Si alloys produced with traditional casting process, there are usually many coarse Si particles in the matrix, which lead to low tensile strength, poor turning properties and rough surface after mechanical working[4]. The previous researches[5, 6] indicated that, for particulate reinforced metal matrix composites(MMCs), if the particles are smaller than 20 μm and uniformly distributed, the composites will present high mechanical properties, smooth surface and improved turning properties. Therefore refinement of primary Si crystals is the key technology for production of castings with hypereutectic Al-Si alloy by traditional casting process.

Presently the refinement of primary Si is mainly achieved by phosphorus modification internationally. The phosphorus is usually added by means of phosphorus alloy or phosphorus compound, representatively Cu-P alloy or phosphate. The traditional theory on P modification is that the AlP compound is formed when P is added into the melt of hypereutectic Al-Si alloy. Based on the principle of similarity of crystal structure and lattice, the small AlP compound particles act as heterogeneous nucleus, and the primary silicon is refined because of the increase of nucleus[6, 7].

Sodium is generally added as a modifying element into hypoeutectic Al-Si alloys to refine eutectic silicon. For the united modification of P and Na on hypereutectic Al-Si alloys in the previous research[7], it was considered that P and Na could easily combine to form a steady compound Na_3P. This means that Na not only cannot refine eutectic structure, but also destroy the refining effect of phosphorus on primary silicon. But Ohmi et al[8] found that when P and Na are added orderly for united modification, primary silicon can be modified under certain conditions. However, researches on the modification mechanism of P-Na united modification are seldom. The modification mechanism and the distribution of refining elements and their effects on microstructure need to be studied.

In this paper the Al-Si-Cu-Mg alloys containing 22%Si were modified with a P-Na dual modifier, and the effects were compared with P addition. Effects of P-Na modification on crystallization and microstructure of hypereutectic Al-Si alloys were studied with Electron-Scanning Microscope, Electron-Probe and X-ray diffractometer.

2 EXPERIMENTAL

The experimental Al-Si alloy was designed simi-

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lar to the generally used piston alloy, and the nominal chemical compositions of the alloy were as following: 22% Si, 1.0% Cu, 0.5% Mg, 0.5% Mn, ≤0.4% Fe, balance Al. The purities of raw materials used to make this alloy were pure Al (A00 grade), 99.9% Si, 99.99% Mg, respectively, and Al-10% Mn master alloy and Al-50% Cu master alloy were used.

Two kinds of modifiers were added into melt of the above alloys respectively. One was P modifier, which was added in the form of Cu-13% P master alloy, and the master alloy was added at 1.0% amount. Another was P-Na united modifier, in which P was added in the form of Cu-13% P master alloy, and Na was added in the form of sodium salt. The master alloy was also added at 1.0% amount, and the sodium salt was added at 2.0% amount.

The alloy was melted in a graphite crucible in an electric furnace. The melting processes were that, Mg was added into the melt at 700 ℃, the melt was refined with blowing Ar gas bubbles at 760−780 ℃, and the modifier was added at 800−850 ℃. The melt was poured at 820 ℃ into metallic moulds to make specimens, which were preheated to about 200 ℃. The specimens have diameters of 20 mm. The strength test specimens were also by pouring the melt into the metallic mould under the same condition above mentioned.

The microstructures of the specimens were examined with an optical microscope and an SEM-500 scanning electron microscope. A JXA-8800 electron probe microanalyser was used for EPMA analysis. A D/max-ⅢC model X-ray diffractometer analyser was used for analysis of compounds in Si phase of Al-Si alloy. The Si particles for X-ray analysis were extracted from specimen of hypereutectic Al-Si alloy by deep etching method.

3 RESULTS AND DISCUSSION

3.1 Comparison of microstructure

The microstructure of un-modified specimen of Al-22% Si-1.0% Cu-0.5% Mg-0.5% Mn alloy is shown in Fig. 1(a), where there are large primary Si particles about 80−150 μm in size, and long flake-shape eutectic Si. The microstructure of the alloy modified by P is shown in Fig. 1(b), the size of the primary Si is about 35−50 μm, and the eutectic Si is still in long flake-shape, which is in an un-modified state. Fig. 1(c) shows the microstructure of the alloy modified by P-Na, and the size of the primary Si is only about 20−25 μm. In addition to the refining of eutectic Si, the size of the primary Si modified by P-Na is smaller than that modified by P only. For the specimens with a diameter of 5mm, the primary Si particle size was only about 18 μm with P-Na modification[9, 10]. This means that the particle size can be less than 20 μm. But the size of primary Si with P modification was still at 35−45 μm for the specimen with a diameter of 5 mm, which was still larger than 20 μm.

Therefore, it is obvious by comparison that the modification by P-Na addition has smaller primary Si particles, and has certain refining effect on eutectic Si. But the eutectic Si modified with P is still in un-modified state.

