

EPMA analysis of calcium-rich compounds in near eutectic Al–Si alloys

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Abstract

The effect of Ca impurity on solidification structure of near eutectic Al–Si piston alloy (ZL109), the origin of the presence of calcium (Ca) and the transformation of Ca compounds in the alloy were investigated. It has been found that many kinds of Ca compounds exist in commercial pure silicon, which are the main source of the Ca impurity in ZL109 alloy. It has also been shown that calcium can modify eutectic Si and enhance the formation of α -Al dendrites and fibrous eutectic Si in the alloy, even retaining the structural characteristics after addition of sodium. The abnormal phenomenon is due to the formation of $\text{Ca}_x\text{Si}_y\text{P}_z$ compounds which are more stable than AlP phases in the melt. However, the Ca level can be reduced from 216 ppm to 30 ppm and then the P modification efficiency can be recovered after a refinement treatment by C_2Cl_6 because of the reaction: $\text{Cl}_2 + \text{Ca} \rightarrow \text{CaCl}_2(\text{s})$, and the transformation: $\text{Al} + \text{Mg} + \text{Ca}_x\text{Si}_y\text{P}_z(\text{s}) + \text{Cl}_2 \rightarrow (\text{Al}_5, \text{Mg}_{0.85} + \text{Ca}_{0.15})\text{P}(\text{s}) + \text{CaCl}_2(\text{s}) + \text{MgCl}_2(\text{s})$, the $(\text{Al}_5, \text{Mg}_{0.85}, \text{Ca}_{0.15})\text{P}$ compounds serving as heterogeneous nucleating sites of the primary Si phases. © 2004 Elsevier B.V. All rights reserved.

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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]. But a refinement treatment of bulky primary silicon particles is an important aspect in the casting technology of hypereutectic Al–Si alloys in order to improve mechanical properties, especially elongation. For near eutectic compositions Al–Si multi-component alloys, the precipitation of fine primary silicon particles and the acquirement of a hypereutectic structure is widely applied in piston industry because of an improvement in strength at elevated temperatures and a reduction in thermal expansion coefficient.

It is generally recognized that primary silicon can be effectively nucleated by AlP particle [4,5]. Therefore adding

phosphorus is necessary in most casting technologies of piston production.

Presently this is obtained by adding a copper–phosphorus master alloy, typically containing between 6% and 15% P, which is added in the form of small ingots or occasionally as rods in the furnace. Another method of refining primary Si grains in practice involves adding specialty commercial fluxes containing red phosphorus as the active agent and other salts to prevent rapid oxidation/combustion of the phosphorus. Safety and environmental concerns, low P recovery, and the degree of effectiveness are major drawbacks of these fluxes. Other techniques adding P to Al–Si alloys have been developed, for example, by addition of Al–P or Al–Cu–P master alloys [5,6], containing a high concentration of P as AlP. These alloys are effective at lower melt temperatures, lower addition rates and short contact times.

However, the 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

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Table 1
Chemical compositions of raw materials and produced ZL109 alloys ss(wt.%)

Samples	Si	Cu	Mg	Ni	Al	Fe	Ca	Na	P	Sr
Pure Si	Bal.	–	–	–	0.23	0.48	0.85	–	–	–
Pure Al	0.107	0.002	0.005	0.003	Bal.	0.137	0.0012	0.0129	< 0.0001	0.0003
ZL109	12.67	1.026	1.013	0.954	Bal.	0.218	0.0467	0.0013	< 0.0001	0.0002
ZL109-1	12.77	1.029	0.993	0.960	Bal.	0.238	0.0258	0.0003	< 0.0001	0.0002
ZL109-2	12.80	1.474	0.967	0.944	Bal.	0.223	0.0216	0.0003	0.0016	0.0002
ZL109-3	12.75	1.489	0.755	0.952	Bal.	0.221	0.0030	0.0001	0.0067	0.0002

reaction to form Na_3P . Doping with calcium (Ca) instead of Na produces a similar poisoning effect [7]. Trace Ca and Na can cause P modification inefficiency. The abnormal phenomenon is due to the formation of $(\text{Ca}_{n-x}, \text{Na}_x) \text{P}_m$ compounds which are more stable than the AlP phases in the melt [8]. In this paper, the origin of the presence of calcium in Al–Si alloys, the formation and transformation of Ca compounds, the influence of the Ca-rich compounds on the structures of the Al–Si piston alloy and the methods of removing Ca from the alloy melt are discussed.

