

# Refinement of Primary Silicon Crystals by Novel Al-ZnS Master Alloy in Solidification of Hypereutectic Al-Si Alloys

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## Abstract

A novel Al-ZnS master alloy was developed by in situ reaction of Zn and Na<sub>2</sub>S in the Al melt. The results from this study left little doubt that this novel Al-ZnS master alloy was a promising refiner in solidification of hypereutectic Al-Si alloys. It refined the primary silicon to the same extent as that achieved by adding P via Cu-P following the same refinement mechanism. The SEM work confirmed that there were many pre-formed ZnS particles contained in the master alloy. The optical metallography showed that the morphologies of the primary silicon crystals in the solidified Al-22Si alloy were drastically changed from irregular coarse morphology to fine regular particles. The primary silicon crystal was refined from 74 μm to 26, 22, 24 μm by adding 0.05, 0.1, 0.15 wt% ZnS respectively with holding time of 20 min, whereas the average particle size of the primary silicon refined by 200 ppm P reduced to 20 μm. With the increase of the holding time up to 1.5 hr, the primary silicon size will increase up to 33 μm in adding 0.1 wt% ZnS.

**Key words** Hypereutectic Al-Si alloys, refinement, primary silicon, master alloy.

## Introduction

Hypereutectic Al-Si alloys are of increasing interest for applications that require a combination of light weight and high wear resistance, such as pistons, liner-less engine blocks and pumps. The wear resistance of this class of alloys is due to the presence of hard primary Si particles formed during casting [1, 2]. For hypereutectic Al-Si alloys, the final properties in the cast component are controlled by the size and distribution of the primary silicon phase in addition to the degree of modification of the eutectic silicon matrix [3]. To maximise machine tool life while taking advantage of the high wear resistance of hypereutectic Al-Si alloys, the primary Si crystals formed during solidification should be as fine and uniformly dispersed as possible. The current commercial practice is to add phosphorous in the form Cu-P, Al-Cu-P and Al-Fe-P master alloys, such that primary Si nucleates heterogeneously on AlP particles. The crystal structure and lattice parameter of AlP are close to that of silicon with the minimal mismatch between them, less than 1% [4].

Refining agents like Ga, Ge, Se, Be, Te, Li, Cd, Zn, Mn, V, Cb, Bi, Mo, Hf and S either individually or in combination have also been studied. These agents along with Na would give simultaneous silicon refinement and eutectic modification [5]. A significant refinement of primary silicon in 390 alloy has been reported with the use of Germanium, Gallium, Selenium, Tellurium, Lithium, Cadmium, and Lithium Chloride [6].

Due to the structural similarity of ZnS in its zincblende form, and its similar lattice parameter to those of Si and AlP, its use as an inoculant to refine the primary Si in solidification of hypereutectic Al-Si alloys was examined in this study. ZnS occurs in two common polytypes, zincblende (also called sphalerite: cubic with lattice parameter  $a_0 = 5.41 \text{ \AA}$ ) and wurtzite (hexagonal with lattice parameters  $a_0 = 3.2495 \text{ \AA}$ ,  $c_0 = 5.2069 \text{ \AA}$ ). ZnS crystallizes with the cubic zincblende structure below 1020 °C and with the hexagonal wurtzite structure above this phase transition temperature [7]. The refinement efficiency of ZnS in solidification of the hypereutectic Al-Si alloys has been investigated. Experiments were conducted to refine the primary silicon particles in Al-Si alloy by adding the new Al-ZnS master alloy.

## Experimental procedures

The initial batches of Al-Si alloys were prepared in an electric resistance furnace by melting and diluting an Al-50Si master alloy with commercial purity aluminium LM0 at 1100 °C for 3 h in a clay crucible. The compositions of raw materials are listed in Table 1. For homogeneity, the molten alloy was manually stirred for a few seconds and then cast.

