A NEW METHOD FOR MELT REFINEMENT OF AL CAST ALLOYS IN SAND CASTING PROCESS

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Aluminium castings have played an integral role in the industrial growth since their inception during the late 19th century. Their early applications include domestic components, such as cooking utensils, decorative parts, etc. These early applications rapidly expanded to address the requirements of a wide range of engineering specifications, particularly, in automobile and aerospace industries. In the present work, an attempt was made to modify the micro-structure of Al-17.0Si-0.5 mg alloy by adding barium to the melt at 4.0% and 5.0% and the modified melts were cast in sand moulds. The cooling conditions were varied for different experiments. Barium metal additions refined the primary and eutectic silicon phases of Al-17.0Si-0.5 mg alloy through simultaneous refinement of both primary and eutectic silicon morphology. Results clearly indicate that barium metal in varying proportions at faster cooling rate exhibited remarkable refinement over the existing methods of refinement for hyper-eutectic Al-Si alloys. The SEM micrographs of the samples, modified by 4.0% Ba and 5.0% Ba, show that when barium was added to the melt, the morphologies of the primary silicon and eutectic silicon changed from coarse blocky shape to irregular morphology to fine blocky columnar shape with reduced primary silicon size. The quantity of refinement increased with the amount of modifier addition and cooling rate. Appearances of such morphology of silicon in the alloy can be attributed to the crystallization behaviour of silicon that has barium in the form of solid solution. Hardness of the modified samples of Al-17.0Si-0.5 mg-4.0Ba and Al-17.0Si-0.5 mg-5.0Ba increased by 10% and 12% respectively in comparison to an unmodified sample (Al-17Si-0.5 mg). Experiments were also conducted with the combined additions of Barium and Al-5.0Ti-1.0B grain refiner and the results were found to be favourable.

Keywords: Al-Si alloy, Micro-refinement, Barium addition, Grain refiner addition, Crystallization of silicon, Hardness

INTRODUCTION

Hypereutectic Al-Si alloys are widely used in the automobile and aerospace industries because they exhibit several specific and interesting properties, such as excellent wear resistance, high strength-to-weight ratio, low

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coefficient of thermal expansion, good corrosion resistance, excellent fluidity, and good castability. They are used in various applications such as liner-less engine blocks, automotive pistons, compressor bodies, and pumps. Hypereutectic Al-Si alloys are used to produce engine blocks without cylinder liners, automotive pistons, and a number of other products primarily because of their high wear resistance properties resulting from a large volume fraction of the silicon phase. However, the desirable properties of hypereutectic Al-Si alloys depend on the characteristics of their cast microstructures, namely secondary dendrite cell size or arm spacing, and the size, morphology (or shape), and distribution of eutectic and primary Si particles. The morphology of primary silicon particles can be rather complex, such as plate-like, star-shaped, polygonal, blocky, and feathery varying with solidification conditions, chemical composition, and alloying elements.

The phase diagram of Al-Si binary system (Massalsky, 1990) reveals that a hypereutectic alloy is formed with a silicon composition that exceeds 11.7 wt% silicon, as shown in Figure 1. The microstructure of hypereutectic alloys contains two major components, the primary phase and the eutectic phase. Conventional casting resulting in hypereutectic Al-Si alloys in which the primary silicon phase appears as large particles exhibiting a variety of morphologies such as coarser platelets, star-like and blocky, while the eutectic structure consists of an aluminum-rich solid solution of silicon and virtually pure silicon, forming the matrix of the microstructure. The three main groups of aluminium alloys which contain silicon are as follows.

1. Hypoeutectic 2.0-7.0%
2. Eutectic 8.0-13.0%
3. Hypereutectic 14.0-25.0%

![Figure 1: The Al-Si Eutectic Phase Diagram](image)

