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# A new nucleation mechanism of primary Si by like-peritectic coupling of AlP and $Al_4C_3$ in near eutectic Al–Si alloy

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# Abstract

The effect of TiC particles on the phosphorous modification efficiency in near eutectic Al–Si alloy and a new nucleating mechanism was studied in this paper. The results show that the phosphorous modification efficiency can be significantly improved and the sizes of the primary Si can be obviously refined after the addition of trace TiC particles. EPMA shows there is a coupling of AlP and  $Al_4C_3$  particles in the center of primary Si, and a new 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 the particles was also discussed.

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Keywords: Al-Si alloy; Primary silicon; Modification; Nucleation mechanism

# 1. Introduction

Considerable effort has been devoted to the development of lightweight engineering materials during the past decades [1–3]. Recently, near-eutectic and hypereutectic Al–Si alloys have been widely used in automotive applications, especially in the piston industry, because of their excellent combination of properties, including good abrasion and corrosion resistance, low coefficient of thermal expansion and high strength-to-weight ratio [4,5]. As the desirable combination of characteristics of Al-Si near-eutectic and hypereutectic alloys depends on the primary Si grain size to a large extent, the modification of primary Si is being studied more widely with increasing usage. Various methods have been used for the modification of primary Si particles, such as rapid cooling [6], low temperature casting [7] and various alloying additions [8]. Microstructure control using minor element addition has been the most popular method due to its simplicity. Phosphorous has been the most widely used minor 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 hypoeu-

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tectic Al–Si alloys, can be used to refine  $\alpha$ -Al dendrites [9]. While some researchers [10,11] have found that the addition of TiC particles significantly improves the phosphorous modification effect, the effect mechanism has not been understood until now.

This article discusses the effect mechanism of TiC particles on P modification efficiency in near eutectic Al–Si alloys by using EPMA and crystal lattice coherence analysis. This also provides new practical and theoretical information for the neareutectic and hypereutectic Al–Si production industry.

#### 2. Experimental procedure

The eutectic Al–Si alloy used in the experiments was produced by a 20 kW medium frequency induction furnace using commercial purity aluminum (99.85%) and super-purity crystalline Si (99.999%). The TiC particles were added in the form of Al–8Ti–2C master alloy. The chemical compositions of the experimental alloy are shown in Table 1 (all compositions quoted in this work are in wt.% unless otherwise stated).

The eutectic Al–Si alloy was re-melted in a clay-bonded graphite crucible, heated in an electric resistance-heating furnace at 800 °C and held at this temperature for 30 min. Part of the melt was poured into an iron chill mould with dimensions of 70 mm  $\times$  35 mm  $\times$  20 mm and Sample-1 was obtained without any additions or further treatment. Sample-2 was obtained 40 min after the addition of 1%Al–3.5P master alloy to the melt. Then, following the addition of 0.2%Al–8Ti–2C master alloy, Sample-3 was obtained after 10 min. More Al–8Ti–2C master alloy was added until there was 2%Al–8Ti–2C master alloy in the melt. After 10 min, the melt was cast and Sample-4 was obtained.

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Table 1		
Chemical	compositions of produced eutectic Al-Si alloy and Al-Ti-C master alloy (w	t.%)
		-

Samples	Si	Cu	Mg	Ni	Ti	С	Р	Sr	Al
Al-12.6Si Al-8Ti-2C	12.61 <0.15	0.002	0.004 <0.01	0.002	0.218 7.98	0.0046 1.99	<0.0001	0.0002	Bal. Bal.

Another four samples were obtained in the same experiment process without the addition of Al–8Ti–2C master alloy for comparison. 1%Al–3.5P master alloy was added to the eutectic Al–Si alloy and samples were taken after 40, 50, and 60 min, respectively. All the samples were poured into the same type of iron chill 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 10 mm above the bottom of the ingots and mechanically ground and polished using standard routines. The structure and qualitative analysis were conducted by using a high scope video microscope (HSVM) and JXA-8840 electron probe micro-analyzer (EPMA).

### 3. Results and discussion

Fig. 1 shows the microstructures of Al–12.6Si alloy before and after the addition of Al–3.5P and Al–8Ti–2C master alloys. There are a few primary Si grains in Al–12.6Si alloy, and their sizes are large block-like and unequal, as shown in Fig. 1(a). After the addition of 1%Al–3.5P 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 Al–P modified Al–12.6Si alloy, which is consistent with the previous result [12]. The phosphorous modification effect is retained after the addition of 0.2%Al–8Ti–2C master alloy in the melt. The average size of the primary Si decreased from 40  $\mu$ m to approximately 20  $\mu$ m, indicating that the Al–8Ti–2C master alloy improved the phosphorous modification effect. In addition, when 10 times the Al–8Ti–2C master alloy was added to the melt, the positive phosphorous modification effect was retained as before without any poisoning phenomenon.

According to the literature [13–15], AlP and Si are both diamond cubic with very similar lattice parameters. Primary Si nucleates heterogeneously on the solid AlP particles with a cubecube orientation relationship and solidifies [13], which promotes the precipitation and refinement of primary silicon. In terms of this theory, Al–P master alloy can modify primary silicon effectively, as shown in Fig. 1(b).

Fig. 2 presents the EPMA of a primary silicon nucleus in Sample-4 (Al–12.6Si with the addition of both 1%Al–3.5P and 2%Al–8Ti–2C master alloys), and there is a light particle inside the dark nucleus of the primary silicon. The X-ray images show that the dark nucleus contains Al and P elements, indicating that it was AlP compound. While the light particle contains Al and C, without Ti, which indicates that the particle is not TiC but Al<sub>4</sub>C<sub>3</sub> compound. Furthermore, the Al<sub>4</sub>C<sub>3</sub> particle lies in the core of the AlP compound.

Fig. 3 shows another nucleus of the primary silicon in Sample-4, and the compositions of the magnified nucleus are illustrated in Fig. 4. It is noted that the nucleus contains Al, P and C elements, without Ti. Furthermore, the P and C are not overlapping each other, while they both overlap the Al, indicating that they are AlP and Al<sub>4</sub>C<sub>3</sub> compounds, respectively. This is similar to the result of Fig. 2, since the Al<sub>4</sub>C<sub>3</sub> compound

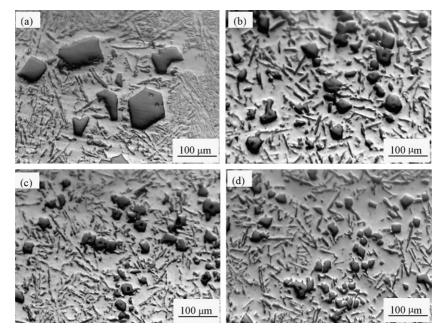


Fig. 1. Microstructures of Al–12.6Si alloy before and after the addition of Al–3.5P and Al–8Ti–2C master alloys: (a) Al–12.6Si; (b) Al–12.6Si + 1%Al–3.5P; (c) Al–12.6Si + 1%Al–3.5P + 0.2%Al–8Ti–2C; (d) Al–12.6Si + 1%Al–3.5P + 2%Al–8Ti–2C.

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