Table 1 Aluminium alloys composition wt%

| Alloy   | Cu   | Mg   | Si   | Fe   | Mn   | Ni   | Zn   | Pb   | Sn   | Ti   | Cr   | Al   |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|
| LM0     | 0.03 | 0.03 | 0.30 | 0.40 | 0.03 | 0.03 | 0.07 | 0.03 | 0.03 | -    | -    | Bal. |
| Al-50Si | 0.08 | 0.28 | 51.0 | 0.32 | 0.02 | 0.01 | 0.02 | 0.02 | 0.01 | 0.09 | 0.03 | Bal. |

One synthesis method for zincblende ZnS nanoparticles is by chemical reaction using Zn and Na<sub>2</sub>S [8]. Experiments were carried on to prepare the Al-ZnS master alloy by adding the stoichiometric amount of Zn metal followed by adding 50% excess of Na<sub>2</sub>S powder to high purity aluminium melt with gentle mixing at 800 °C for 20 min. The produced master alloy cast in cylindrical mould pre-heated to 200 °C, and cooling in air at a cooling rate of approximately 16 K/s.

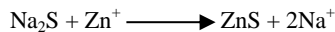
Another set of experiments was conducted to refine Al-22Si alloy by adding different amount of the Al-ZnS master alloy for different holding time. In order to compare with P refinement, the Al-Si alloy was remelted to 800 °C and then P was added in the form of CuP shot (Supplied by Aura Metals Ltd). The molten alloy was manually stirred for a few seconds and sample was taken after 20 min. Samples for all above experiments were taken by a Boron Nitride coated steel mould (35mm in diameter and 40mm in height with long handle) preheated at 200 °C which was then water cooled at approximately 15 K/s. Longitudinal sections of resulting samples were prepared by the standard technique of grinding with SiC abrasive papers and polishing with 1 μm

diamond suspension followed by silica suspension. The chemical composition of all alloys was analysed using a “Worldwide Analysis System (WAS) AG, Foundry master”. Microstructure characterization was accomplished using an optical microscope (Carl Zeiss Axioskop 2 MAT) equipped with image analysis software. The scanning electron microscopy (SEM) examination was carried out using a Zeiss Supera 35 FEG and JEOL 840 microscopes. The microscope equipped with an energy dispersive spectroscopy (EDS) facility, operated at an accelerating voltage of 5-20 KV.

## Results and discussion

### Preparation of Al-ZnS Master Alloy

Al-ZnS master alloy was prepared by adding the stoichiometric amount of Zn followed by adding excess amount of Na<sub>2</sub>S to high purity aluminium at 800 °C. The SEM micrographs and EDX analysis confirm the formation of ZnS particle in the master alloy as shown in Figure 1. The higher Al content can be attributed to the small size of the ZnS particle and large beam size used for EDX measurement. It is clear that ZnS particle can be precipitated in the melt and its formation is according to the following chemical equation;



The same principle is used to remove Zn from the wastewater or etching solution as ZnS by adding Na<sub>2</sub>S [9]. ZnS crystallizes with the cubic zincblende structure below 1020 °C and with the hexagonal wurtzite structure above this phase transition temperature [10]. Since, the master alloy prepared at 800 °C so the precipitated particles are zincblende ZnS. From the chemical analysis of the master alloy and according to the chemical equation, the composition of the master alloy is Al-1.5wt%ZnS. Further work is in progress to separate these ZnS particles for full characterisation and optimize the master alloy composition and results will be reported elsewhere.