2. Experimental procedure

A commercial purity crystalline Si and aluminum were used to produce eutectic Al–Si piston alloys (ZL109), their compositions being shown in Table 1 (all compositions quoted in this work are in wt.% unless otherwise stated). The ZL109 alloys were prepared in a 20 kW medium frequency induction furnace and poured into an iron chill mould, and ingots with a size of 70 mm × 35 mm × 20 mm were fabricated. Metallurgical samples were cut directly from 10 mm above the bottom of the ingots.

The ZL109 alloy for each test, weighing approximately 5 kg was re-melted in an electronic resistance-heating furnace at 780 °C and kept at this temperature for 30 min. Part of the melt was poured into the mould and the ZL109-1 sample was obtained without addition of anything and without treatment.

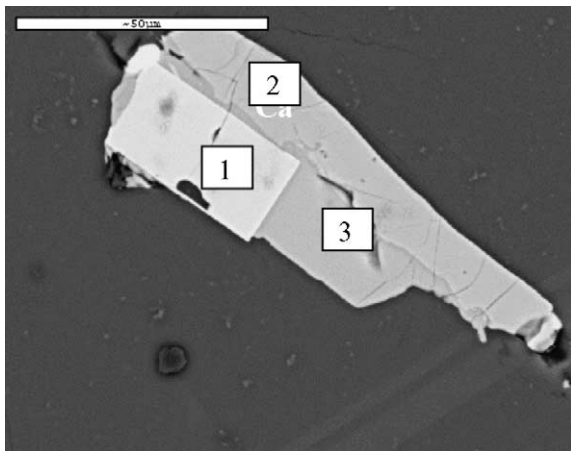


Fig. 1. Compounds in commercial purity crystalline Si. (1) TiFeSi_2 ; (2) $\text{Ca}_5\text{Fe}_{17}\text{Al}_{25}\text{Si}_{35}$; (3) FeAlSi_{10} .

The ZL109-2 sample was obtained 40 min after addition of 0.5% Cu–10% P master alloy to the melt. Degassed with C_2Cl_6 for 5 min, the melt was cast and the ZL109-3 sample was obtained (all the samples were poured into the same mould).

The microstructure analysis was carried out on as-cast samples to investigate the morphologies and transformation of Ca-rich compounds and the effect of Ca on P modification efficiency for the ZL109 alloy. Metallographic specimens were mechanically ground and polished through standard routines and were characterized as to the structure and qualitative analysis were conducted on selected samples using a high scope video microscope (HSVM) and JXA-8840 electron probe micro-analyzer (EPMA).

3. Results and discussion

3.1. The origin of the presence of the Ca impurity in ZL109 alloy

In order to understand the sources of Ca impurity pick-up during the melting of ZL109 alloy, the main raw materials were analyzed. Ca, Fe, Al and O are the main impurity elements in commercial purity crystalline Si (0.85% Ca). It usually contains several kinds of Ca-rich compounds, such as $\text{Ca}_5\text{Fe}_{17}\text{Al}_{25}\text{Si}_{35}$, $\text{Al}_2\text{Si}_8\text{Ca}_5$, $\text{Ca}_5\text{Si}_{11}\text{Al}_{10}\text{O}_{46}$ and $\text{Ca}_9\text{Si}_{12}\text{Al}_4\text{O}_{54}$, present in blocky or strip-like shapes. Besides 0.24% Ca is present as solute in the Si, as shown in Figs. 1 and 2.

It is found that 467 ppm Ca exists in ZL109 alloy, which likely results from the commercial pure Si since there is only 12 ppm Ca in commercial pure Al. Moreover, the $\text{Al}_2\text{Si}_8\text{Ca}_5$ compound is detected in the ZL109 sample by electron probe micro-analyzer (EPMA) in combination with Ni phases containing, as shown in Fig. 3. This indicates that the Ca level is directly related to the commercial purity Si.

