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Relationship between microstructures and contents of Ca/P in near-eutectic Al–Si piston alloys

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Abstract

The relationship between microstructures and contents of Ca/P in near-eutectic Al–Si piston alloy (ZL109) was investigated by optical microscopy and electron probe microanalyzer (EPMA). Ca was found to have an obvious influence on the microstructures of ZL109 alloys. It is difficult to present phosphorus refinement effect when the Ca content in the ZL109 alloy exceeds 100 ppm. In order to obtain a good phosphorus refinement effect, the content of Ca impurity in the alloy should be under 50 ppm. It has also been shown that Ca can modify eutectic Si and enhance the formation of α-Al dendrites and fibrous eutectic Si in the alloy. Controlling the content of Ca impurity by the addition of C_2Cl_6 to the melt resulted in the appearance of phosphorus refinement effect. With the decrease of Ca content from 100 ppm to 12 ppm, the average primary silicon particle size is reduced to 16.2 μm from 31.7 μm.

Keywords: Al–Si alloy; Refinement; Microstructure; Calcium

1. Introduction

Near-eutectic and hypereutectic Al–Si alloys are widely used in automotive applications, especially in piston industry, because of excellent abrasion and corrosion resistance, low coefficient of thermal expansion and high strength-to-weight ratio [1–3]. These properties led to the application of Al–Si alloys in automobile industry, especially for cylinder blocks, cylinder heads, pistons and valve lifters [4]. However , with the increase of Si content, the mechanical properties of Al–Si alloys are reduced notably, especially elongation. So the low expansion group of Al–Si eutectic or near-eutectic alloys, referred to as 'piston alloy', need to be modified. As the desirable combination of characteristics of Al–Si near-eutectic and hypereutectic alloys depends on the primary Si grain size to large extent, the refinement of primary Si are considered more and more widely with increasing usage of them. Research is required to develop a microstructure with uniformly distributed fine primary Si particles in a modified eutectic matrix. Various methods have been used for the refinement of primary Si particles, such as rapid cooling [5], low temperature casting [6] and various alloying additions [7,8]. Microstructure control using minor element addition has been the most popular method due to its simplicity. Phosphorus has been most widely used as minor element for the refinement of primary Si in near-eutectic and hypereutectic Al–Si alloys.

However, most metallurgical process needs a precise control of liquid metal quality in terms of trace impurities. Some trace impurities are detrimental to the final product quality, for example, a trace sodium (Na) impurity can poison the catalytic effect of the AlP particles, probably by a preferential reaction to form Na_3P. Calcium is a common impurity in silicon metal and is brought into the melt in the course of smelting [9]. The results of Kobayashi et al. [10] showed that Ca can refine the intermetallic compounds as well as the eutectic silicon particles. Knuutinen et al. [11] reported that Ca can cause a depression of the eutectic arrest and result in fibrous eutectic Si. In this

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Table 1
Chemical compositions of ZL109 alloys and refinement effect

Samples	Element, wt-%											refinement effect
	Si	Cu	Ni	Mg	Fe	Ti	P*	Ca*	Na*	Sr*	Al	
(1)	12.71	1.019	0.862	0.958	0.221	0.018	3	457	4	5	Bal.	N
(2)	12.72	1.091	0.870	0.915	0.236	0.017	101	282	2	5	Bal.	N
(3)	12.75	1.089	0.872	0.831	0.231	0.017	92	208	2	5	Bal.	N
(4)	12.72	1.093	0.870	0.743	0.240	0.017	79	141	2	4	Bal.	N
(5)	12.67	1.095	0.932	0.635	0.229	0.017	72	100	<1	2	Bal.	Y
(6)	12.70	1.082	0.873	0.558	0.239	0.017	57	49	<1	1	Bal.	Y
(7)	12.81	1.110	0.905	0.431	0.240	0.017	41	12	<1	1	Bal.	Y

Y——with refinement effect N——no refinement effect.
* Levels of P, Ca, Na and Sr are given in parts per million.

paper, the relationship between microstructures and contents of Ca/P in ZL109 piston alloys was investigated through control of Ca content by the addition of C_2Cl_6 in the melts.

2. Experimental procedures

A commercial purity crystalline Si and aluminum, which Ca content is 0.67% and 0.0012%, respectively, were used to produce eutectic Al–Si piston alloys (ZL109). The ZL109 alloys were prepared in a 20 kW medium frequency induction furnace and poured into an iron chill mould, and ingots with dimensions of 100×40×30 mm were obtained.

