

# Influence of Titanium & Carbon Additions on the Phosphorous Modification Efficiency in Near Eutectic Al–14Si alloy

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## Abstract

The influence of Titanium (Ti) & Carbon (C), as gray cast iron master alloy, additions on the structure modification efficiency of the phosphorous (P) in near eutectic Al–14Si alloy and the nucleating mechanism was studied in this work. The results show that the phosphorous modification efficiency can be significantly affected by this addition and the sizes of the primary Si particles can be obviously refined after the addition of trace Ti&C. Micro probe Analyzer (MPA) shows there is a coupling of aluminium phosphides (AlP) and  $Al_4C_3$  particles in the center of primary Si. Moreover, the nucleation mechanism of primary Si by like-peritectic coupling of AlP and  $Al_4C_3$  was presented. The formation mechanism of like-peritectic coupling of these particles was also discussed.

**Keywords:** Al–14Si alloy; Primary silicon; Modification; Nucleation mechanism

## الخلاصة:

في هذا البحث تمت دراسة تأثير اضافة التيتانيوم والكربون، على شكل حديد الزهر الرمادي كسبيكة اشابة، على كفاءة الفوسفور في تعديل البنية البلورية لسبيكة الالمنيوم - 14% سليكون، كما تم ايضا دراسة سلوك التتوي لهذه السبيكة. لقد اظهرت النتائج بان كفاءة تعديل الفوسفور للبنية البلورية تتاثر كثيرا بهذه الاضافة وان الحجم الحبيبي لدقائق السليكون الاولي تاثر هو الاخر بشكل ملحوظ باضافة التيتانيوم والكربون. ويظهر مجس التحليل المايكروبي (MPA) ان هناك ارتباط بين دقائق فوسفيد الالمنيوم ودقائق كربيد الالمنيوم في مركز حبيبة السليكون الاولي. علاوة على ذلك فقد تم عرض الية تخليق دقائق السليكون الاولي بواسطة مزدوج شبه بيرتكتك لفوسفيد وكربيد الالمنيوم ( $AlP$  and  $Al_4C_3$ ). تم ايضا مناقشة الية تكوين مزدوج شبه بيرتكتك لتلك الدقائق.

## 1. Introduction

The excellent mechanical and casting properties of Aluminium-Silicon alloys promote to use these alloys widely in aerospace and transportation [ M. Harun *et al*, 1996], [S Nagarajan and B Duttaand, 1999], [ Henghua *et al*, 2008 ]. Al–Si alloys that contain more than 12 wt.% Si exhibit hypereutectic microstructures, normally consisting of the primary silicon phase in the eutectic matrix [Henghua *et al* 2008]. More attentions are paid to hypereutectic Al–Si alloys than other aluminium alloys for aeronautic, astronautic, vacuum pumps and on automobile owing to their corrosion resistance good thermal conductivity, high wear resistance, lower density, higher thermal stability, and machinability, etc [Tomida *et al*, 2003]. The brittleness of coarse Si phases (both eutectic and primary silicon particles) is the main reason for the poor properties of Al-Si alloys because coarse silicon crystals have sharp edges that lead to premature crack initiation and fracture in tension [Sanoh, 1994].

As the desirable combination of characteristics of Al–Si near-eutectic and hypereutectic alloys depends on the topography and morphology of primary Si particles to a large extent, the modification of primary Si is being studied more widely. Various methods have been used for the modification of primary Si particles, such as rapid cooling [Nikanorov *et al*, 2005], low temperature casting, high cooling rate [Peijie Li *et al*, 2002] and various alloying additions [Teak-soo Kim *et al*, 2000]. Controls the microstructure using small addition of elements has been the most popular method due to its simplicity. Phosphorous has been the most widely used element for the modification of primary Si in near-eutectic and hypereutectic Al–Si alloys. Al–Ti–C, as a grain refiner of commercial purity aluminum and binary hypoeutectic Al–Si

alloys, can be used to refine  $\alpha$ -Al dendrites[C.L.Xu *et al*,2007],[J.R.Davis *et al*, 2001].

The present work discusses the effect mechanism of TiC particles, which added using gray cast iron and titanium powder with fluxes, on P modification efficiency in near eutectic Al–14Si alloys by using MPA and crystal lattice coherence analysis. This also provides new practical information for the neareutectic and hypereutectic Al–Si production industry.