3.2 Micro-analysis of elements distribution

In order to investigate the difference of mechanism of the two kinds of modifier, microanalysis on composition and compounds was carried out for the

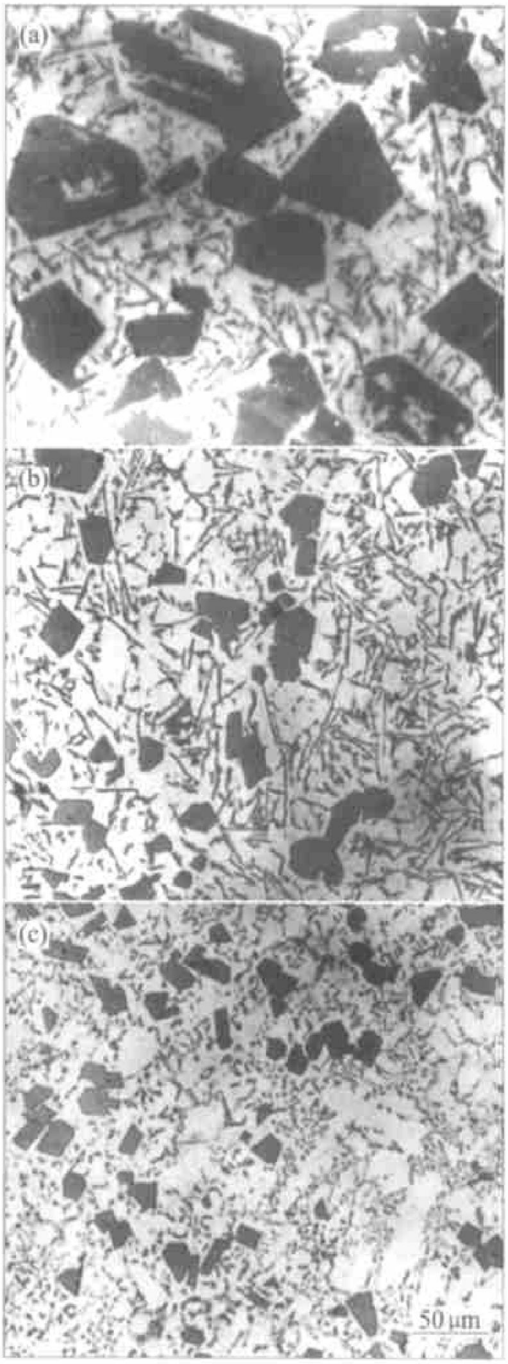

Fig. 1 Microstructures of different treated specimens
(a) —Un-modified; (b) —Modified with P;
(c) —Modified with P-Na

two kinds of specimens, respectively. Results of EDS analysis on primary Si modified by P is shown in Fig. 2. Fig. 3 shows the result of EDS analysis on primary Si modified by P-Na. It is known from Fig. 2 and Fig. 3 that there is a very small AlP particle, acted as nuclei, in the primary Si particle both in P and P-Na addition. However, the remarkable difference is that, for the alloy modified by P-Na, content of P element in primary Si is obviously higher than that in other region(Fig. 3), and the distribution region of P element is very clear, with identical contour to that of the primary Si. But there is no such phenomenon for the alloy modified by P(Fig. 2).

Fig. 4 shows the result of EDS analysis by line scanning on primary Si in a specimen modified by P-Na, but the specimen is from a different batch to the specimen of Fig. 3. From the line scanning curves of Al, Si, Cu, Mg, Mn, P(Fig. 4), we know that the primary Si phase is mainly composed of Si and P.

From the above results we know that the primary Si in the Al-Si alloy modified by P-Na is