The ZL109 alloy, weighing approximately 3 kg, was re-melted in a graphite clay bonded crucible by an electric resistance furnace, and held at 780 °C for 30 min after melting. Firstly, part of the melt was poured into the mould preheated at 100 °C with dimensions of 70×35×20 mm and sample (1) was obtained without addition of anything and no treatment. Secondly, the Al–3.5% P master alloy, which was produced by Shandong Shanda Al and Mg Melt Technology, was added into the melt with amount of 1.0%. After keeping for 30 min, sample (2) was obtained. Hexachloroethane (C_2Cl_6) treatment was subsequently carried out to reduce the content of Ca by plunging it into the melt, with an addition of 0.1% of the weight of melt for each treatment. After holding at 780 °C for 10 min, the melt was poured into a metal mould to investigate the relationship between microstructures and contents of Ca and P in ZL109 alloys. The chemical compositions of all the ZL109 alloy ingots are given in Table 1.

The microstructure analysis was carried out on as-cast samples to investigate the effect of Ca and P on microstructure for the ZL109 alloy. Metallographic specimens were mechanically ground and polished through standard routines and were characterization as to the structure and qualitative analyses were conducted on selected samples using a High Scope Video Microscope (HSVM) and JXA-8840 Electron Probe Microanalyzer (EPMA). Five points were chosen at random to measure the average size of primary Si particles.

3. Results and discussion

The microstructure of sample (1) with 457 ppm Ca is shown in Fig. 1. The figure shows an obvious hypoeutectic

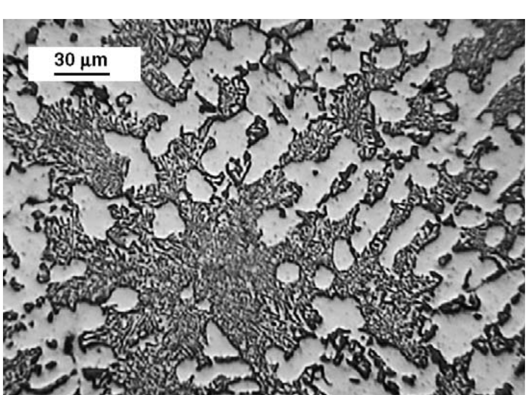

Fig. 1. Microstructure of unmodified ZL109 alloy with 457 ppm Ca.

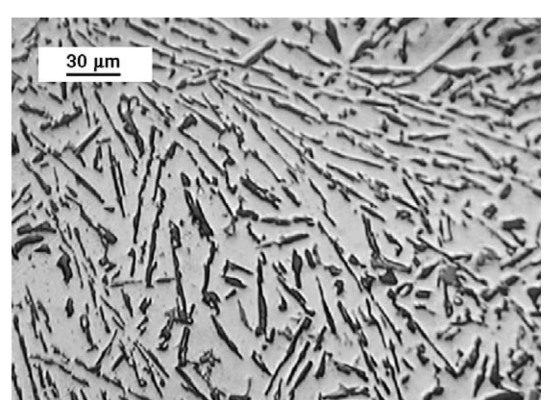

Fig. 2. Typical Microstructure of eutectic Al–Si alloy with 17 ppm Ca.

Table 2
Chemical compositions of eutectic Al-Si alloy

Si	Cu	Ni	Mg	Fe	P*	Ca*	Na*	Sr*	Al
12.58	0.890	0.953	0.682	0.223	5	17	2	4	Bal.

* Levels of P, Ca, Na and Sr are given in parts per million.

structure by the appearance of α-Al dendrites and fibrous eutectic Si. It reveals that trace amounts of Ca can effectively modify the eutectic Si shape, just similar to that of a sample modified with sodium or strontium. Under the same melting and casting conditions, Fig. 2 shows a typical microstructure of eutectic Al–Si alloy with coarse plate-like eutectic silicon morphology. The chemical compositions of the eutectic Al–Si alloy ingots are given in Table 2.

Fig. 3 shows the microstructure of the ZL109 alloy with different contents of Ca and P. Although Al–3% P master alloy is a highly effective modifier for near-eutectic and hypereutectic Al–Si alloys, it seems now to have no phosphorous refinement effect in the ZL109 alloy with 282 ppm Ca and 101 ppm P, as shown in Fig. 3(a). It did not present phosphorous refinement effect until the content of Ca is reduced to100 ppm through C_2Cl_6 treatment.