## 2. Experimental procedure

The Al–Si alloy used in the experiments was produced by electric resistance-heating furnace using commercial purity aluminum (99.87%) and commercial pure silicon 99.97%. The chemical composition analysis was performed by using x-ray fluorescence spectrometer XRF type (X-Met 3000 TX, horizon 600 series), model 2004 as shown in Table 1. The near eutectic Al–14Si alloy was re-melted in a clay-bonded graphite crucible, heated in an electric resistance-heating furnace at 870 °C and held at this temperature for 20 min. under a cover was measured by of flux (45%NaCl + 45% KCl + 10% NaF). Part of the melt was poured into a copper-zinc alloy mould cooled by flowing cold water Figure (1) and sample no.1 was obtained without any additions or further treatment. Sample no.2 was obtained 20 min after the addition of 0.2%Cu<sub>3</sub>P master alloy contains 15%P to the melt. Sample no.3 was obtained after 10 min. then a 0.016% of pure titanium powder and 0.058% of gray cast iron (3.47 wt% C) duly packed in aluminium foil and added to the melt. More Ti and cast iron was added until there was 0.16%Ti and 0.58%cast iron in the melt.

Table 1 Chemical composition of prepared samples

Samples	Wt.%Si	Wt.%Cu	Wt.%Mg	Wt.%Ni	Wt.%C	Wt.% p	Wt.%Ti	Al
1	14.11	0.002	0.001	0.002	0.001	0.001	0.001	Bal.
2	14.21	0.070	0.001	0.001	0.001	0.030	0.001	Bal.
3	14.23	0.070	0.001	0.001	0.002	0.028	0.016	Bal.
4	14.18	0.068	0.001	0.001	0.02	0.029	0.16	Bal.

After 10 min, the melt was cast to prepare sample no.4. All samples were performed under a cover of flux (45%NaCl + 45% KCl + 10% NaF).

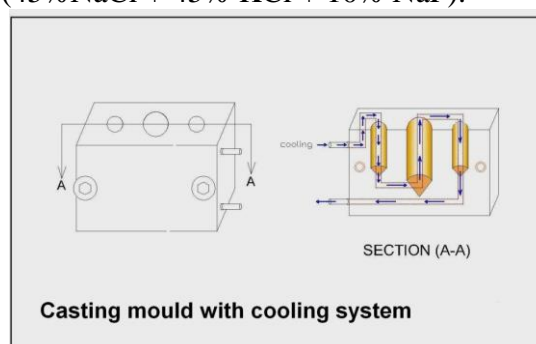


Figure 1 Casting mould

Another four samples were obtained in the same experiment process without the addition of Ti powder and cast iron chips for comparison. 0.2% Cu<sub>3</sub>P master alloy was added to the near eutectic Al–14Si alloy and samples were taken after 30, 40, and 50 min, respectively. All the samples were poured into the same type of copper-zinc mould, preheated to 150 °C before casting.

The microstructure analysis was carried out on as-cast samples to investigate the morphologies and transformation of the silicon phase. Metallographic specimens were cut directly from 10mm above the bottom of the ingots and mechanically ground and polished using standard routines. The structure and qualitative analysis were conducted by using computerized light optical microscope, type LEICA DMRM connected equipped with a Sony video colour digital camera and also, some samples

were investigated using a Hitachi S-3700N SEM equipped with a micro probe analyzer (MPA) and Energy Dispersive Spectrometer (EDS). The images were treated and analyzed with a *Kapa Image Base Launcher program*, in laboratories of Royal Institute of Technology (KTH) in Sweden

### 3. Results and discussion

Figure1 shows the microstructures of Al–14Si alloy before and after the addition of  $\text{Cu}_3\text{P}$  master alloy, Ti and C. There are a few primary Si grains in matrix of eutectic, and their sizes are large block-like and unequal, as shown in Figure 1(a).