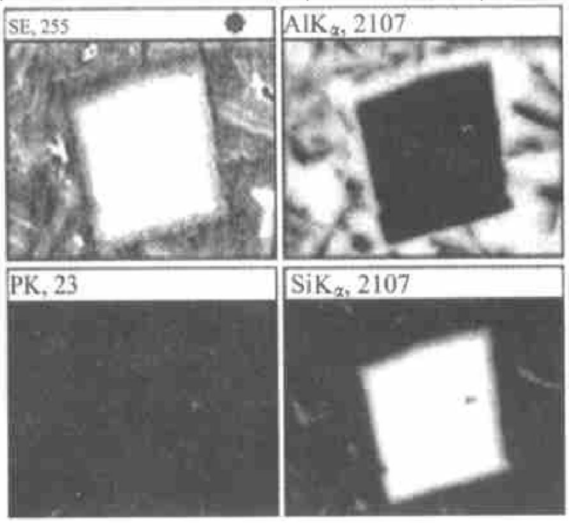

Fig. 2 EDS analysis on primary Si modified with P

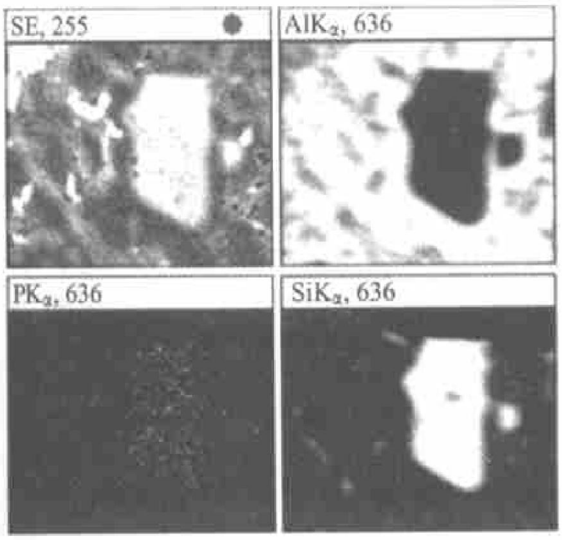

Fig. 3 EDS analysis on primary Si modified with P-Na

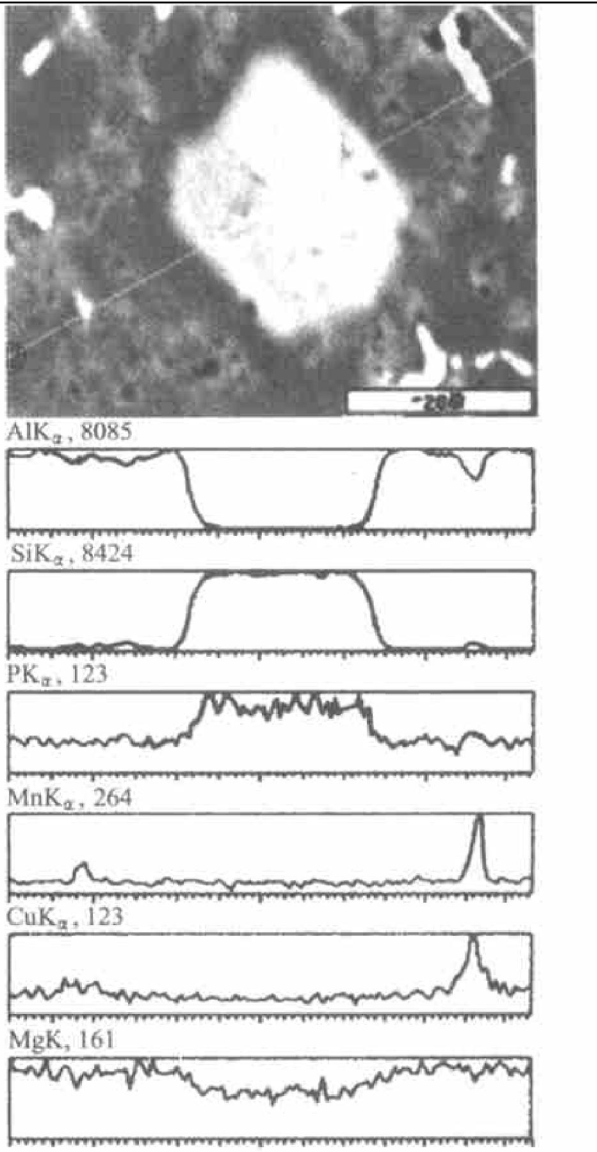

Fig. 4 EDS analysis with line scanning on primary Si of alloy modified with P-Na

mainly composed of two elements, Si and P. But the actual material and structure cannot be distinguished only from above mentioned results. Therefore, the Si particles were extracted from specimen of hypereutectic Al-Si alloy by deep etching technology, and the actual material of the Si phase was determined by a D/max-IIIC model X-ray diffractometer. The XRD patterns for the Si particles is shown in Fig. 5, in which the upper curve(a) is that modified by P-Na, and the bottom curve is that modified by P. The diffraction patterns indicated that the SiP compound is discovered in Si crystals of the alloy modified by P-Na, and the Si phase is composed of Si and SiP. But there was no SiP in Si crystals in the alloy modified by P.

