Effect of rapid solidification on the microstructure and refining performance of an Al–Si–P master alloy

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\textbf{Abstract}

A new Al–18Si–2.5P master alloy has been successfully prepared to refine primary Si in hypereutectic A390 alloys, and the relationship between the microstructure and refining performance was investigated. 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. The rapid solidification has a significant improvement on the refining performance and the P recovery of Al–18Si–2.5P master alloy. It is suggested that the difference in refining performance of Al–18Si–2.5P master alloy is related to the morphology, size and quantity of AlP particles in master alloy, which could influence the dissolution rate of AlP and thereby affect the refining performance.

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1. Introduction

Considerable efforts have been concentrated on the improvement of modifiers to meet the requirements of environmental protection and industry applications. Among these modifiers, P is one of the most effective refiner of primary Si particles with wide application and can be added into the melt in many forms such as Cu–P, Al–Cu–P, and Al–Fe–P. Several investigations with these master alloys have been carried out in literatures. For example, Zhang et al. (2008) have investigated the microstructure and mechanical properties of hypereutectic Al–Si alloy modified with Cu–P. However, Maeng et al. (2000) reported that in comparison with Al–Cu–P master alloy, the Cu–P master alloy is known to be more stable to use as modifier but needs higher modification temperature. Kyffin et al. (2001) have used Al–Fe–P master alloy to investigate the effect of phosphorus additions on the spacing between primary Si in a Bridgman solidified hypereutectic Al–Si alloy. Faraji et al. (2005) have studied the effect of solidification cooling rate and Al–Fe–P inoculation on the number of primary Si per unit volume in hypereutectic Al–Si alloys. While, the addition of Al–Fe–P master alloy would cause the contamination of impurity element Fe in composition, which has the deleterious influence on the mechanical properties, especially the elongation and impact resistance. Therefore, the AlP-containing master alloy without other impurity elements is thought to be an ideal P addition for the modification and refinement of primary Si in Al–Si alloys.

As a kind of preparation process, the Rapid Solidification Process (RSP) of metals and alloys means extraordinarily high rates of cooling during solidification from the molten state (Jones, 1984). Significant modification can be obtained by RSP treatment, e.g. the remarkable refinement of the as-solidified microstructure, the refinement of the scale of segregation, the extended solid solubility and the formation of non-equilibrium phases (Majumdar and Muddle, 1993). Jones (1991) reviewed the formation of microstructure in rapidly solidified materials and its effect on properties. Trivedi (1994) proposed that under rapid solidification conditions, non-equilibrium conditions at the interface and a modified diffusional instability condition played critical roles in the selection of morphology and its microstructural scales. Zhang et al. (2003) reported that RSP could lead to the great improvement of nucleation rate and thus improved the grain refining performance of Al–5Ti–1B master alloy.

In this study, a new type of Al-based master alloy—ternary Al–18Si–2.5P master alloy has been developed, and the effect of rapid solidification on the microstructure and refining performance of this master alloy is investigated.

2. Experimental procedures

The base alloy used in this experiment was A390 alloy with the chemical composition given in Table 1 (all compositions quoted in this work are in wt.% unless otherwise stated). The samples of
Table 1
Chemical composition of A390 alloys (in wt.%).

<table>
<thead>
<tr>
<th>Material</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Fe</th>
<th>Zn</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A390</td>
<td>16.01</td>
<td>4.74</td>
<td>0.50</td>
<td>0.10</td>
<td>0.004</td>
<td>0.003</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Table 2
Preparation of Al–18Si–2.5P master alloy.

<table>
<thead>
<tr>
<th>Alloy designation</th>
<th>Cooling condition</th>
</tr>
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<tbody>
<tr>
<td>Al–18Si–2.5P master alloy</td>
<td>Cast-iron mold</td>
</tr>
<tr>
<td>A</td>
<td>Graphite crucible</td>
</tr>
<tr>
<td>B</td>
<td>Copper mold</td>
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</table>

Al–18Si–2.5P master alloy with different solidification rates were prepared using commercial grade Al–18Si–2.5P master alloy which were supported by Shandong Shanda Al&Mg Melt Technology Co. Ltd. After the ingot-like Al–18Si–2.5P master alloy was remelted at 1600 °C by high-frequency induction heating under a controlled Ar atmosphere, the melt was blown into different pouring molds. Then the samples of Al–18Si–2.5P master alloy with different microstructures caused by the different solidification rates can be obtained, and the preparation data for the samples were given in Table 2.