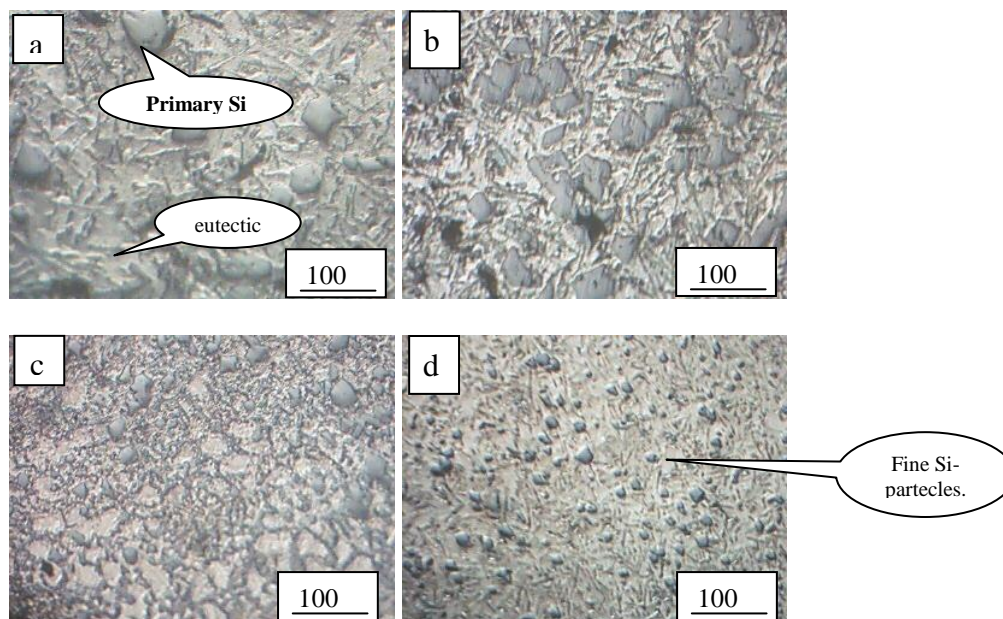


Figure1 Microstructures of eutectic Al–Si alloy before and after the addition of 0.2%  $\text{Cu}_3\text{P}$ , Ti and cast iron master alloys: (a) Al–Si; (b) Al–Si + 0.2%  $\text{Cu}_3\text{P}$ ; (c) Al–Si + 0.2%  $\text{Cu}_3\text{P}$  + 0.016% Ti and 0.058% cast iron; (d) Al–12.8Si + 0.2%  $\text{Cu}_3\text{P}$  + 0.16% Ti and 0.58% cast iron.

After the addition of 0.2%  $\text{Cu}_3\text{P}$  master alloy, there is an obvious phosphorous modification effect and the size of the primary Si decreased significantly. The holding time used in this experiment has no influence on the phosphorous modification effect of phosphorus modified Al–14Si alloy, which is consistent with the previous result [Min Zuo *et al*, 2009].

The phosphorous modification effect is retained after the addition of 0.2%  $\text{Cu}_3\text{P}$ , and 0.058% cast iron master alloy to the melt. The average size of the primary Si decreased from  $60\mu\text{m}$  to approximately  $12\mu\text{m}$ , indicating that the Ti and C improved the phosphorous modification effect.

In addition, when 10 times the Ti and cast iron master alloy was added to the melt, the positive phosphorous modification effect was retained as before without any poisoning phenomenon.

As mentioned in the literature [C.R. Ho, B. Cantor, 1995], AlP and Si are both diamond cubic with very similar lattice parameters. Primary Si nucleates heterogeneously on the solid AlP particles with a cube-to-cube orientation relationship and solidifies, which promotes the precipitation and refinement of primary silicon. According to this theory,  $\text{Cu}_3\text{P}$  master alloy can modify primary silicon effectively, as shown in figure1 (b).

Figure 2 presents the MPA image of a primary silicon nucleus in sample (4), (Al–14Si with the addition of both  $\text{Cu}_3\text{P}$  and  $\text{Fe}_3\text{C}$  master alloys), and there is a light particle inside the dark nucleus of the primary silicon.