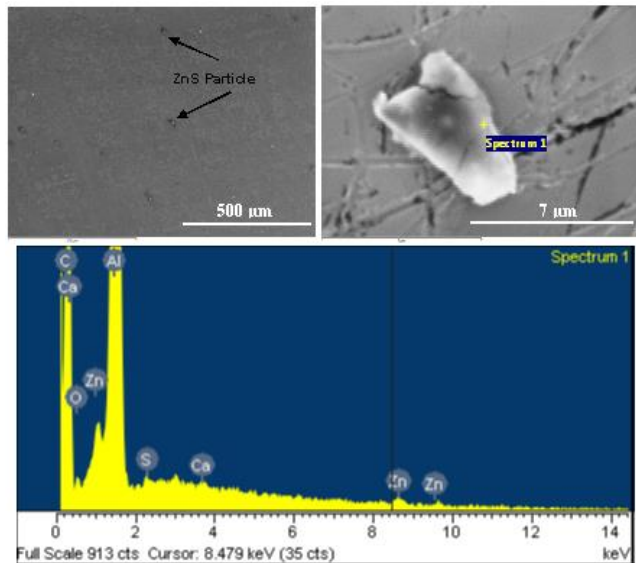


Figure 1 SEM micrographs and EDX analysis graphs showing the formation and structure of precipitated ZnS particles.

### Refinement of Primary Silicon by Al-ZnS Master Alloy

Primary results encouraged us to use this master alloy to examine its refinement performance in solidification of the higher Si content of hypereutectic Al-Si alloys. The optical micrographs in Figure 2 show the refinement performance of Al-1.5ZnS master alloy in solidification of Al-22Si alloy. The untreated Al-22Si, Figure 2 (a&b) contained irregular coarse primary Si with average particle size of approximately 74 µm and because of high Ca content in commercial purity alloy (> 200 ppm) the eutectic Si had a mostly fibrous morphology.

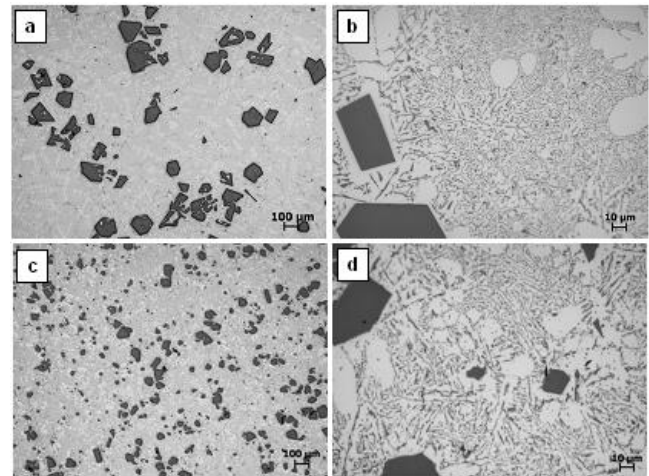


Figure 2 The optical micrographs of; (a, b) Al-22Si, (c, d) Al-22Si with the addition of 0.05wt% ZnS cast after 20 min. (a, c) low magnification and (b, d) high magnification.

Refinement with Al-1.5ZnS master alloy show that the particle size of primary silicon reduced to 26, 22 and 26 µm in adding 0.05, 0.1 and 0.16 wt% of ZnS respectively with 20 min holding time as shown in Figure 2 (c&d) and 3. The morphologies of primary silicon crystals in solidification of Al-22Si alloy are drastically changed from irregular morphologies to regular morphologies with some lose in the modification of the eutectic Si matrix.

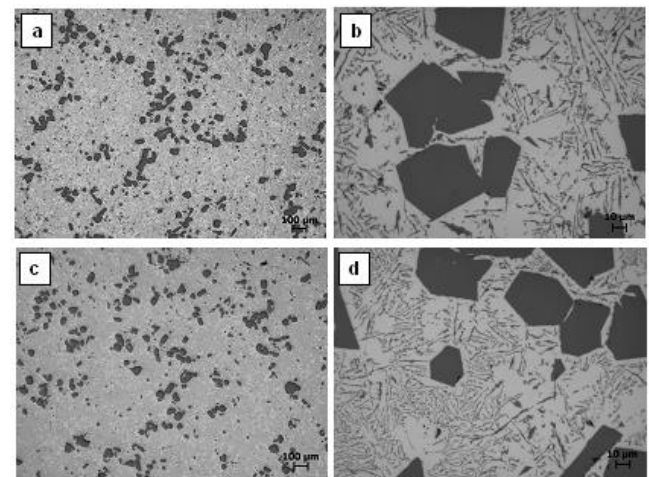


Figure 3 The optical micrographs of Al-22Si cast after 20 min; (a, b) Si with the addition of 0.1% ZnS, (c, d) with the addition of 0.16% ZnS (a, c) low magnification and (b, d) high magnification.