The comparisons of refining performances and P recoveries between different samples of Al–18Si–2.5P master alloy were carried out using A390 alloys as the base alloys with the same procedures. The base alloy was remelted in a graphite crucible using an electrical resistance furnace and held at 730 °C for 30 min. After the melt was degassed with C2Cl6 for 15 min, the refinement treatment was carried out by addition of Al–18Si–2.5P master alloy. The designed addition level of P was fixed to 150 ppm. After holding the melt from 5 min to 60 min, it was poured into a permanent mold with a size of 70 mm × 35 mm × 20 mm.

Metallographic specimens were all cut from the same position of the casting samples, then mechanically ground and polished through standard routines. Statistical analysis was conducted to determine the average size of primary Si. Microstructure analysis was carried out by high scope video microscope (HSVM), JXA-8840 electron probe microanalyzer (EPMA), and transmission electron microscope (TEM). The P recoveries in A390 samples were measured using the Emission Spectrometer. The identification of small grains was carried out using selected-area electron diffraction (SAED) and energy dispersive analysis of X-rays (EDAX). Thermal analysis was performed using differential scanning calorimeter (DSC).

3. Results

3.1. Microstructures of Al–18Si–2.5P master alloy with different solidification rates

Fig. 1 shows the microstructures of three types of Al–18Si–2.5P master alloy. As seen in Fig. 1, all the samples A, B and C are composed of three phases: α-Al, Si phase (primary Si and eutectic Si) and AlP particles. Meanwhile, it can be obviously found that there are remarkable differences in the microstructures of the three samples. As shown in Fig. 1(a), the AlP particles contained in sample A (with a solidification rate of about 10 K s⁻¹) exhibit agglomeration to some extent, while they have both plate-like and rod-like appearances with the quite wide size distribution. In comparison with sample A, AlP particles contained in sample B (with a solidification rate of 60–80 K s⁻¹) exhibit flake-like morphology with length of 120 μm. Quite different from those of samples A and B mentioned above, AlP particles in sample C with rapidest solidification rate (about 300–500 K s⁻¹) take the form of finer grains, about 12 μm in size.
Fig. 2. EPMA analysis of sample C: (a) SEI and (b–d) the X-ray images for respective elements: Al, Si and P.

Fig. 2 shows the EPMA analysis of sample C. From the comparison of microstructure of the samples, it can be observed that RSP has an obvious impact on the microstructure of AlP particles. With the faster cooling rate, the distribution of AlP particles and their morphologies can be improved, and the sizes can also be refined at the same time. Table 3 summarizes the marked difference in microstructural parameters of AlP particles in Al–18Si–2.5P master alloy.

Fig. 3. Typical microstructures of A390 alloy before and after the addition of Al–18Si–2.5P master alloy: (a) unrefined; (b–d) refined by samples A, B and C, respectively.
Table 4
Variation of average grain size of primary Si refined by three kinds of Al–18Si–2.5P master alloy.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mean particle size of primary Si (μm)</th>
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<tbody>
<tr>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>A/ (Standard deviation)</td>
<td>36.1/5.73</td>
</tr>
<tr>
<td>B/ (Standard deviation)</td>
<td>22.8/2.83</td>
</tr>
<tr>
<td>C/ (Standard deviation)</td>
<td>17.5/2.23</td>
</tr>
</tbody>
</table>

Fig. 4. P recoveries in A390 alloys refined by three kinds of Al–18Si–2.5P master alloy. (P addition level: 150 ppm, melt temperature: 730 °C).

3.2. Refining performance of Al–18Si–2.5P master alloy

Refining tests were carried out to quantify the refining performance of the three types of Al–18Si–2.5P master alloy. Fig. 3 shows the typical microstructures of A390 alloys unrefined and refined by Al–18Si–2.5P master alloy. As illustrated in Fig. 3, the primary Si in unrefined A390 alloys presents irregular morphologies such as coarse platelet and star-like. As evident in Fig. 3(b)–(d), A390

Fig. 5. TEM analysis for the primary Si in A390 alloys refined by sample C of Al–18Si–2.5P master alloy: (a) the morphology; (b) the corresponding EDAX analysis for the spot A; (c) the TEM diffraction spots for AlP.

Fig. 6. DSC results for Al–18Si–0.9P master alloy: (a) the solidification curve for Al–18Si–0.9P and (b) the corresponding differential curve of curve (a).
alloys have shown fast grain refinement response to the addition of Al–18Si–2.5P master alloy, with the average size of primary Si significantly decreasing from 80 µm to less than 20 µm. Meanwhile, most of primary Si particles are near-spherical in morphology with homogeneous distribution.

