Article ID: 1003-6326(2003)01-0092-05

United modification of Al-24Si alloy by Al-P and Al-Ti-C master alloys ①

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Abstract: The modification effect of a new type of Al-P master alloy on Al-24Si alloys was investigated. It is found that excellent modification effect can be obtained by the addition of this new type of Al-P master alloy into Al-24Si melt and the average primary Si grain size is decreased below 47 μm from original 225 μm. It is also found that the TiC particles in the melt coming from Al8Ti2C can improve the modification effect of the Al-P master alloy. When the content of TiC particles in the Al-24Si melt is 0.03%, the improvement reaches the maximum and keeps steady with increasing content of TiC particles. Modification effect occurs at 50 min after the addition of the Al-P master alloy and TiC particles, and keeps stable with prolonging holding time.

Key words: Al-P master alloy; Al-Si alloy; modification; TiC
CLC number: TG 146 **Document code:** A

1 INTRODUCTION

Hyper-eutectic Al-Si alloys are widely used in the automotive engineering, especially in piston industry, with excellent abrasion and corrosion resistance, low coefficient of thermal expansion, high strength-to-mass ratio and so on[1-4]. As the desirable combination of characteristics of hyper-eutectic Al-Si alloys depends on the primary Si grain size to large extent, the refinement and modification of primary Si are considered more and more widely with increasing usage of them. The common method of modifying primary Si is to add phosphorus into melt in practice and the modification effect of it is the best at present[5-9], although there are many other ways by which the primary Si can be modified, such as chilling, superheat melting, low-temperature casting, high-pressure casting. The most common technique of adding phosphorus to Al-Si alloys is the usage of red phosphorus, special commercial fluxes and Cu-P master alloy. While the drawbacks of them, for example safety and environmental concerns, segregation and degree of effectiveness, are brought in at the same time.

So far, there are a few references available on modifying Al-Si alloy by Al-P master alloy and factors that affect modification effect of Al-P master alloy. In this paper, the Al-24Si alloy is modified by Al-2.5%P master alloy, and the influence of TiC on the modification effect of the Al-P master alloy is also investigated.

2 EXPERIMENTAL

Al-24%Si alloy (mass fraction) used in the experiments was prepared with commercial pure aluminum and silicon in medium frequency induction furnace, the compositions of which are shown in Table 1. The new type of Al-P master alloy was produced with a patent technology[10], the content of phosphorus of which is 2.5%. The Al-Ti-C master alloy used in the experiments was Al-8%Ti-2%C master alloy prepared with a new technology in Ref.[11]. After degassed by DSG, the melt was poured into a permanent mould, then a sample was achieved with the dimension of d 25 mm × 60 mm.

Table 1 Chemical compositions of commercial pure Al and Si (mass fraction, %)

Raw material	Si	Fe	Cu	Ca	Impurities	Al
Pure Al	0.13	0.12	0.01	–	0.30	Bal.
Pure Si	Bal.	0.2	–	0.04	1.0	0.5

Al-24Si alloy was melted in graphite clay crucible via a resistance-heating furnace at 800 ℃. The Al-P master alloy with amount of 0.8% was added into the

① **Foundation item:** Project(50171037) supported by the National Natural Science Foundation of China; Project(01105) supported by Key Project of Science and Technology Research of Ministry of Education of China
Received date: 2002-03-11; **Accepted date:** 2002-07-02
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melt at 800 ℃, about 2 min later, the melt was degassed by 1% DSG. The melt was poured into a permanent mould prior to addition and at one hour after addition of the Al-P master alloy at 800 ℃, then a sample was achieved with the dimension of d 25 mm × 60 mm. Under some situation, Al-P mater alloy was added into the melt together with Al-8Ti-2C in the experiments to evaluate the function of TiC particles, and the other process was the same as the above. The melt was poured into the permanent mould at 10, 20, 30, …, 180 min after addition of Al-P master alloy and Al-8Ti-2C to estimate the influence of holding time on modification effect of Al-P master alloy.