3.2. Influence of Ca impurity on the structures of ZL109 alloy

It is readily apparent from Fig. 4 that the ZL109-1 sample shows a hypoeutectic structure by the appearance of α -Al dendrites and fibrous eutectic Si, just similar to that of a sample modified with Na or Sr. Knuutinen et al. [9] reported that Ca can cause a depression of the eutectic arrest and result

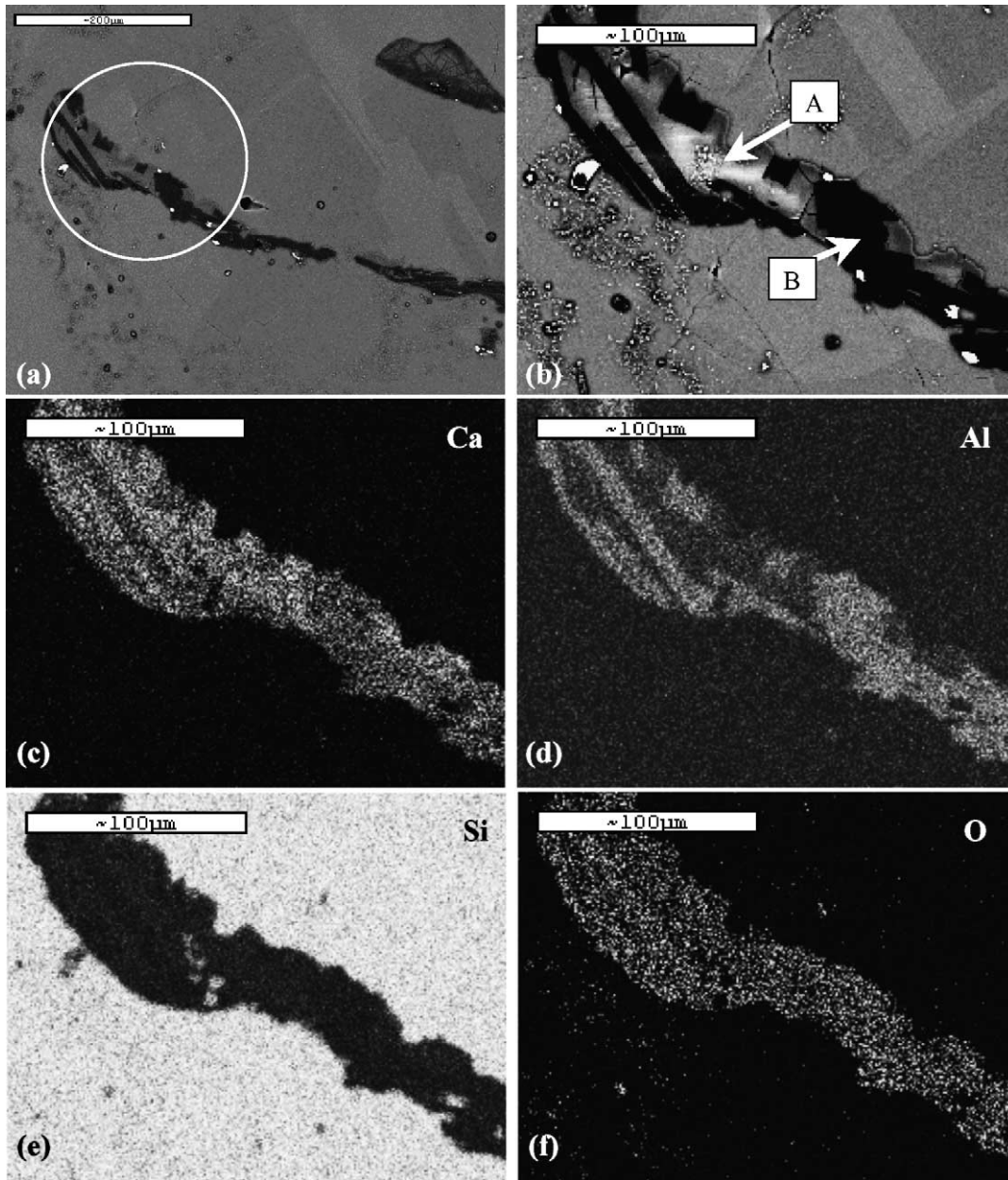
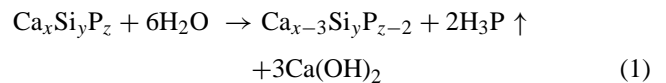


Fig. 2. A strip-like compounds in commercial purity crystalline Si and its EPMA analysis. (A) $\text{Ca}_9\text{Si}_{12}\text{Al}_4\text{O}_{54}$; (B) $\text{Ca}_5\text{Si}_{11}\text{Al}_{10}\text{O}_{46}$. (a–b) SEI of a strip-like compound; (c–f) the X-ray images for respective element: Ca, Al, Si and O.