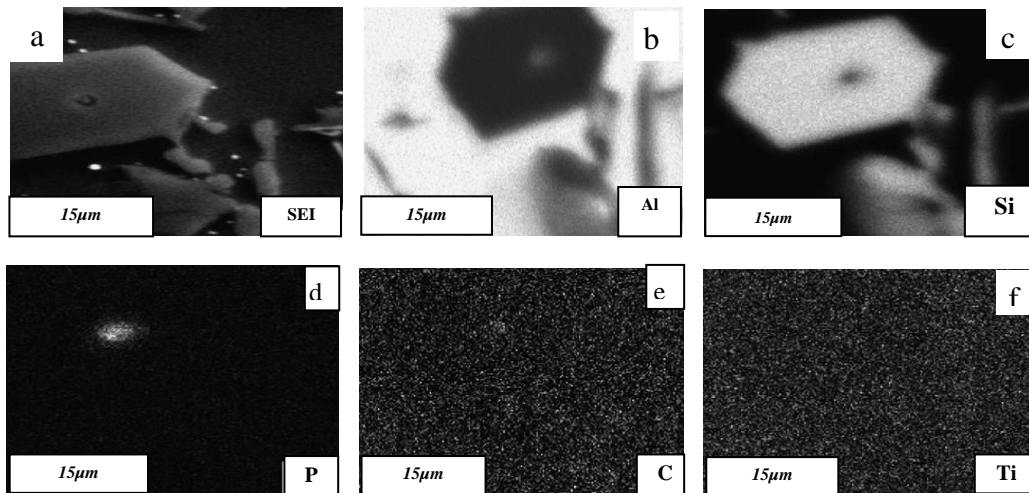


Figure 2 MPA of a primary silicon nucleus: (a) SEI of the primary Si; (b–f) the X-ray images for respective elements, Al, Si, P, C and Ti.

The X-ray images show that the dark nucleus contains Al and P elements. This indicates that it was AlP compound. While the light particle contains Al and C, without Ti, which indicates that, the particle is  $Al_4C_3$  compound. Furthermore, the  $Al_4C_3$  particle lies in the center of the AlP compound.

Figure 3 shows another nucleus of the primary silicon in sample (4), and the compositions of the magnified nucleus in Figure 4. It is noted that the nucleus contains Al, P and C elements, without Ti.

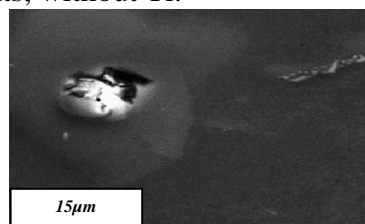


Figure 3 Another nucleus of the primary silicon in the Al–12.6Si added  $Cu_3P$  and cast iron master alloys.

Furthermore, the P and C are not overlapping each other, while they both overlap the Al, indicating that they are AlP and  $Al_4C_3$  compounds, respectively.

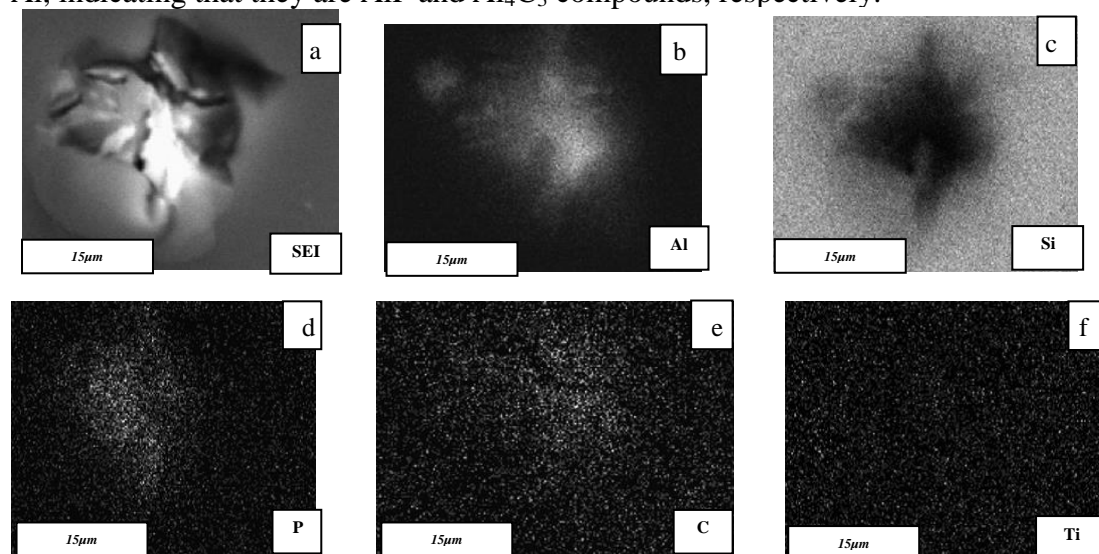


Figure 4 MPA of another primary silicon nucleus: (a) SEI of the primary Si; (b–f) the X-ray images for respective elements, Al, Si, P, C and Ti



This is similar to the result of Figure 2, since the  $Al_4C_3$  compound is not surrounded with AIP compound but adjacent to AIP compound.

