Effect of Various Refinement Methods on the Morphologies of Primary Si in a Hypereutectic Al-18Si Alloy

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The present study investigates the effect of different molten metal processing methods on the modification of primary silicon and the microstructure and mechanical properties of hypereutectic Al-18wt%Si alloy. The effects of melt treatment with the addition of electromagnetic vibration, AlCuP, bubbling of argon gas and their combination has been examined and an optimum procedure has been suggested for the treatment of molten Al-Si alloys, which resulted in the finest primary silicon particles with the highest tensile, impact hardness properties and features of ductile fracture. This optimum procedure includes bubbling of the melt with argon gas for 15 min, the addition of 50 ppm of AlCuP master-alloy and stabilization of the melt for 15 min. [doi:10.2320/matertrans.M2015071]

1. Introduction

Hypereutectic Al–Si alloys (with more than 12.6 wt% Si) are widely used in the automotive and aerospace industries for manufacturing of high integrity engine blocks, air compressors, rotary engine and pistons. The widespread use of these alloys is due to their high-temperature strength and excellent wear resistance caused by dispersion of the Si as a reinforcing phase within the matrix. Furthermore, these alloys possess excellent combined properties, such as high specific strength, good cast-ability, excellent weld-ability, high thermal conductivity, high resistance to corrosion and low coefficient of thermal expansion.1–4

However, the presence of star-shape or irregular-shape coarse primary Si deteriorates the mechanical properties of this alloy family. Upon loading, the coarse primary Si particles act as plausible stress concentration sites, which lead to premature failure. Therefore, many researchers have investigated the refinement of Si particles to improve the mechanical properties of these alloys and variety of methods for this purpose. These methods include the addition of modifiers, ultrasonic vibration,5 quench modification, adding trace-levels of nucleation agents, rapid cooling and superheating.5–10 Some of these methods have difficulties that limit their use in full scale industrial practices. For example, for the ultrasonic vibration process, continuously maintaining the molten metal at high temperatures for a period of time is difficult to perform, and the process is practically difficult to implement in large scale industrial practices.5

 Modification of Al-Si alloys with Ce,11–14 Sc,15,16 La,14,17 Y,18 Yb,14,19 Eu20 and misch metals21 has been the subject of many studies. Phosphor is another modifier element that can be added to the melt in the form of SiP, CuP and AlCuP to form AlP nuclei within the molten Al-Si alloys.22,23 Zhagn et al.24 reported that the Cu-P master alloy modifies the primary silicon phase, but it has no or little modifying effect on eutectic Si. Liu et al.25 found two modification mechanisms for eutectic Al-Si alloy. The first mechanism is heterogeneous nucleation and refining of the primary Si phase using AlP particles. This mechanism is in agreement with the findings of Chen et al.26 regarding the ability of P to refine the primary Si. In the second mechanism, P atoms modify the morphologies of the Si phase. However, Liu et al.25 stated that the modification of hypereutectic Al-Si alloy mainly depends on the heterogeneous nucleation mechanism induced by AlP particles (the first mechanism). It is reported26 that excess P is unfavorable to the refinement of primary Si and can repress the modification of RE on the eutectic Si. As indicated above, the use of the ultrasonic vibration process to continuously maintain the molten metal at high temperature for a period of time is problematic and is practically difficult to meet the needs of industry due to the limitations of refining with insufficient vibration.9 Recently, Lee et al.27,28 reported that injecting an inert gas bubbling into the Al-Si melt reduces the amount of dissolved hydrogen in the melt, while increasing the nucleation rate of primary Si phase.

This study aimed to compare the effects of electromagnetic vibration, gas bubbling and AlCuP addition as well as their combination on the modification of the primary Si phase in an Al-18Si alloy and its mechanical properties.

2. Experimental Procedure

Tables 1 and 2 present the chemical composition of the hypereutectic Al-18Si alloy (free from any refining elements such as Sr, Sb, Ca and P) and the AlCuP master-alloy used in this study. Al-18Si alloy ingots were melted in an electric furnace at 1023 K; then, different melt treatments were applied. Subsequently, molten alloy was poured into the metallic mold (Fig. 1) that was preheated to 473 K. Five different melt treatments were studied as described below:
2.1 Experiment 1: no melt treatment
No melt treatment was used in this experiment. After melting at 1023 K and subsequently cooling down to 1003 K, the melt was degassed with addition of FOSECO 790 degasser flux and then was stabilized by holding at 1003 K for 10 min before being poured into the mold.