To refine the melt, several methods such as electromagnetic stirring (Jung et al., 2001; Yu et al., 2011, Lu et al., 2007, Robles Hernández and Sokolowski, 2006), melt vibration (Jung et al., 2001; Lu et al., 2007), pulse treatment, rapid solidification (Zuo et al., 2009), minor element addition (modifier) (Zhang et al., 2012), Zhang et al., 2010, Booth-Morrison et al., 2011, Knuutinen et al., 2001) and melt overheating treatment (Dai and Liu, 2009) carried into execution. However, the minor element addition (modifier/grain refiner) has proven to be the most effective and simple method. The mechanical properties such as tensile strength at room temperature, hardness, high wear resistance and so on were considered in correlation with the structure and good casting properties and these improved mechanical properties are results of the fine eutectic microstructure formed after solidification. Recently, Shamusuzzoha (2012) revealed that the dual refinement of the primary and eutectic silicon
phases in shape casting of hypereutectic Al-Si alloys is possible with Ba metal addition. Weixi et al. (2010) and Xu et al. (2006) reported that with the Nd addition in hypereutectic Al-15 wt% Si alloy, the morphologies of primary silicon changes from coarse blocky shape and irregular morphology (20-40 μm) to fine blocky shape, with primary silicon size reducing to 10-20 μm. Jiang et al. (2005) investigated the effect of new Al-P-Ti-TiC-Y modifier on primary silicon in hypereutectic Al-Si alloy. The primary silicon in unmodified Al-20 wt.% Si and Al-29 wt.% Si alloys exhibit coarse platelets, star-like and other irregular morphologies (100 and 250 μm respectively), changing drastically to fine blocky shape (20 and 35 μm respectively).

Zuo et al. (2009) investigated the effect of rapid solidification on the microstructure and refining performance of an Al–18Si–2.5P master alloy. The results show that as the solidification rate increases, the size of AlP particles in Al–18Si–2.5P master alloy reduces and the morphology of AlP evolves from plate-like to the fine nodular shape. Shin et al. (2012) investigated the effect of Sr addition on the microstructure and mechanical properties of Al–10.5Si–2.0Cu recycled die-casting alloy. The addition of Sr of the order 0.01–0.02 wt% in the Al–10.5Si–2.0Cu recycled alloy transformed the morphology of the eutectic Si from an acicular shape to lamellar. Li et al. (2011) investigated the effects of ytterbium (Yb) on the microstructure and eutectic solidification behaviour of Al–7.5%Si–0.45%Mg alloys. The micro-structural observations show that the addition of Yb causes a structural transformation of eutectic silicon from a coarse plate to a fine flake-like and some branched morphology. Zhang et al. (2012) reported that the Sc addition in varying proportion to Al-7% Si alloys, modify the microstructure of the eutectic Si from a coarse, plate-like and acicular to a finely branched and fibrous pattern.

Bo et al. (2010) investigated the effect of Sb on the microstructure and mechanical properties of Mg2Si/Al-Si composite. When the mass fraction of Sb is 0.4%, the average size of primary Mg2Si is refined to 25 μm, and the morphology of primary Mg2Si changed from coarse dendritic shape to fine particles. Morrison et al. (2011) revealed the effect of substituting 0.01 or 0.02 % Er for Sc in an Al–0.06 Zr–0.06 Sc % alloy to develop cost-effective high-temperature aluminum alloys for aerospace and automotive applications. Knuutinen et al. (2001) studied the effects of different concentrations of separate additions of Ba, Ca, Y and Yb on the eutectic arrest in an A356 (Al–7%Si–Mg) alloy by thermal analysis and concluded that addition of Ba resulted in a very fine fibrous structure. Zhang et al. (2010) studied the effects of barium modifier content on the mechanical properties, microstructures, and wear resistance of Al–Mg–Si alloys at room temperature. The Ba modifier at 1 wt% exhibited the best results for the mechanical properties of alloy. The modification caused the disappearance of primary silicon with the formation of solid solution dendrites and fine fibre or rod-like eutectic silicon instead of plate-like structures, resulting in a highly branched filamentary form with a better distribution of Si particles.

Modification of the Al–Si eutectic from a flake-like to a fine fibrous silicon structure can be achieved in two ways; by chemical
modification or with quench modification, but no work was done on the simultaneous refinement by addition of certain elements at rapid cooling rate. The wear resistance decreases with increasing load in case of unmodified alloys when subjected to varying load conditions in engineering applications, but this has not been verified for the grain refined and barium modified alloys which are likely to offer higher wear resistance with increasing load. The modifying effect of Ba, Ca, Y and Yb (2001) on Al-7%Si-Mg hypoeutectic alloy showed that all elements modify the eutectic to different degrees, but no work was done to reveal the modifying effect of Ba, Ca, Y and Yb on Al-17%Si-0.5%Mg hypereutectic alloy.

The effects of barium modifier content on the mechanical properties, microstructures, and wear resistance of hypoeutectic Al–Mg–Si alloys at room temperature caused the disappearance of primary silicon with the formation of solid solution dendrites and fine fibre or rod-like eutectic silicon instead of plate-like structures, resulting in a highly branched filamentary form with a better distribution of Si particles hence improve the wear resistance of the alloy.