The variation of average size of primary Si refined by three kinds of Al–18Si–2.5P master alloy is illustrated in Table 4. It is clear that the refining performance of Al–18Si–2.5P master alloy with rapid solidification rate is much better than those of two other samples, especially in shorter holding time. The primary Si in A390 alloy refined by sample C are very small with average size of 17.5 µm even holding for only 5 min, compared with those in alloys refined by sample A or B. This indicates that rapid solidification has a significant improvement on the refining performance of Al–18Si–2.5P master alloy.

3.3. Comparison of P recoveries

The comparison of P recoveries was carried out with the same designed addition level of 150 ppm P at 730 °C. The result is illustrated in Fig. 4. It can be seen that there is no large difference between samples A and B. While, there is an obvious increase of P recovery in A390 alloy refined by sample C, and it goes up to 60% after holding for 60 min.

4. Discussion

According to the literature, Si can nucleate heterogeneously on a substrate of AlP with a cube–cube orientation relationship and solidify to form a faceted Si particle due to the very similar lattice parameters with AlP (Ho and Cantor, 1995). While Cantor (1997) proposed that heterogeneous nucleation behaviour was highly sensitive to the presence of ppm levels of potent impurities, which could sometimes produce dramatic changes in liquid undercooling and final solidified microstructure. Directly demonstrating the heterogeneous nucleation behaviour of AlP, Fig. 5 shows the TEM analysis of the primary Si in A390 alloy refined by sample C. It can be seen that there is a sphere-like grain (~1 µm) embedded inside the primary Si (Fig. 5(a)). The black spot (designated as A) in the grain is caused by the electron-beam of EDAX analysis. The chemical composition is about 49.63 at.% Al and 50.37 at.% P, which proved to be AlP (Fig. 5(b)). The corresponding SAED pattern of AlP in zone axis of [1 1 0] is shown in Fig. 5(c).

In order to analyze the solidification behaviour of hypereutectic Al–Si alloys, the DSC thermal analysis was performed with Al–18Si–0.9P alloys and result is shown in Fig. 6. It can be found that besides the peaks at 667.94 °C and 570.44 °C which correspond to the precipitation of primary Si and the eutectic reaction respectively, there is still a small peak at about 1122.94 °C. The small peak can be speculated to be the precipitation peak of solvent AlP. In terms of the DSC result (Fig. 6) and the extremely low solubility of AlP as investigated by Beer (1969) and Lescuyer et al. (1998), the solidification process of A390 alloys after addition of Al–18Si–2.5P master alloy can be deduced as follows: after adding Al–18Si–2.5P master alloy into the melt, the AlP particles gradually start to dissolve, which results in the reductions in their size and the dissolution from large particles into smaller ones. Due to the lower solubility of phosphorus and the density difference, a large quantity of AlP particles cannot uniformly distribute in the melt. These undissolved AlP would become the dregs and float to the surface and cannot act as the nucleation sites of primary Si. With the temperature decreasing during solidification, the AlP which are homogeneously dissolved in the melt would precipitate, and this part of AlP particles is usable for the nucleation of primary Si (Yu et al., 2007). In comparison with the samples A and B with solidification rate less than 100 K s−1 in conventional processing (Jones, 1984), the fine nodular-like AlP particles prepared by RSP are at the non-equilibrium state with high energy, which means lower stability. After the addition of sample C into the A390 melt, these AlP particles in sample C are easier to dissolve into the melt due to the high energy, which improves the P recovery and nucleation rate and thus leads to improved refining performance.

From the comparison of microstructure of different Al–18Si–2.5P master alloy (Fig. 1), it can be observed that besides the morphologies and sizes of AlP particles, the distribution of them in sample C is also improved due to rapid solidification. The homogeneous distribution would also be beneficial to increase the dissolution rate of AlP particles and thus do good to the improvement of the refinement efficiency of the master alloy.

5. Conclusions

(1) A new Al–18Si–2.5P master alloy with a large number of preformed AlP particles has been successfully prepared.

(2) The rapid solidification has significant impact on the microstructure of Al–18Si–2.5P master alloy, and improves obviously the refining performance. With addition of rapidly solidified Al–18Si–2.5P master alloy, the primary Si of the A390 alloy can be remarkably refined to 17.5 µm on average even holding for only 5 min.

(3) Increased dissolution rate of AlP particles due to the fine nodular-like morphology and homogeneous distribution may be the reason for the improvement of refining performance of Al–18Si–2.5P master alloy.

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References