2.2 Experiment 2: gas bubbling
In the second treatment, after melting, the degasser equipment that blows argon gas (at a flow rate of 8 L/min) through a porous ceramic filter with a pore size of 2 µm was used for gas bubbling of the 8 kg molten metal. The bubble size and its relation to the gas flow rate were determined as in the previous experiment based on the water model and the molten metal. After gas bubbling, the metal was cooled to 983 K, at which temperature, the gas bubbled for 5 to 30 min; next, the molten metal was poured into the mold.

2.3 Experiment 3: addition of AlCuP
For the third treatment, after melting at 1023 K and subsequently cooling down to 1003 K, 50 ppm of AlCuP was added to the melt, and then the melt was stirred with a rotating alumina blade (rpm of 150) for 5 min. Thereafter, the melt was stabilized by holding at 1003 K for 0 to 30 min. Next, the melt was poured into the mold. The temperature of 1003 K was adopted from the results of previous studies that indicated it is the best temperature for the treatment of Al-18Si alloy melt that contains 30–100 ppm of P (in the form of AlCuP or CuP).

2.4 Experiment 4: gas bubbling + addition of AlCuP
In the fourth treatment, after melting and cooling down to 1003 K, the melt was gas bubbled for 15 min. Next, 50 ppm of AlCuP was added to the melt, and then the melt was stirred with an alumina blade (rpm of 150) for 5 min. Thereafter, the melts was stabilized by holding at 1003 K for 0 to 30 min. Finally, the melt was poured into the mold.

2.5 Experiment 5: electro magnetic vibration
The electromagnetic vibration (EMV) used in the experiment consisted of a D.C magnetic field generator and an alternating current generator. The stationary D.C magnetic field generator was fixed at 0.35 T. The sample was placed into a pre-heated electric furnace, which was located between the cores of magnetic field generator, as shown in Fig. 2. The sample was first heated to 1073 K and then cooled naturally to 973 K, at which time, an electric field was applied. Subsequently, the sample was cooled (at approximately 1.5 K/s) until it fully solidified at a fixed AC frequency, changing current density by 20, 40, 60, 80 and 100 A/m² at 1 kHz under the applied field of 0.35 T.

To study the effect of different melt treatments on the microstructure of the alloy, metallographic specimens were prepared and etched using Keller solution (175 ml distilled water + 20 ml HNO₃ + 3 ml HCl + 2 ml HF). The microstructure of the samples was studied using an optical microscope (Olympus, PMG3) and a scanning electron microscope (Hitachi S-4800). Subsequently, the size and morphology of the primary Si particles were determined using image analysis software (Image-Pro Plus). Wear tests were performed using a conforming pin-on-disc test machine (PLINT TE770). The samples (Φ6.5 mm × 13 mm) were prepared from the hypereutectic Al-Si alloy castings, which were fabricated via various molten treatment methods, and the surface of each of the wear test specimens had a roughness of 0.02 µm following the test. The disc having a rectangular of 37 mm × 58 mm × 3 mm was made of S45C steel and hardened to approximately 58 ± 1 HRc. The wear tests were performed at a constant pressure of 2 MPa, and a test of each sample was conducted for 6 h at room temperature. Each wear sample was ultrasonically cleaned and weighed before the wear test using a balance with the accuracy of 0.01 mg. After the wear test, the samples were cleaned in the solvents and then reweighed to determine the weight loss due to wear. To evaluate the effects of different melt treatments on the tensile properties of the alloy, 10 tensile test specimens were prepared according to ASTM-EM8 for each melt treatment. The tensile tests were conducted using an Instron-8516 universal tester at a constant crosshead speed of 1 mm/min. In addition, the effect of melt treatments on the hardness of the alloys was determined using...
a Vickers hardness tester (Akashi, HM-122) with a diamond indenter at a load of 50 gf. Furthermore, Standard Charpy V-notch specimens (10 mm × 10 mm × 55 mm, longitudinal orientation) were prepared in each experimental condition and tested at room temperature using a Tinius Olsen impact tester (JTT, ASCI-360), and the fracture surfaces of the samples were examined using SEM. To indirectly evaluate the changes in the microstructure of the primary Si, the electric conductivity of the alloys was measured at room temperature via the eddy-current method using an electrical conductivity meter (Auto-Sigma 3000). All of the test samples were cut from the center of the cast alloys in a rectangular bar with the dimensions of 20 mm × 20 mm × 20 mm.