Taghavi et al. (2009) found that mechanical vibration effectively refined the dendritic structure of A356 aluminum alloy, and that the level of refinement was directly related to the vibration frequency and the duration of the vibration treatment, although the refinement was not as significant as that observed with chemical modification. Lu et al. (2007) focused on the study of refinement of primary Si in hypereutectic Al–Si alloy by electromagnetic stirring basically a physical modification method and did not work in the direction of chemical modification.

Robles et al. (2006) in their research work on comparison among chemical and electromagnetic stirring and vibration melt treatments for Al–Si hypereutectic alloys, focused on the chemical refinement by the material other than barium. Chemical modification using sodium, phosphorus, or rare-earth metals (Booth-Morrison et al., 2009, Jiang, 2005, Li et al., 2011, Bo et al., 2010) has been widely used as a method for modification but no work was done with barium modifier and/or grain refiner like Al-5Ti-1B. Several researchers worked on various methods like electromagnetic stirring (Jung et al., 2001, Yu et al., 2011, Lu et al., 2007, Robles Hernández and Sokolowski, 2006), melt vibration (Yu et al., 2011, Robles Hernández and Sokolowski, 2006), pulse treatment, rapid solidification (Zuo et al., 2009), minor element addition (modifier) (Zhang et al., 2012, Zhang et al., 2010), Booth-Morrison et al., 2011, Knuutinen et al., 2001) and melt overheating treatment (Dai and Liu, 2009) carried into execution exclusively. However simultaneous action of the combined effect of two or more methods may result in better refining efficiency. Very few researchers Knuutinen et al. (2001), Zhang et al. (2010) and Shamusuzzoha (2012) selected barium as focus of study but either they remain specific to the barium percentage or limited to the hypoeutectic Al-Si alloys. Recently (Shamusuzzoha and Juretzco, 2007, Shamusuzzoha and Juretzco, 2008, Shamusuzzoha et al., 2011), based upon the concept of the solubility of barium metal in the silicon phase, the dual refinement of primary
and eutectic silicon has been attributed to the solidification morphology of Si that has barium in solution. However, barium metal addition in varying proportions at faster cooling rate exhibits marked refinement over the existing similar hypereutectic Al-Si alloys.

The present work investigates the effect of barium addition on primary silicon particles refinement in hypereutectic Al-Si alloys. In order to accomplish this, first designing and assembling a casting apparatus, that would allow the effective application of rapid cooling to a solidifying molten material for the development of barium modified hypereutectic Al-Si alloys, is exercised. Subsequently Ba metal addition in varying proportions at faster cooling rate in hypereutectic Al-Si alloys. Finally testing of microstructure, measurement of mechanical and tribological (wear resistance etc.) properties of modified alloys are carried in to execution.

**EXPERIMENTAL PROCEDURE**

**Fabrication of Mould and Water Cooling Attachment for Casting**

A metallic cylindrical pipe was designed to hold and support sand mould cavity for the solidification. The moulding material was selected as mild steel because its machinability is good and easy to manufacture, over and above, it is easily available. The material for the mould has following properties:

- Melting point: 1410°C
- Thermal conductivity: 45.006- 64.9125 W/ (m K)

The dimensions of the mould, shown in Figure 2, are as follows.

Height = 150 mm
Diameter = 25 mm

A stainless steel box of dimensions 305 mm X 305 mm X 204 mm was fabricated to serve as platform for mould and helps achieve unidirectional solidification through water cooling action flowing through the inlet and outlet ports provided for. The casting was carried out in two steps- the master alloys (Al-30%Si, Al-10%Mg and pure Al) were melted in pit furnace and then sand casted to get ingot.
Material Preparation
Commercial pure Al (99.9%) was used as the base element, and binary Al–30%Si (by wt) and Al–10%Mg (by wt) master alloys were added to synthesize hypereutectic Al–Si alloy (Al–17 wt% Si in this experiment). The nominal chemical compositions of the pure Al, Al–30Si master alloy and Al-10Mg master alloy, as well as that of the prepared Al–17Si alloy were measured by a spark spectrometer.