In order to further confirm whether that the P and C elements overlap each other or not, the composition along the line C–D across the primary silicon in Figure 5(a) is illustrated in Figure 5(b). It can be concluded that there are two types of compound, AIP and  $Al_4C_3$ , in the nucleus of the primary silicon.

Liquid aluminium is capable of dissolving iron [John A. Taylor, 2000], this leads to thought that the aluminium melt dissolves the cast iron to free iron and carbon at 700°C.

In a pure Al system, a maximum in reactivity was observed in the liquid-state, between 700 and 750 °C, and carbon reacts with aluminium to form  $Al_4C_3$  [V.H. Lo´pez *et al*, 2003]. And then, Ti and Al combined together to form  $TiAl_{13}$  [G.S. Vinod Kumar *et al*, 2005].

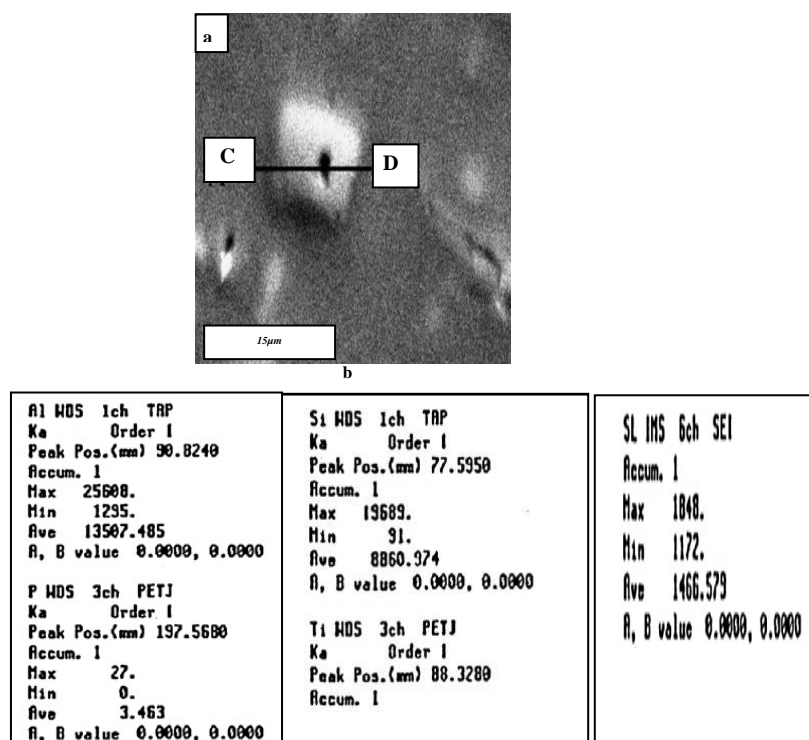


Figure 5 The distribution of chemical composition along the line across the primary silicon: (a) line (C–D) across the primary silicon; (b) chemical composition distribution along line C–D.

In this work, the melt was heated to a temperature of 780 °C. This is below the stable temperature of  $TiC$  in the melt. And then some  $Al_4C_3$  compounds were formed through the following reaction:



When  $Cu_3P$  master alloy is added into the melt, the below reaction can occur at 720°C [Min Zuo *et al*, 2009], then AIP particles formed.



Many of AIP particles may not be absorbed by the Al melt because of the lower solubility of phosphorus and the density difference. The undissolved AIP particles don't act as the nuclei of the primary Si crystals during solidification. It is well understood that there are only Ti, C and the Al in the melt. Thus, the improvement in the phosphorous modification effect is only due to the C. When C as cast iron form is added to the melt, the  $Al_4C_3$  formed can absorb the AIP, coupling together as a like-peritectic reaction to form an AIP-rich transition layer around the  $Al_4C_3$  particles, which can act as heterogeneous nucleating sites for the primary Si grains during