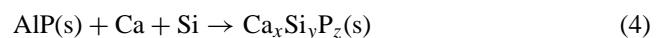
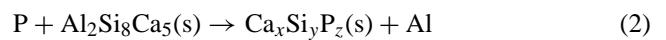
in fibrous eutectic Si. The addition of Ca results in an instantaneous effect with the first addition already and no further significant changes occur with increased concentration. Therefore, it is the Ca impurity that causes the modification performances of the eutectic Si phases.

The Ca modified structure is retained even after addition of 0.5% Cu–10% P master alloy, and there is not any primary Si particle in the alloy, as shown in Fig. 5. On the other hand, by EPMA analysis, it is easily found that there are a few holes distributed in α -Al containing residual Ca, P and Si, as shown in Fig. 6. It is difficult to carry out a quantitative analysis because of losing of some the phosphorus due to reaction (1) during fabricating the sample, so the compound

is indicated by $\text{Ca}_x\text{Si}_y\text{P}_z$.



It implies that the $\text{Ca}_x\text{Si}_y\text{P}_z$ compounds are more stable than AlP particles in the melt. The following reactions may be involved:



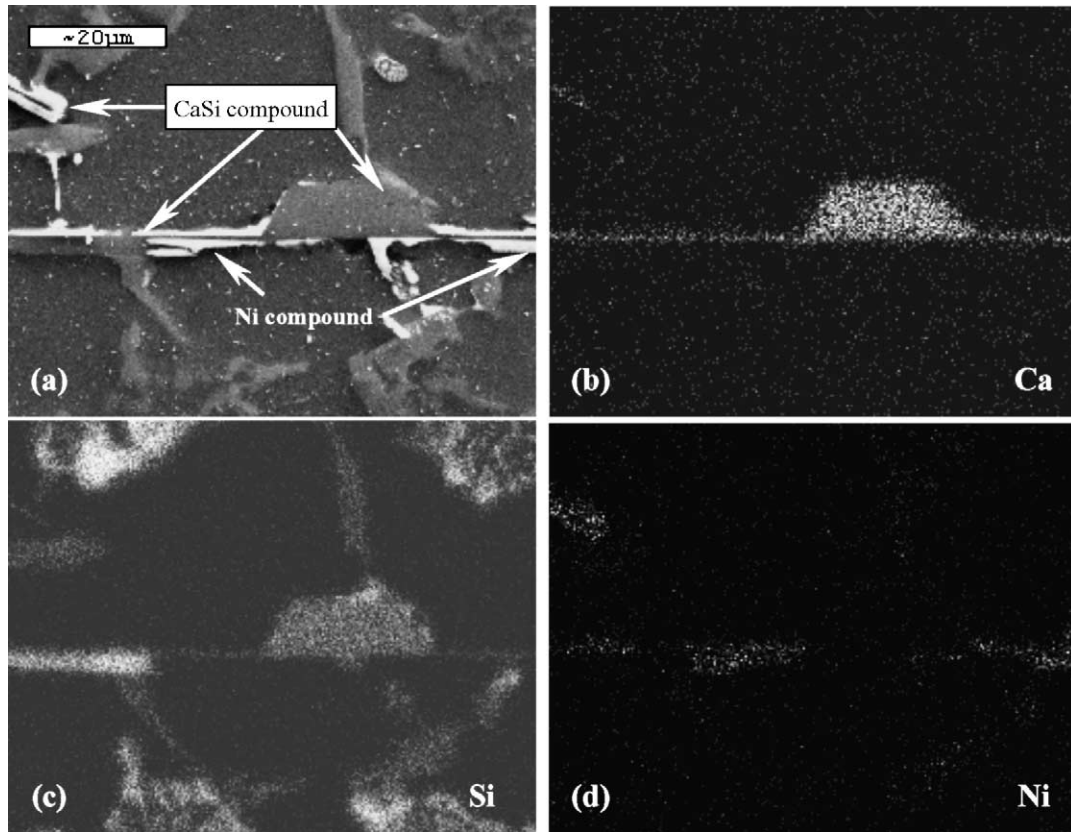


Fig. 3. EPMA analysis of ZL109 sample. (a) SEM (b–d) the X-ray images for respective element: Ca, Si and Ni.