The metallographic sample was taken from the center of casting sample and polished. SEM and metallographic microscope were employed for metallographic examination and measurement of primary Si grain size. Three points were chosen at random to measure ten largest primary Si particles, and take the average and maximum size from them.

3 RESULTS AND DISCUSSION

Fig. 1 shows the microstructure of Al-P master alloy, and the facial scanning of P of the same point is shown in Fig. 2. As shown in the two figures, block-like aluminum phosphide (AlP) lumps exist in the Al-P master alloy, which provide ready substrate for the nucleation of primary Si in the Al-Si alloy. Fig. 3 and Fig. 4 show, respectively, the microstructures of Al-24Si alloy before and after addition of 0.8% Al-P master alloy. The primary Si is coarse, plate-like and irregular, and the average primary Si grain size is 225 μm more or less in unmodified Al-24Si alloy, as shown in Fig. 3. The size, shape and distribution of primary Si are greatly improved in Al-24Si alloy modified by addition of 0.8% Al-P master alloy. The average primary Si grain size is decreased below 47 μm, the largest size is less than 75 μm, the shape is more regular, and the distribution is more uniform than before. Fig. 5(a) shows the morphology of a primary Si particle, and facial scanning of Al and P are respectively shown in Figs. 5(b) and (c). The results indicate that there are phosphorus and aluminum in the center of the primary Si particle, that is, AlP serves as the heterogeneous nucleus of primary Si. The modification of primary Si in Al-24Si alloy is attributed to the AlP lumps in the Al-P master alloy. When the Al-P master alloy is added into Al-24Si melt, the AlP lumps in the master alloy disperse into fine AlP particles gradually and then distribute in the melt uniformly. In this process, most of AlP particles don't dissolve because the solubility of P in Al-Si alloy is small, while a part of AlP particles may dissolve in the melt. As we know, the crystal lattice of AlP is face centered cubic lattice, similar to that of Si, the lattice constants of AlP and Si are 5.42 Å and 5.43 Å, and the least atomic distance of them are 2.56 Å and 2.44 Å respectively[12, 13]. So AlP particles can effectively act as heterogeneous nuclei in the crystallization of Al-Si alloy.