It was clear that with the increase of ZnS content the average particle size of the primary silicon decrease with up to 0.1wt% ZnS. Above 0.1wt% ZnS the size of primary silicon increases again, this could be due to the agglomeration of ZnS particles in the melt. With the increase of the holding time up to 90 min, the average particle size of primary silicon reduced from 74  $\mu\text{m}$  to 33  $\mu\text{m}$  by adding 0.1 wt% of ZnS in solidification of Al-22Si as shown in Figure 4.

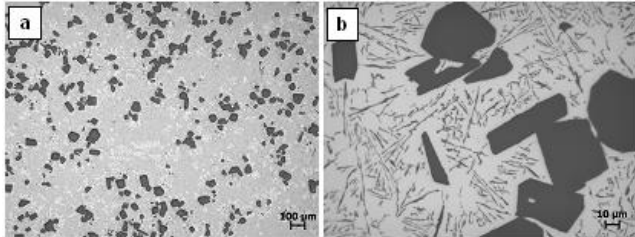


Figure 4 The optical micrographs of Al-22Si with the addition of 0.1% ZnS cast after 1.5 hr. (a) low magnification and (b) high magnification.

This inefficiency in the refinement of primary Si at high holding time could be due to the agglomeration of ZnS particles which then produce larger size if compared with that produced in 20 min holding time. Also, the high holding time leads to continuous removal of the Ca by oxidation, and then the eutectic Si matrix loses its modification.

The chemical composition of Al-22Si alloy after adding the master alloy (0.1%ZnS) analysed using a “Worldwide Analysis System (WAS) AG, Foundry master” showed that the Si composition reduced to around 20%Si because of dilution. Hence, to compare with P refinement, an experiment was conducted by adding 200 ppm of P to Al-20Si alloy. The average particle size of primary silicon was reduced to 20  $\mu\text{m}$ , as shown in Figure 5.

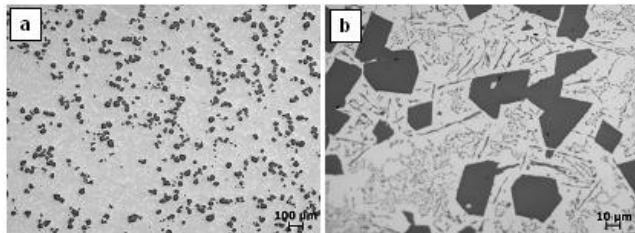


Figure 5 The optical micrographs of Al-20Si alloy with the addition of 200 ppm P. (a) low magnification and (b) high magnification.

In using P for refinement of primary silicon in hypereutectic Al-Si alloy, AIP particles will form in-situ which has a zincblende crystal structure with a lattice constant of 5.431  $\text{\AA}$ . These particles are suspended in the melt and act as potent sites for epitaxial nucleation of primary silicon [11].

It is very clear that the in-situ prepared zincblende ZnS have the same efficiency of P refinement of primary silicon and follow the same refinement mechanism.

### Summary

The conclusions from the results of this study are:

1. According to the heterogeneous nucleation theory, ZnS particles act as potent substrate for nucleation of primary silicon. The lattice parameter of zincblende cube ZnS is 5.41  $\text{\AA}$  which is

similar to that of silicon with a lattice mismatch of less than 1 %. The primary Si nucleates and then grows by wrapping around the ZnS nucleant to develop as a compact particle.

2. The results from this study leave no doubt that the novel Al-ZnS master alloy is a promising refiner in solidification of hypereutectic Al-Si alloys. It has the same efficiency of CuP in the refinement of primary silicon and follows the same refinement mechanism. It seems that there is no interaction between ZnS and the Ca exists in the melt and hence there was no drop in modification of the eutectic Si in commercial purity Al-Si alloy.

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