3.3. The recovery of the P modification effect and methods of removing Ca

There is a remarkable structural change in the ZL109-2 sample after addition of C_2Cl_6 . Many primary Si grains

precipitate in the eutectic matrix, as shown in Fig. 7. It is also found that there are holes in the centers of some Si grains, and some remaining Al, P, Mg and Ca elements, as shown in Fig. 8. Quantitative analysis shows the compound consists of 36.3 at.% P, 53.7 at.% Al, 9.0 at.% Mg and 1.6 at.% Ca,

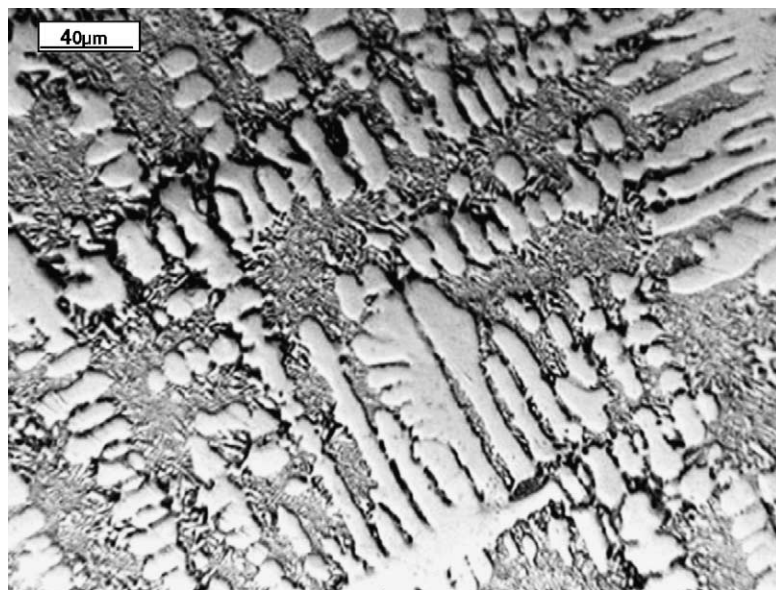


Fig. 4. Microstructure of ZL109-1 sample.

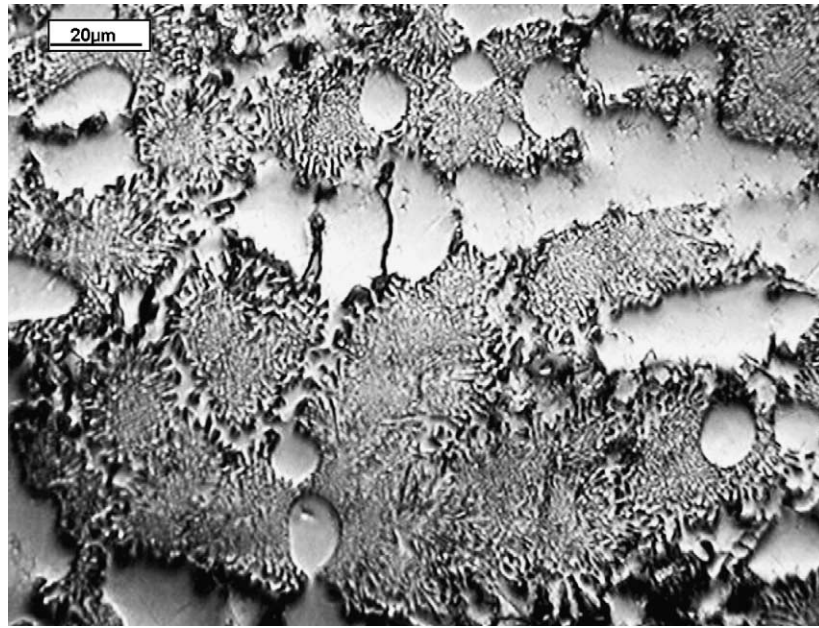


Fig. 5. Microstructure of ZL109-2 sample.

so the compound may be expressed by $(Al_5, Mg_{0.85}, Ca_{0.15})P_{3.4}$.