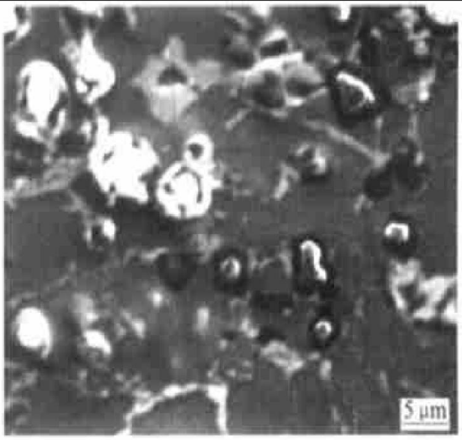

Fig. 1 Microstructure of Al-P master alloy

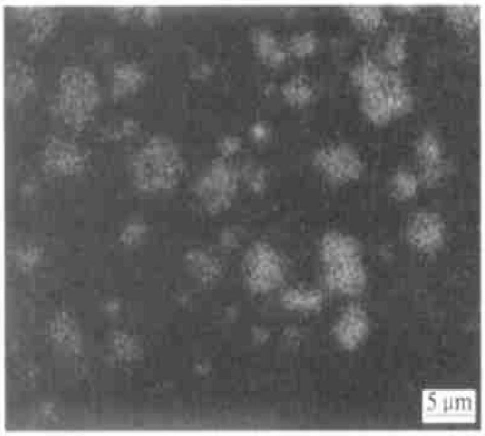

Fig. 2 Facial scanning of P

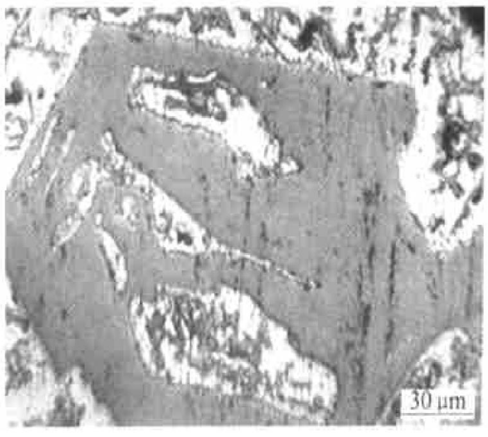

Fig. 3 Microstructure of unmodified Al-24Si alloy

$$\Delta G^*_{\text{hom}} = \frac{16}{3}\frac{\pi\sigma^3_{\text{LC}}T_0^2}{L^2\Delta T^2} \quad (1)$$