3. Results and Discussions

3.1 The microstructure of non-treated alloy
Figure 3 shows the typical microstructure of Al-18Si alloy in non-treated condition (experiment 1). From this figure, the microstructure of the non-treated alloy contains coarse hexagonal and plate-like primary Si particles within the microstructure. The results from image analysis showed that the average equivalent diameter of the Si particles was approximately 52 µm. In addition, it appears that the primary Si particles have a non-uniform distribution within the microstructure.

3.2 The effect of bubbling treatment
The effect of the bubbling time on the microstructure of the alloy is shown in Fig. 4. Figure 4(a) shows the microstructure of the non-treated alloy (from experiment 2) and Fig. 4(b) to (g) is taken from the melts that were treated by gas bubbling for 5, 10, 15, 20, 25 and 30 min, respectively. Figure 5 shows the effect of bubbling time on the average equivalent diameter of the primary Si particles. Figures 4 and 5 shows that bubbling of the melt for only 5 min decreased the average Si particle size by approximately 50%. This observation is consistent with the conclusions of Lee and coworkers\(^\text{27}\) that the gas bubbles serve as heterogeneous nucleation sites for the primary Si particles in Al-Si melts. Furthermore, it has been suggested\(^\text{5}\) that the transient cavitation of gas bubbles breaks up the clusters of primary Si particles and results in fine and uniform distribution of Si particles within the microstructure (see Figs. 4(c) and (d)). Increasing the bubbling time from 5 to 10 and further to 15 min decreased the average Si particle size slightly. A recent report described the refining of that coarse morphology...
of primary Si phase by the cavitation effect with the formation of bubbles in the Al melts.\(^{27}\)

### 3.3 The effect of AlCuP

Figures 6 and 7 show the effects of the melt stabilization time (after addition of AlCuP) on the microstructure and the size of primary Si in Al-18Si alloy. Comparison of Figs. 6(a) and (b) show that the addition of AlCuP itself (without any melt stabilization) significantly decreased the size of the primary Si particles. As indicated in Fig. 7 and Figs. 6(a) to (c), increasing the stabilization time to 10 min resulted in finer Si particles. However, stabilization of the melt for longer than 10 min increased the Si particle size slightly and steadily. This behavior can be attributed to the fading of P (added as AlCuP).\(^{30,31}\)

### 3.4 The effect of gas bubbling + AlCuP

Figures 8 and 9 show the effect of melt stabilization time (after bubbling for 15 min, adding AlCuP and stirring for 5 min) on the microstructure and the size of the primary Si particles in the Al-18Si alloy, respectively. From Fig. 8, using both gas bubbling and AlCuP addition significantly reduced the size of the primary Si particles. However, stabilization of molten metal for more than 15 min increased the size of the Si particles slightly. Figure 9 also shows that simultaneous treatment of the melt by gas bubbling and AlCuP addition changed the morphology of the Si particles from elongated,
plate-like and coarse particles to more compacted, less elongated near-spherical ones. In addition, Fig. 8 shows that this melt treatment increased the number density of Si particles, which could be due to the cavitation of bubbles during the gas bubbling\(^5\) and the presence of AlCuP particles that act as a preferred heterogeneous nucleation sites. Furthermore, this figure clearly indicates that sequential application of gas bubbling and AlCuP resulted in more uniform dispersion of the Si particles within the microstructure of the alloy.