solidification. With the dissolved AlP precipitating to  $\text{Al}_4\text{C}_3$  compound, more AlP will dissolve into the Al melt. Therefore, most undissolved P can provide a modification effect after the addition of Ti and C particles ( $\text{Al}_4\text{C}_3$  is unstable in air). Thus more AlP particles act as the nuclei of the primary silicon. And then increasing the quantity of the primary Si and decreasing the size, as shown in Figure 1(c) and (d). It can be concluded that the addition of Ti and C particles can significantly increase the absorptivity of P in the melt, greatly improving the modification effect of the  $\text{Cu}_3\text{P}$  master alloy. Heterogeneous nucleation can be regarded as a geometrically modified case of homogeneous nucleation by which the activation barrier is decreased by the presence of a foreign substrate. A purely geometrical calculation shows that when the solid/liquid interface of the substance is partly replaced by an area of low energy solid/solid interface between the crystal and a foreign solid, nucleation can be greatly facilitated. Normally, the potential of the foreign substrate in facilitating the nucleation process is estimated from the following relation:

$$f(\theta) = (2 + \cos \theta)(1 - \cos \theta)/4 \quad \text{equation (3)}$$

where  $\theta$  is the wetting angle between the growing crystal and the foreign substrate within the melt. Under conditions of good solid/solid wetting, i.e. small  $\theta$ , the foreign substrate can have an important effect on the nucleation process. Good solid/solid wetting is expected when there are planes of low lattice disregistry between the foreign substrate and the growing crystal. Therefore, the need for near-perfect epitaxial of AlP on at least one of the crystal faces of the  $\text{Al}_4\text{C}_3$  substrate has been suggested as being essential for effective nucleation [Doru Michael Stefanescu, 2008]. It is well known that AlP is a diamond cubic with lattice parameter:  $a = 5.42$  [C.R. Ho, B. Cantor, 1995], as shown in Figure 6. The Al atoms, shown in yellow, form a normal face-centered cubic, while the P atoms, Shown in blue, are distributed in the tetrahedral interstices of the crystal cell, with each P atom surrounded by four proximate Al atoms.  $\text{Al}_4\text{C}_3$  is hexagonal with the lattice parameters:  $a = 3.335$ ,  $c = 24.96$ , with the Al atoms located on the corner angles of a hexagon and in the centre of the back surface.

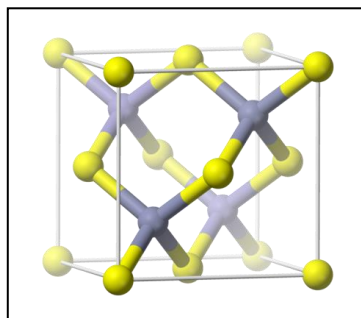


Figure 6 Crystal structure of (AlP) [en.wikipedia.org].

The holding time used in this experiment has no influence on the phosphorous modification effect. When there is a good coherent relationship existing on the interface of two types of phases, one phase can act as very fine heterogeneous nucleating site for the other phase [M.-X. Zhang et al, 2005]. The interatomic distance of the crystal face of the two phases should be close to each other, besides the atomic arrangement of the crystal faces should be similar. When the interface of two phases has a good coherent relationship, the interplanar distances should be also similar to each other. Based on the interplanar distances of  $\text{Al}_4\text{C}_3$  and AlP crystals, and according to Turnbull–Vonnegut equation, the degree of disregistry  $\delta$  is below 5% [Min Zuo et al, 2009]. This indicates that  $\text{Al}_4\text{C}_3$  compound is a good nucleation substrate

for AlP compound, and AlP can easily nucleate. And then a large number of evenly distributed nuclei are available for the primary silicon, so the quantity of the primary Si increases significantly. This leads to obtain fine primary silicon particles.

#### Conclusions:

1. After the addition of 0.2% Cu<sub>3</sub>P master alloy, there is an obvious phosphorous modification effect and the size of the primary Si decreased significantly.
2. The holding time used in this experiment has no influence on the phosphorous modification effect.
3. The phosphorous modification effect is retained after the addition of 0.2% Cu<sub>3</sub>P, and 0.058% cast iron master alloy to the melt. The number of primary silicon particles increased and the average size of the primary Si decreased from 60μm to approximately 12μm, and the indicating that the Ti and C improved the phosphorous modification effect.
4. When 10 times the Ti and cast iron master alloy was added to the melt, the positive phosphorous modification effect was retained as before without any poisoning phenomenon.
5. There is an AlP-rich transition layer around or near to Al<sub>4</sub>C<sub>3</sub> compound, which can act as the heterogeneous nuclei for the primary silicon grains, which is a possible mechanism for the improvement of phosphorous modification efficiency after the addition of trace TiC particles.

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