Materials added for alloy (Al-17%Si-0.5%Mg) preparation are:
1. Master alloys
   A. Al-30%Si
   B. Al-10%Mg
2. Pure Al (99.99%)
3. Barium Hydroxide (Mol. Wt. - 315.4 gm)

A. Quantity of Barium Hydroxide required for 4% Barium addition = 60.81 gm
B. Quantity of Barium Hydroxide required for 5% Barium addition = 77.51 gm

Charge Calculation
Materials added for master alloy (Al-17%Si-0.5%Mg) preparation are master alloys Al-30%Si, Al-10%Mg, Pure Al (99.99%) and Barium Hydroxide (Mol. Wt. - 315.4). The compositional details of these two master alloys and pure Al in terms of direct weights with due considerations of melting losses are given hereunder in Table 1, followed by the details of barium in the form of Barium Hydroxide (Mol. Wt. –

<table>
<thead>
<tr>
<th>Table 1: Details of Charge Calculation</th>
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<tr>
<td>Composition</td>
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<td>-------------</td>
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<tr>
<td>Wt. of charge (in Kg) (A)</td>
</tr>
<tr>
<td>Melting loss (in % wt) (B)</td>
</tr>
<tr>
<td>Total required composition (in Kg) (C=A+B)</td>
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</table>

a. Quantity of Si master alloy (Al-30%Si) = 1.717× (100/30) = 5.723 kg
   Al content in Al-30%Si = 5.723 kg - 1.717 kg = 4.006 kg
b. Quantity of Mg master alloy (Al-10%Mg) = 0.0515× (100/10) = 0.515 kg
   Al content in Al-10%Mg = 0.515 - 0.0515 = 4.635 kg
c. Total Al in master alloy = 4.006 kg + 0.4635 kg = 4.4695 kg
   Required pure Al = 8.332 kg - 4.469 kg = 3.863 kg

Sequence of Experiments
After fabrication of cylindrical mild steel mould of height 150 mm and diameter 150 mm, two cylindrical castings, each of height 150 mm and diameter 25 mm, were prepared in the fabricated mould to see the difference of microstructure in hypereutectic Al-Si alloys and the effect of barium addition on the silicon particle refinement as shown in Figure 3. The castings were prepared in two steps- the master alloys [Al-30%Si (5.723Kg)], [Al-10%Mg (0.515Kg)] and pure Al [(3.863Kg)]
were melted in a pit furnace and then sand casted to get ingots. The composition of these ingots was Al-17%Si-0.5%Mg and from these two ingots by weight 0.665 kg and 0.772 kg (depending upon the graphite crucible capacity) were again melted separately. Then barium hydroxide in appropriate quantity was added to get different proportions of barium in the alloy. The molten alloy was then solidified one by one in the fabricated mould at faster cooling rates. Two alloys having percentage of barium as 4 and 5% were cast.

**Specimen Preparation**

After the casting process, two disc shaped samples of size 20 mm X 10 mm were taken from the centre of the cylindrical castings. The samples were initially polished by files and then fine polishing was done with silicon carbide paper of various sizes (220, 320, 400, 600, 800, 1000 and 2000) on rotating disc mechanism. Further, the samples were polished using velvet cloth with alumina powder. Etching was done with HF reagent (hypereutectic Al-Si alloy) for 20 seconds for each sample. Photographs of microstructures were taken at different magnification of 1000X, 2000X, and 5000X at three different locations. The microstructure was analyzed by the Image J software.

**RESULTS**

SEM micrographs of longitudinal samples of cast alloys thus developed, have the compositions of Al-17%Si-4% Ba and Al-17%Si-5% Ba respectively. Energy dispersive x-ray spectrometry equipped with SEM for the specimens showed an overall composition that is close to Al-17 wt% Si. The microstructure in micrographs is free of any large idiomorphic primary silicon as evident by the unmodified sample micrograph shown in Figure 4. The microstructure in both the longitudinal samples appears similar in appearance and exhibits very fine eutectic matrix, as shown in Figure 5. Figures 6 and 8 show the SEM image at magnification of 1000X for full image of sample 1 and sample 2 which are further used as input file to the software to generate the EDX result at magnification of 1000X at locations [1 1] of sample 1 and [2 1] of sample 2. The silicon
crystals in these micrographs are of eutectic silicon phase and assume a very fine flake-like morphology. The data collected from this study are of two types: (i) quantitative temperature measurements from each casting sample, and (ii) quantitative measurements for each sample.

**SEM/EDX Analysis**

EDX results of the specimens at different locations are shown in Figures 7 and 9. The image taken by SEM is used for EDX. EDX gives the approximate percentage of the constituents of the alloy at a certain location or a selected region. At first the whole area at a magnification of 1000X was selected to check the composition of the alloy. At higher magnifications (5000X), the eutectic silicon particle was clearly visible. In this case, EDX analysis was done for a small area. EDX results confirmed the approximate percentage of individual components of the alloy as shown in Table 3 corresponding to Figure 7 and Table 4 corresponding to Figure 9. In the second case, the selected small area shows the high aluminium percentage. In the third case, the selected point shows the high silicon percentage. Hence, the eutectic silicon particle is clearly differentiated. The specimen in Figure 7 shows the phase elements at location [1 1] of the sample 1. The specimen Figure 9 shows the phase elements at location [2 1] of the sample 2.