$$\Delta G^*_{\text{heter}} = \Delta G^*_{\text{hom}} f(\theta) \quad (2)$$

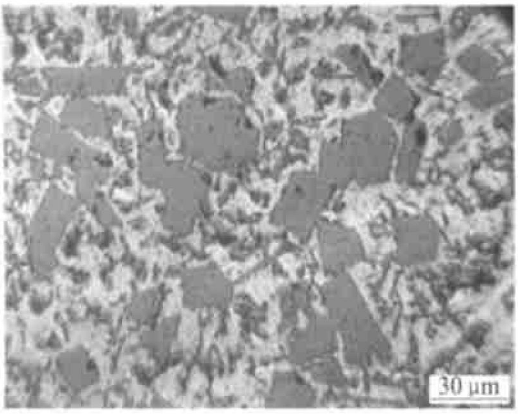

Fig. 4 Microstructure of Al-24Si alloy modified by 0.8% Al-P master alloy

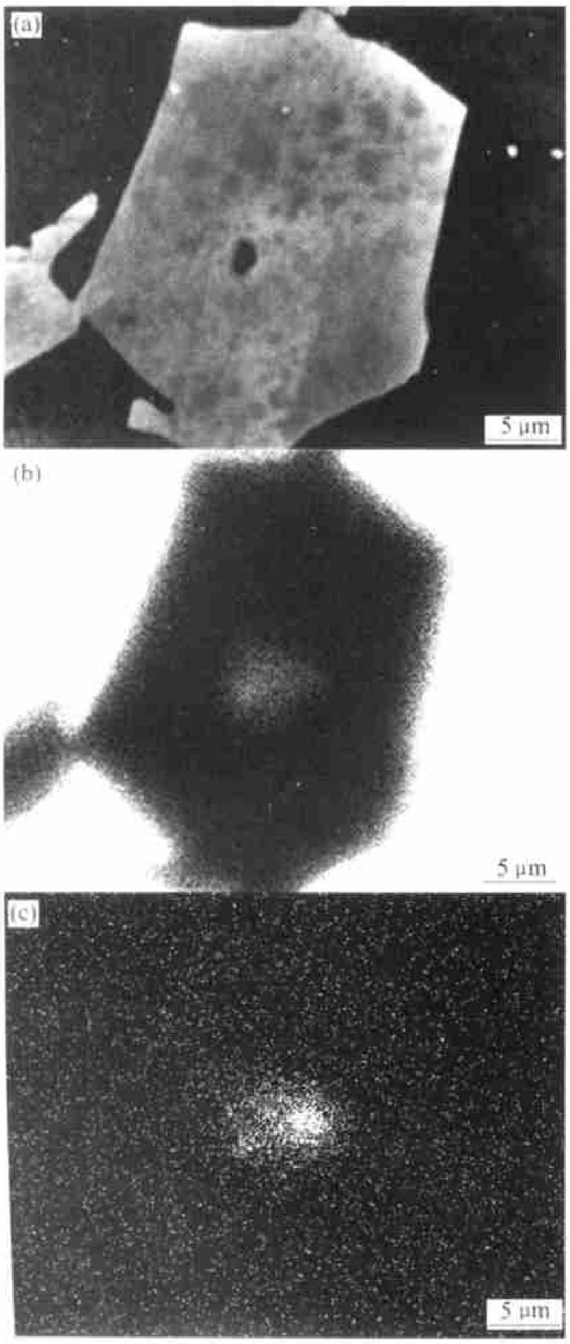

Fig. 5 EPMA analysis of primary Si crystal
(a) —Morphology of primary Si; (b) —Facial scanning of Al; (c) —Facial scanning of P

$$f(\theta)=\frac{2-3\cos\theta+\cos^3\theta}{4} \quad (3)$$

where ΔG^*_{hom} is the critical nucleation energy of homogeneous nucleation, ΔG^*_{hete} is the critical nucleation energy of heterogeneous nucleation, and θ is the wetting angle between nucleus and melt[14].

According to Eqns. (1) and (2), the influence of heterogeneous nuclei on the critical nucleation energy is in the form of $f(\theta)$. From Eqn. (3), it is predicted that the value of $f(\theta)$ is between 0 and 1. So the AlP particles in the melt reduce greatly the critical nucleation energy, energy undulation for the formation of critical nuclei, and the critical nucleation degree of super-cooling of primary Si, which is also reported in Ref. [3]. Thus, the nucleation rate of primary Si is increased greatly under the same conditions as homogeneous nucleation. As a result, the number of primary Si particles is enhanced, and the primary Si grain size is decreased.

It is also found that the addition of Al8Ti2C master alloy in the melt can improve the modification of Al-P master alloy on Al-24Si alloy. The phases in Al8Ti2C master alloy with few $TiAl_3$ plates are mainly Al and TiC. The Al and $TiAl_3$ dissolve rapidly except TiC particles after adding Al8Ti2C into the melt. So the improvement in modification of Al-P master alloy is caused by the steady TiC particles in the melt. The microstructure of Al-24Si alloy with 0.03% TiC particles modified by 0.8% Al-P master alloy is shown in Fig. 6. Compared with that in Fig. 4, the average primary Si grain size is smaller. Fig. 7 shows that the primary Si grain sizes for Al-24Si alloy are related to the content of TiC particles in the melt. The average and largest primary Si grain size decrease with increasing content of TiC particles in Al-24Si melt. At the point of 0.03%, they reach the minimum value basically, and the primary Si grain size doesn't change greatly but keeps steady with more TiC particles.

From the above results, it is shown that TiC particles in the melt promote the modification effect of Al-P master alloy really. In the authors' opinion, the essential reason of improvement in modification effect is that TiC particles activate the dissolved phosphorus in the melt. As mentioned before, not only many fine AlP particles are reserved, but also a part of AlP lumps in Al-P master alloy are dissolved when Al-P master alloy is added into the melt. The dissolved phosphorus in the melt can't form AlP nuclei, which can nucleate and accelerate the precipitation of primary Si during the solidification of Al-24Si alloy. Fig. 8 shows the EPMA analysis of Al-P master alloy with TiC particles. From these figures, it is found that AlP lumps are interwoven with TiC particles in the Al-P