The following reactions may take place during refinement treatment of the melt by C_2Cl_6 :

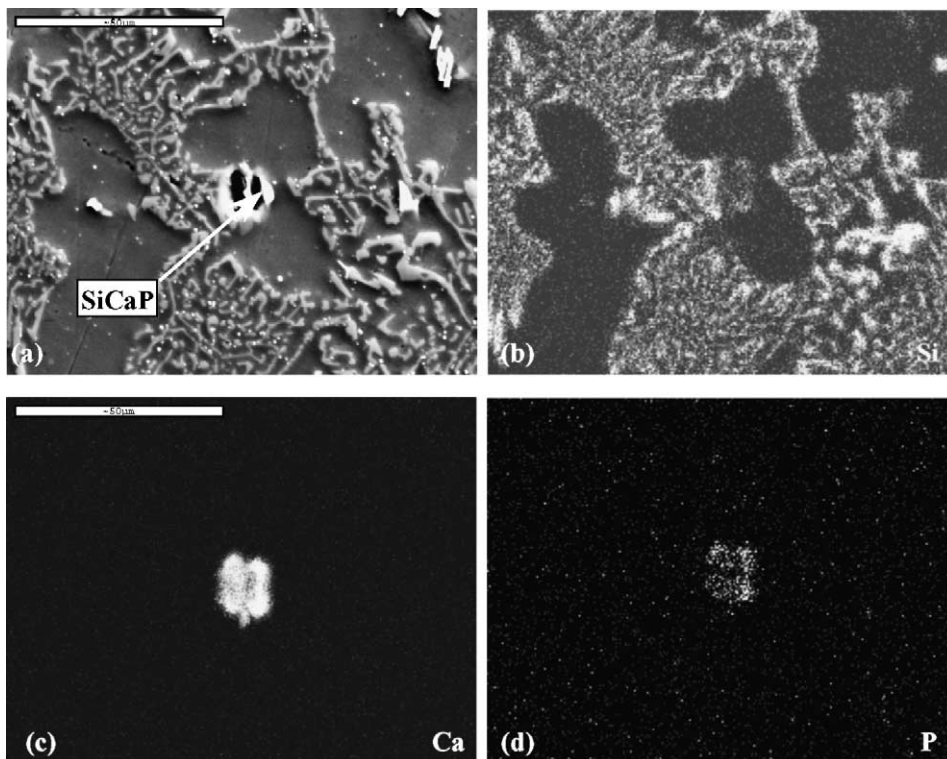
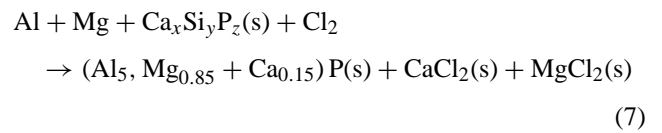


Fig. 6. EPMA analysis of ZL109-2 sample. (a) SEM; (b–d) the X-ray images for respective element: Si, Ca and P.

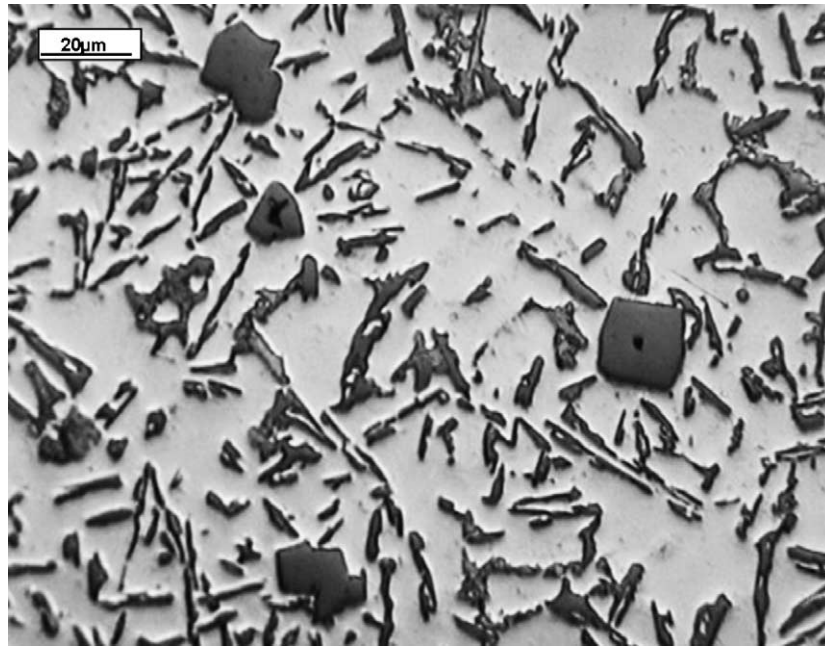


Fig. 7. Microstructure of ZL109-3 sample.