### 3.5 The effect of electromagnetic vibration (EMV)

Figure 10 represents the microstructure of the EMV processed alloy. The intensity of the magnetic field, the induced frequency and the cooling rate are 0.35 T, 1 kHz and 1.5 K/s, respectively. Figure 10(a) shows that the primary Si phase exhibits a traditional morphology, with the growth occurring faceted manner. Figures 10(b)–(f) show the microstructure of the samples induced at the same frequency (1 kHz) and at different currents (20, 40, 60, 80 and 100 A). According to the study of the electromagnetic vibration, the microstructure is considered to be modified when the frequency reaches 1000 Hz.\(^{32}\) Figure 10 shows that the coarse morphology of the primary Si phase was transformed to a fine morphology with the increase of current density. In particular, at the current setting of 60 A, a decrease in the size of the primary Si phase and a uniform distribution in the matrix are observed. However, when the current is increased to above 80 A, the primary Si phase is refined, but the eutectic Si phase becomes coarse. Figure 11 shows the variation of the primary Si size with increasing current density of electromagnetic vibration in the alloy. Figure 8 shows that the primary Si size is significantly reduced from 52 to 26 µm by applying 20 A to the melt because the primary Si phase is modified to 21 µm at the current setting of 60 A. That is, the primary Si phase is refined with increasing the current. As a result, the preferential growth along (112) in Si was suppressed and the twin density was increased by preventing the Si atom from attaching to the growing interface of the Si phase and by changing the solid-liquid interfacial energy of Si due to the electromagnetic vibration during solidification. For this reason, the primary Si phase is believed to be modified. In addition, the strong impact coupled with the locally high temperatures in a very short time could also

![Fig. 9](image-url) Variation of average equivalent diameter of primary silicon particles with holding time after melt treatment with gas bubbling + AlCuP.

![Fig. 10](image-url) (a) microstructure of alloy with no treatment and microstructure of the alloy after electromagnetic vibration (b) 20 A, (c) 40 A, (d) 60 A, (e) 80 A and (f) 100 A (Cooling rate: 1.5 K/s, 0.35 T, 1 kHz).

![Fig. 11](image-url) Variation of average equivalent diameter of primary silicon particles with increasing current density of electromagnetic vibration in the alloy.
remelt the primary Si phase, causing their edges to be circular.26)

Figure 12 compares the finest primary Si sizes that were obtained from each melt treatment. This figure shows that the finest primary silicon particles were obtained after treatment of the melt with bubbling and subsequent addition of AlCuP. However, all of the treatments were found to greatly decrease the size of the primary silicon particles compared to the non-treated alloy. Many researchers have reported that bubbling of the molten aluminum introduces a large number of oxides into the melt.33–35) Because the primary Si size decreased only slightly for the gas bubbling + AlCuP treatment compared with the AlCuP treatment, it is reasonable to conclude that gas bubbling + AlCuP has almost no benefits over the AlCuP treatment. The primary Si phase of electromagnetic vibration (EMV) is modified to 21 µm at the current setting of 60 A. The primary Si phase is refined with increasing the current. However, to judge such a conclusion, the effects of these melt treatments on the mechanical properties shall be considered, which are discussed in section 3.6.

As such, the degree of Si refinement was quantified again by measuring the electric conductivity of the alloys. This quantification was based on the dependence of the electric conductivity on the morphology of the primary Si and eutectic Si due to the interaction between the flow of free electrons and the nonconductive Si, as shown by the schematics in Fig. 13(a).36–38) coarse Si phase hinders the flow of electrons, which decreases the electric conductivity, and vice versa, indicating that measuring the electric conductivity of the alloys can be used to judge the changes in the structure, especially the morphology of primary and eutectic Si associated with the molten treatment methods. Indeed, as shown in Fig. 13(b), the electrical conductivity of the alloy increased with various molten treatment methods, especially AlCuP + gas bubbling processing; this observation further indicated that the morphology of the primary Si changed from coarse polygonal, platelet-like and star-like shapes to fine blocky shapes, which is consistent with the results shown in Fig. 13, which indicate variation of the mean size of the primary Si phase for the different molten treatment methods.