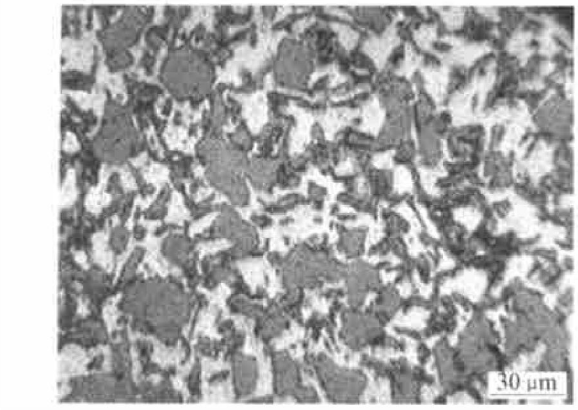

Fig. 6 Microstructure of Al-24Si with 0.03%TiC modified by Al-P master alloy

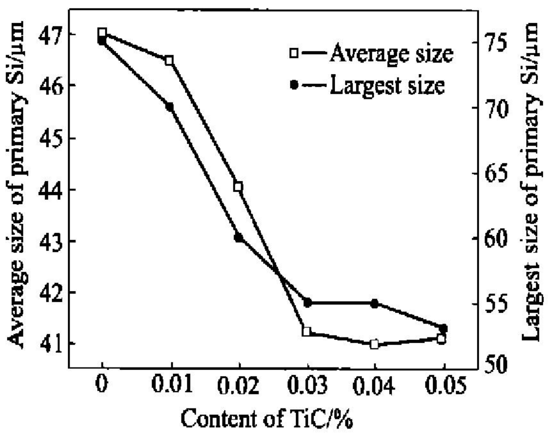

Fig. 7 Primary silicon grain size for Al-24Si as a function of content of TiC particles

master alloy, and there is a better wetting performance between AlP and TiC. So, although the content of AlP and TiC in Al-P master alloy is low, it is possible for AlP to adhere to TiC particles. Furthermore, the crystal lattice of AlP is the same as that of TiC, face centered cubic lattice, with the lattice constants of them being 5.42 Å and 4.32 Å[15] respectively. Despite large difference in lattice constants between them, the atomic distance on crystal face(001) of AlP is 5.42 Å and the double atomic distance on crystal face(011) of TiC is 6.11 Å. If TiC particle serves as the substrate of AlP, the unmatched rate(δ) between them at these two crystal faces is 12.7%. This value is between 5% and 25%, which indicates that the interface between them is partial mutual lattice interface[14]. With partial mutual lattice interface and large wetting power between AlP and TiC particles, the dissolved P may congregate on the surface of TiC particles, and form a transition layer of AlP on TiC particles when there are TiC particles in the melt. Thus the compound structure of TiC particles and AlP transition layer can serve as the nucleus of primary Si in the crystallization of Al-24Si alloy. The dissolved phosphorus is activated in this way, so that the modification effect of Al-P master alloy is improved. However, it is noticed that the dissolved phosphorus is limited and the AlP transition layer on the surface of TiC particles has an extreme value. So, the modification effect reaches the best level at the point of 0.03%, and can't change greatly with more TiC particles. It is necessary to investigate reasonable mechanism more deeply on the improvement of TiC particles in