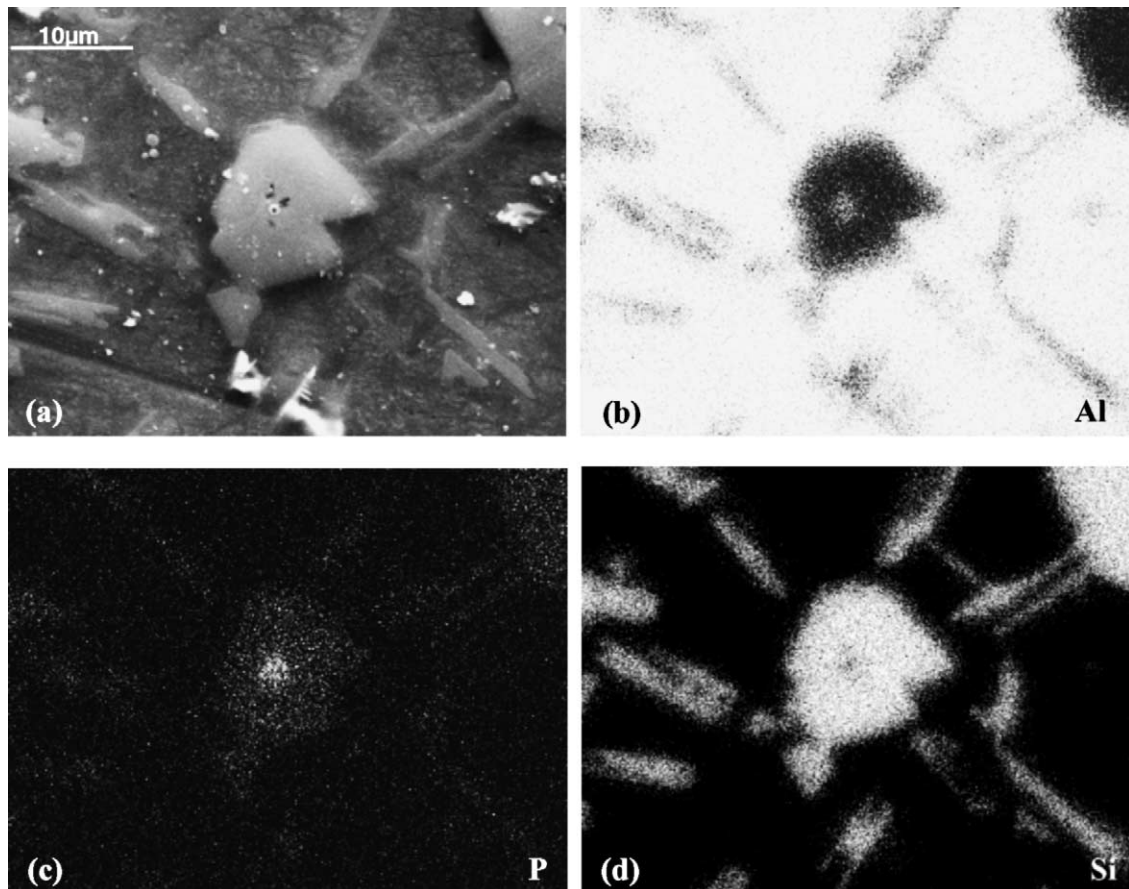


Fig. 8. EPMA analysis of ZL109-3 sample. (a) SEI of a primary Si; (b–f) the X-ray images for respective element: Al, P, Si, Ca and Mg.