According to the data of Table 1 and Fig. 3, we can speculate that it is difficult to present phosphorous refinement effect when the Ca content in the ZL109 alloy exceeds 100 ppm. In order to obtain a good phosphorous refinement effect, the content of Ca in the alloy should be kept under 50 ppm.

It was reported that trace Ca and Na in the melt can cause phosphorous refinement inefficiency. The abnormal phenomenon is due to the formation of $(Ca_{n-x},Na_x)P_m$ ($0<x<n$) compounds, which are more stable than the AlP phases in the melt [12]. From sample (2), we can easily find some Ca_xP_y compounds distributed in α-Al matrix, as shown in Fig. 4. It is difficult to carry out a quantitative analysis to Ca_xP_y because of reaction of Ca_xP_y with water or vapour and loss of some the phosphorus. It is thought that P and AlP react with Ca to form the Ca_xP_y compounds and part of Ca_xP_y compounds maybe slag off, which leads to the decrease of Ca content from 457 ppm to 282 ppm.

Since chloride has a strong affinity for Ca, the content of Ca in the melt reduced to 9 ppm from 238 ppm after C_2Cl_6 treatment, as shown in Table 1. There is a remarkable structural change after addition of C_2Cl_6. Many primary Si grains precipitate in the eutectic matrix, as shown in Fig. 3(b), (c) and (d). And one can clearly see that the primary Si

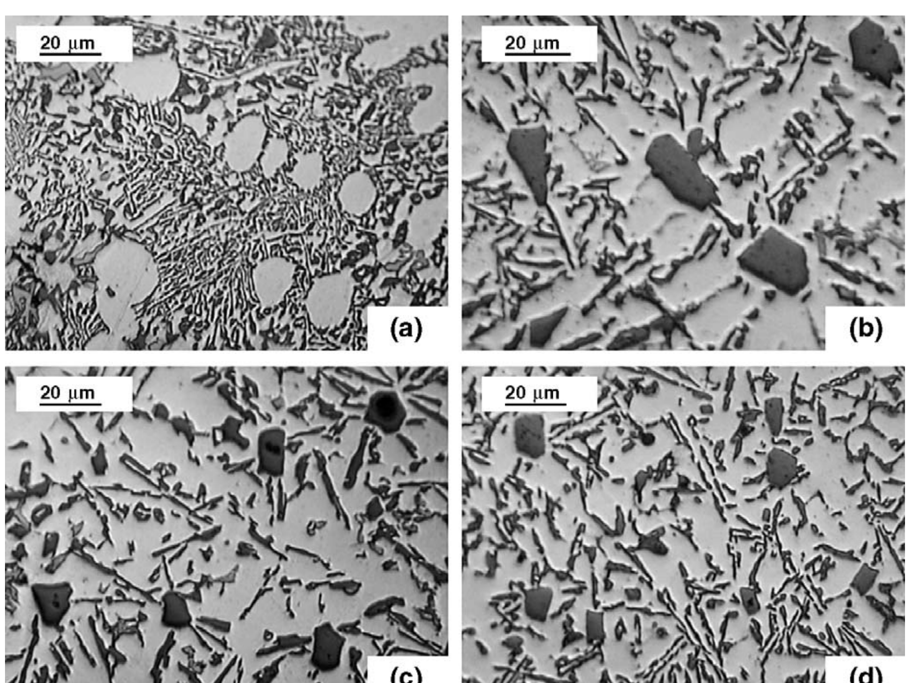

Fig. 3. Microstructure of ZL109 alloy with different contents of Ca and P: (a) 208 ppm Ca+92 ppm P; (b) 100 ppm Ca+72 ppm P; (c) 49 ppm Ca+57 ppm P; (d)12 ppm Ca+41 ppm P.