The mechanism of modification by barium addition of the eutectic silicon particles, is that the atoms of the modifying element are absorbed into the growth steps of the silicon solid-liquid interface (grain boundary), causing a dramatic increase in twinning density, and
thereby modifying the structure by inhibiting further growth of the silicon particle. Further, as the modifying element was absorbed by the silicon solid-liquid interface, the EDX spectrum results at different points are not indicating barium element, which require verification.

**Hardness Results**

The unmodified sample and the two samples which were used for microstructure testing were again used for the hardness testing. Steel ball of diameter 2.5 mm and a load of 31.25 kg were used for the experiment. Three readings at three positions were taken. Then the Brinell hardness number (BHN) was calculated by the formula:

\[
BHN = \frac{2P}{\pi D \left[ D - \sqrt{(D^2 - d^2)} \right]}
\]

where, 

- \(P\) is the applied load in kg
- \(D\) is the diameter of the ball (mm)
- \(d\) is the diameter of the indentation (mm)

After all the values of BHN were calculated, the average of all the three readings at each position was calculated and this gives the hardness at that position. The hardness testing results for each specimen is given in Table 2.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Diameter (mm)</th>
<th>BHN</th>
<th>Average BHN</th>
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<tbody>
<tr>
<td>Unmodified</td>
<td>0.81, 0.78, 0.80</td>
<td>59, 63.8, 60.53</td>
<td>61.11</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td></td>
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<tr>
<td>Al-17%Si-0.5</td>
<td>0.76, 0.78, 0.74</td>
<td>67.3, 63.8, 71</td>
<td>67.37</td>
</tr>
<tr>
<td>Mg-4%Ba</td>
<td></td>
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<tr>
<td>Sample 1</td>
<td>0.75, 0.76, 0.75</td>
<td>69.1, 67.3, 69.1</td>
<td>68.50</td>
</tr>
<tr>
<td>Al-17%Si-0.5</td>
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<tr>
<td>Mg-5%Ba</td>
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**DISCUSSION**

The relatively finer microstructure found at the centre of the presently developed cylindrical samples support an important assumption that the last liquid was solidified at the mould centre, and the initiation of solidification was started either at the mould wall or in the melt that exists between mould wall and the mould centre. Figure 4 is a micrograph of unmodified sample; the silicon phase shows coarse blocky shape and irregular morphology. Figure 5(a) and (b) give the micrographs of samples modified by 4 wt% Ba and 5 wt% Ba, show that when barium was added to the melt the
morphologies of the primary silicon and eutectic silicon changed from coarse blocky shape and irregular morphology to fine blocky columnar shape with reduced primary silicon size. The mechanical property (hardness) test results show that the hardness properties of the modified samples are improved; this improvement may be attributed to refined particles after modification. Hardness of the modified samples Al-17%Si-0.5Mg-4%Ba and Al-17%Si-0.5Mg-5%Ba, having BHN 67.37, 68.50, increased by 10.24 % and 12.09 % respectively in comparison to unmodified sample BHN 61.11.

**CONCLUSION**

The microstructure of the presently developed high-strength hypereutectic Al-Si alloy, discussed in this work, reveals that the entire silicon content of the alloy assumes very
refined flake-like morphology. Appearances of such morphology of silicon in the alloy can be attributed to the crystallization behaviour of silicon that has Ba in the form of solid solution. The solid solution of Ba in silicon effects the crystallization of both the primary and eutectic silicon in the solidification of shape cast hypereutectic Al-Si alloy. The effect allows the hypereutectic melt either not to nucleate any primary silicon crystal or to nucleate those primary silicon crystals that after growth assume small in size and remain indistinguishable from the eutectic silicon phase.

From the results of the experiments, it can be concluded that:

A. Barium addition in hypereutectic Al-Si alloys resulted in refinement of primary silicon particle present in its microstructure.

B. In the modified sample Al-17%Si-0.5Mg-5%Ba, barium addition gives better refinement of the silicon particle in comparison to the modified sample Al-17%Si-0.5Mg-4%Ba.

C. Barium addition doesn’t only refine the primary silicon particle but it also refines the eutectic silicon.

D. Hardness of the modified samples Al-17%Si-0.5Mg-4%Ba and Al-17%Si-0.5Mg-5%Ba, having BHN 67.37, 68.50, increased by 10.24 % and 12.09 % respectively in comparison to unmodified sample having BHN 61.11.

REFERENCES