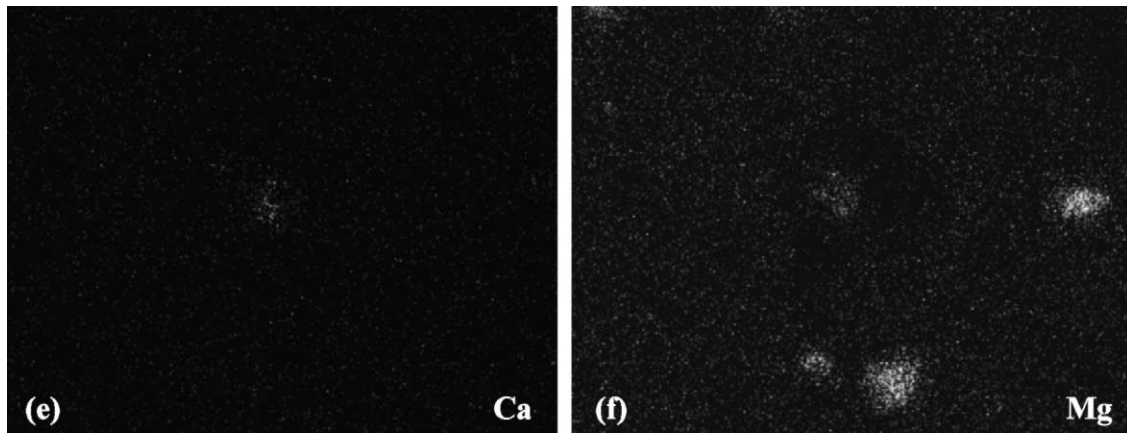


Fig. 8. (Continued).

Table 2
Mg and some trace elements in Al–Si piston alloy after different treatment (wt.%)

	Piston alloy	Re-melted sample	Refinement by C ₂ Cl ₆	Addition of 0.5% Al-3.5% P master alloy	After holding of 60 min at 780 °C
Mg	0.918	0.891	0.657	0.650	0.586
Ca	0.0974	0.0458	0.0086	0.0065	0.0005
Na	0.0063	0.0004	<0.0001	<0.0001	<0.0001
P	<0.0001	<0.0001	<0.0001	0.0028	0.0048
Sr	0.0014	0.0006	0.0001	0.0002	0.0002

The (Al₅, Mg_{0.85} + Ca_{0.15}) P compounds can act as heterogeneous nucleating sites of primary Si grains during solidification. It is clear from Table 1 that the Ca level in the alloy decreased from 216 ppm to 30 ppm after addition of C₂Cl₆, so it is an important method of removing Ca. A similar method was reported able to control the calcium content by the addition of Ti₂Cl₆ to the melt, resulting in successful refinement of the primary silicon particles [10]. In addition, the Ca level in the alloy was also reduced from 467 ppm (ZL109) to 216 ppm (ZL109) after a single re-melting treatment. Similar results reappear in another Al–Si alloy sample, as shown in Table 2, of which the Ca content decreased from 974 ppm to 458 ppm after re-melting treatment. It became further reduced to 86 ppm after refinement by C₂Cl₆, and there was Ca also loss after holding the melt at 780 °C.

4. Conclusions

There are many kinds of calcium-rich compounds in commercial pure Si, such as Ca₅Fe₁₇Al₂₅Si₃₅, Al₂Si₈Ca₅, Ca₅Si₁₁Al₁₀O₄₆ and Ca₉Si₁₂Al₄O₅₄, the Ca impurity in Al–Si piston alloy mainly originating from the commercial pure Si. The developed α-Al dendrites and fibrous eutectic Si in the Al–Si piston alloy are related to this Ca impurity. It has been shown that Ca can lead to P modification inefficiency. The abnormal phenomenon is due to the formation of Ca_xSi_yP_z compounds which are more stable than AlP phases

in the melt. Three kinds of methods can decrease the Ca content, which are a refinement treatment by C₂Cl₆, a re-melting treatment and a holding treatment at melt. The P modification efficiency can be recovered after addition of C₂Cl₆ because of the reaction: Cl₂ + Ca → CaCl₂ and the transformation: Al + Mg + Ca_xSi_yP_z + Cl₂ → (Al₅, Mg_{0.85} + Ca_{0.15}) P + CaCl₂ + MgCl₂. The (Al₅, Mg_{0.85}, Ca_{0.15}) P compounds can serve as the nuclei of the primary Si phases.

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