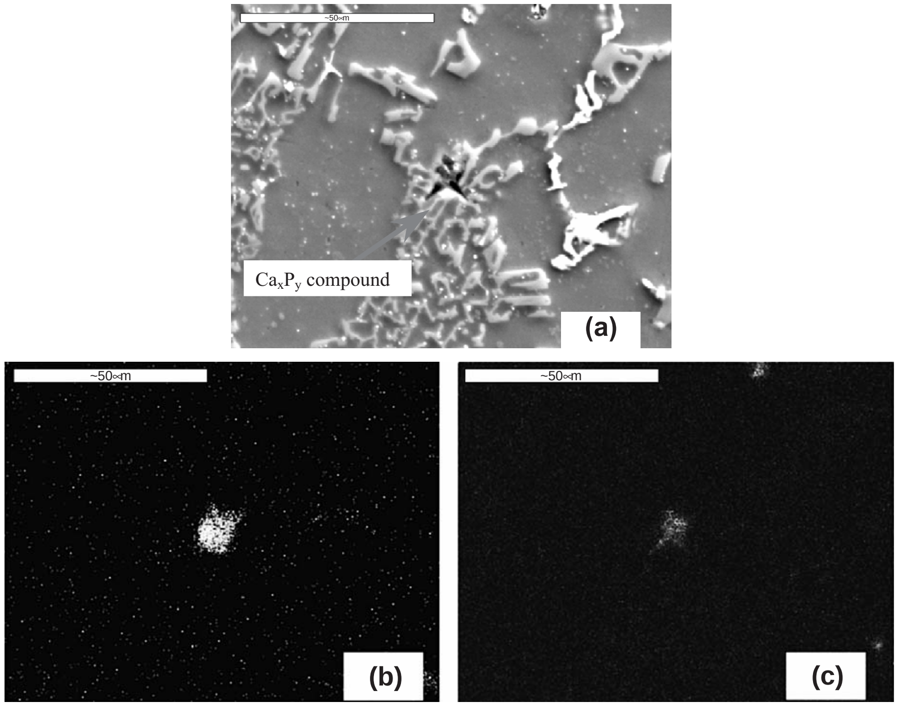

Fig. 4. EPMA analysis of sample (2): (a) SEM; (b) Ca–X-ray image; (c) P–X-ray image.

particles become finer and more uniformly distributed as Ca content reduces. When Ca content was up to 100 ppm, the average particle size of primary Si is about 31.7 μm. For the specimen with 49 ppm Ca, which received four treatments with C_2Cl_6, the particle size is about 17.9 μm. When the content of Ca in the melt is 12 ppm, trace residual P with 45 ppm content can lead to fine primary Si particles with average size of about 16.2 μm.

However, the phosphorous refinement effect disappeared again after adding 0.4% Al–8% Ca master alloy into the remaining melt, as shown in Fig. 5. This fully indicates that Ca impurity has an obvious influence on the microstructures of ZL109 alloy. Reducing Ca content in the melts has proven to be very effective in improving P refinement effect, even refining primary Si particles.

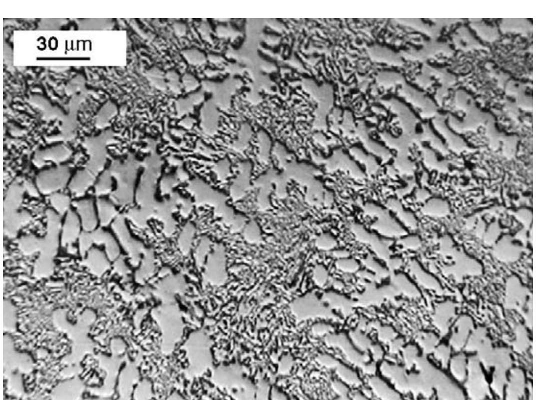

Fig. 5. Microstructure of ZL109 alloy after addition of 0.4% Al–8%Ca master alloy.

4. Conclusions

The relationship between microstructures and contents of Ca/P in near-eutectic Al–Si piston alloy (ZL109) was investigated. The following results were obtained.

1. Calcium was found to have an obvious influence on the microstructures of ZL109 alloys. The developed α-Al dendrites and fibrous eutectic Si in the ZL109 alloys are related to the Ca impurity. It has been shown that Ca can lead to P refinement inefficiency. The abnormal phenomenon is due to the formation of Ca_xP_y compounds, which is more stable than AlP phases in the melt.
2. The control of Ca content to below 100 ppm through the refinement treatment by C_2Cl_6 results in the appearance of phosphorus refinement effect. In order to obtain a good P refinement effect, the content of Ca in the alloy should be under 50 ppm. Primary Si particles were refined as Ca content decreased. Therefore, we should control strictly the content of Ca impurity in the Al–Si piston alloy. A refinement treatment by C_2Cl_6 is an effective method of removing Ca from the alloy melt.
3. With the decrease of Ca content from 100 ppm to 12 ppm, the average primary silicon particles become more uniformly distributed and the average particle size is decreased to 16.2 μm from 31.7 μm.

Acknowledgments

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