3.6 Mechanical properties

Figure 14 shows the effects of different melt treatment processes on the tensile properties of the Al-18 Si alloy. In this
figure, the tensile properties correspond to the conditions with the finest Si particle size in each treatment. From this figure, the treatment of melt with gas bubbling or AlCuP addition was not found to result in a considerable change in the elongation of the alloy. However, treatment of the melt with gas bubbling + AlCuP addition almost doubled the elongation of the alloy (in comparison to the non-treated condition). Furthermore, from this figure, the tensile strength and yield strength of the alloy that has been treated by either gas bubbling or AlCuP are almost the same. However, the melt treatment by gas bubbling + AlCuP agent addition resulted in considerable improvement of both the tensile strength and the yield strength. The mechanical properties improve with the addition of AlCuP combined with degassing because the AlP from AlCuP acts as a heterogeneous nucleation site of primary Si, in addition to each bubble acting as a nucleation site. If the bubble acts as the heterogeneous nucleation site, for a certain amount of gas per unit time is injected into the aluminum melt, smaller bubbles are more effective than larger ones. This improved effectiveness of smaller bubbles occurs because these smaller bubbles are more populated and remain longer than the larger bubbles in the melt, which results in increasing the number of heterogeneous nucleation sites and ultimately leads to improvement of the mechanical properties.27,28 Electromagnetic vibration (EMV) did not result in a considerable change in the elongation of the alloy. Figures 15(a) and (b) show the effects of each melt treatment method on the Vickers harness and the absorbed energy in the Charpy V-notched test of the samples with the finest Si particle size in the corresponding treatment. From Fig. 15, the highest hardness and the absorbed energy values correspond to the samples that were treated by gas bubbling + addition of AlCuP. The samples that were treated by AlCuP addition exhibited the second highest values of harness and absorbed energy. Furthermore, the treatment of the melt with gas bubbling had no significant effect on the hardness and absorbed energy of the alloy.

Figures 16 and 17 represent SEM images from the fracture surface of the alloys with different melt treatments in tension and impact tests, respectively. These figures clearly indicate that the features of the fracture surfaces depend on the molten treatment methods. The fracture surface of the non-treated sample in Figs. 16(a) and 17(a) consist of flat surfaces formed by the fracture of the primary Si flake, indicating that the failure of the samples was dominated by the brittle fracture. However, treatment of the melt with either bubbling...
or AlCuP addition shortened the length of the crack associated with the fracture of the primary Si together with some features of ductile fracture. Finally, the sample that was treated with gas bubbling + AlCuP addition exhibits features of plastic deformation (ductile fracture of the aluminum matrix). The above results are in agreement with the findings of Ref. 39) that, in hypoeutectic Al-Si alloys, the refinement of Si particles (that acts as reinforcing phase) increases the elongation and ultimate tensile strength simultaneously.

Figure 18 illustrates the wear test results of the specimens prepared by various molten treatment methods. Fine, spherical and uniformly distributed primary Si and eutectic Si phases can effectively improve the mechanical and tribological properties of hypereutectic Al-Si alloys.40,41) The results of this study indicated that the wear characteristic of the alloy was enhanced due to the refined primary Si phase through various molten treatments. Wear loss of the alloy is plotted as a function of sliding time in Fig. 18(a). This figure presents the loss of volume of each test specimen for various molten treatments under dry wear conditions. The results indicate that the wear loss of the as-cast sample is better than the other method, under a fixed loading. In addition, wear losses were decreased in the following order; bubbling process (during 15 min), EMV method (60 A), AlCuP (holding time 15 min) and the gas bubbling + AlCuP method (adding the AlCuP after gas bubbling 15 min). These results indicate that the wear loss is proportional to the size and distribution of modified primary Si. Figure 18(b) shows the wear rate as a function of sliding velocity of the alloy. Similar to the results of Fig. 18(a), the wear losses of the processed samples decreased in the following order: as-cast, bubbling, EMV, AlCuP and the gas bubbling + AlCuP. With the results of the wear test reveal the excellent improvement of the wear properties of hypereutectic Al-Si alloys due to the modification and good dispersion of the primary Si phase in the condition of a melt with the gas bubbling + AlCuP treatment.

4. Conclusion

This study confirms that addition of a small amount of P (50 ppm) in the form of AlCuP effectively refines the primary silicon phase in the Al-18Si alloy and transforms the coarse polygonal and platelet-like primary Si particles to fine polygonal and smooth particles. Gas bubbling was also
demonstrated to be effective in the refinement of the primary Si particles, as evidenced by the microstructural evaluations. More importantly, the application of a two-step treatment (gas bubbling + AlCuP addition) was found to refine the primary Si particles more effectively than either single-step refining treatment. The results of the tensile tests show that both UTS and EL% increase by using the two-step treatment instead of either single-step method. The results of the impact test also exhibit an increase in the fracture toughness, which is also confirmed by fractographic evaluations. The study of the fracture surface shows that the tendency toward ductile fracture increases by using a two-step procedure. Based on the results of the present study, the following two-step refining treatment could be recommended for a more effective refinement of the Al-18 Si alloy: 1) Gas bubbling for 15 min, 2) Addition of 50 ppm AlCuP, 3) Stabilization of the melt for 15 min.

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