3.3 Discussion on modification mechanism of P-Na

For Al-Si-P ternary system, many researches confirmed the formation of AlP by reaction of P and Al[7] . The compound AlP(which contains

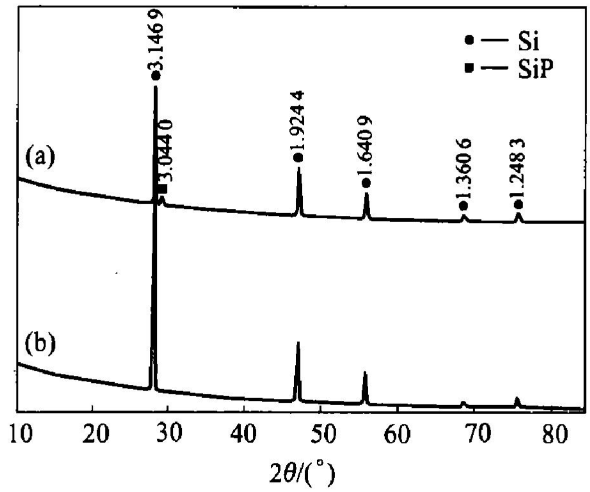

Fig. 5 Comparison of X-ray diffraction patterns of Si phase of alloys with different modifiers
(a) —Modified with P-Na; (b) —Modified with P

53.5% P) has a diamond type FCC lattice, with a lattice constant $a_{AlP}=(5.43-5.47)\times 10^{-10}$ m. The Si phase has the same crystal structure and nearly the same lattice constant as $a_{Si}=5.42\times 10^{-10}$ m[7]. Therefore AlP particles can be the nucleus of Si crystals, and the number of nucleus for Si solidification in the melt can be increased too. Therefore the primary Si can be refined.

For the Al-Si-P-Na quartary system, there may be the following phases in the alloy: Al, Si, $(NaAl)Si_2$, AlP and Na_3P[7]. The appearance of the compound phases is determined by the ratio of Na: P. When this ratio is about 2.2, Na and P react to form Na_3P; if it is higher than 2.2, compound $(NaAl)Si_2$ will be formed; and AlP will be formed when this ratio is smaller than 2.2. In this article, the ratio of Na: P, when modified by the P-Na modifier, is smaller than 2.2. Therefore, AlP was formed when the alloy was modified by P-Na united addition, and it became the heterogeneous nuclei of primary Si crystals and refined the primary Si particles. At the same time, there was a certain content of Na in the melt; it had modification effect on eutectic Si, to get refined eutectic Si. As primary Si and eutectic Si could all be refined, the strength of the alloy P-Na modification was much higher.

Although some researches indicated that P might have certain solubility in Si phase[7], it was discovered that there is SiP compound in the solid Si phase (Fig. 5). We suppose that viscosity of the Al-Si alloy melt be timely increased when Na was added, which weakened the convection in the melt and led to diffusion difficult of atoms. Mondolfo measured that diffusion coefficient of Si atom after Na addition is only 15% of that before Na addition[7]. It is the same for the diffusion of P atoms. Therefore, when P and Na are added at the same time, P atoms in the melt, redistributed by the crystallization of Si phases, are even more not easy to diffuse toward outside liquid, which leads to the formation of SiP compound, and it enters into Si phase. This leads to the increase of P content in Si phase.

During solidification, with the primary Si particles growth, Si atoms in the liquid in front of the growth interface diffuse toward the interface and push Al atoms aside. Viscosity of the Al-Si alloy melt is increased when Na is added, diffusion coefficient of P is decreased, and P atoms enriches on the growth interface of Si phase. It will promote the formation of SiP compound. This obstructs the Si growth and decreases its growth velocity, thus refines the primary Si particles. This is supposed to be the reason why primary Si particles size with P-Na modification is smaller than that modified by P.

As remnant melt will solidify by the mode of eutectic solidification of the Al-Si alloy, P element in remnant melt will not reach the enrichment extent because P content in the remnant melt is lower than that in primary Si, and the two phases of eutectic Si and α(Al) will grow concomitantly. Consequently distribution of P in other regions except primary Si particles is uniform.

Moreover, Na, decomposed by the P-Na modifier, yet has influence on the eutectic growth mode, to refine the eutectic Si, which has the same mechanism to traditional Na modification for eutectic silicon[11, 12]. As P has some restriction on the refining effect of Na, and the refining effect of Na on eutectic Si is not so good as that when Na is individually added in hypoeutectic or eutectic Al-Si alloys. The reason waits for further investigation in the future.

4 CONCLUSSIONS

1) United modification of hypereutectic Al-Si-Cu-Mg alloy with P-Na gets smaller primary Si particles than that with P modification. It can refine eutectic Si at the same time, exhibiting dual modifying effects.

2) The SiP compound is discovered in primary Si particles when modified by P-Na. During the solidification of primary Si, the primary Si is refined by AlP as heterogeneous nucleation, moreover the primary Si particles are further refined because of the presence of Na. It is purposed that the viscosity of the Al-Si alloy melt is increased because of the presence of Na in P-Na addition, P atoms are difficult to diffuse in melt, and then enrich on the growing interfaces of silicon phase and reacted to form SiP compound, which prevents the growth of Si phase and refines Si crystals. Simultaneously Na in the melt has effect of refine-

ment on eutectic Si phase.

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