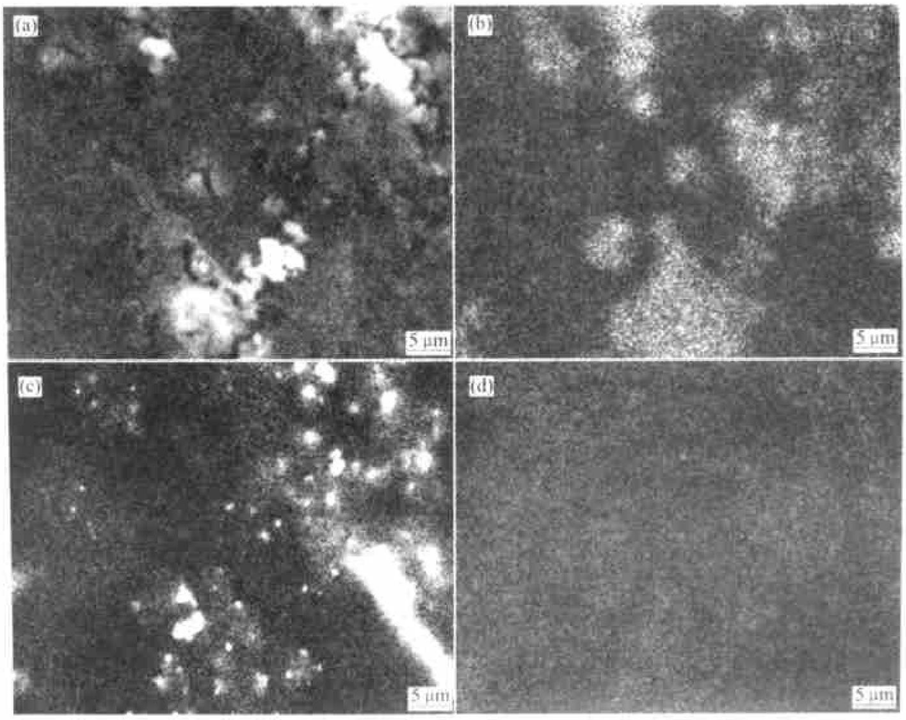

Fig. 8 EPMA analysis of Al-P master alloy with TiC particles
(a) —Morphology of Al-P master alloy with TiC particles; (b) —Facial scanning of P;
(c) —Facial scanning of Ti; (d) —Facial scanning of C

modification effect of Al-P master alloy.

The influence of holding time on modification effect is significant in practice. Fig. 9 shows the primary Si grain size for Al-24Si alloy as a function of time after addition of Al-P master alloy and TiC particles. It is shown that the best modification effect can be obtained at 50 min after addition of Al-P master alloy and TiC particles, which is permitted practically, and the modification effect doesn't increase but keeps stable with long holding time. So, the modification effect of Al-P master alloy on Al-24Si alloy is long-term. The reason is that it takes some time for AlP lumps in Al-P master alloy to disperse and uniform in the melt when it is added. Once the AlP particles distribute uniformly in the melt, they keep balance and serve as nuclei of primary Si in the following solidification.

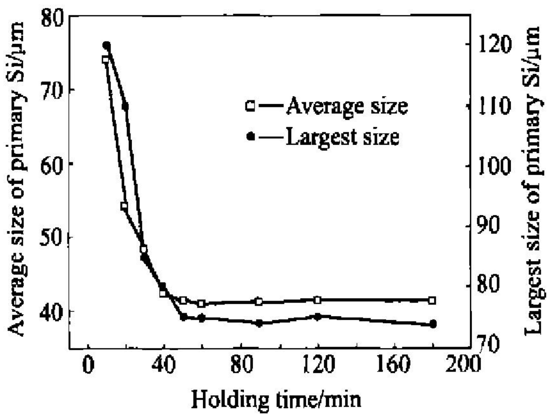

Fig. 9 Primary silicon grain size for Al-24Si as a function of time after addition of Al-P master alloy and TiC

4 CONCLUSIONS

1) Al-P master alloy has excellent modification effect on Al-24Si alloy, and the AlP phases in the Al-P master alloy can act as effective nuclei of primary Si. The primary Si of unmodified Al-24Si is coarse, plate-like and irregular, and the average primary Si grain size is decreased from 225 μm to 47 μm with addition of 0.8% Al-P master alloy intp Al-24Si melt.

2) The TiC particles in Al-24Si melt can improve the modification effect of Al-P master alloy on Al-24Si alloy. When the addition rate of TiC particles in the Al-24Si melt is 0.03%, the improvement reaches the maximum and keeps steady with increasing content of TiC particles.

3) The best modification effect of Al-P master alloy comes forth at 50 min after addition of AlP master alloy and TiC particles, and the modification effect doesn't increase but keeps stable with long holding time. The modification effect of Al-P master alloy on Al-24Si alloy is long-term.

ACKNOWLEDGEMENTS

The authors wish to thank LI Shi-tong for his assistance on SEM analysis.

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(Edited by PENG Chao-qun)