The combined effect of rapid solidification and phosphor addition on the microstructure of hypereutectic A390 alloys.

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Abstract

The influence of the combined effect of rapid solidification and phosphor addition on the morphology of primary silicon particles in A390 Al-Si alloy has been investigated by using light optical microscope (LOM). The P as modifier element was added in the shape of copper phosphor (Cu₃P) master alloy. The results show that as the solidification rate increases, the size of primary silicon particles in A390 alloy reduces and the morphology of these particles evolve from plate-like to the fine nodular shape. The rapid solidification has a significant improvement on the refining performance of P to modify and refine the primary Si particles in A390 alloy. It is suggested that the refining performance of P in Cu₃P master alloy is related to the formation the AIP particles which act as a heterogeneous nucleation. This affects the solidification rate and restricts the Si phase’s growth.
1. Introduction

It is well established that hypereutectic Al–Si cast alloys have the good potential for tribological applications\(^1,\,2\). Silicon as a hard material increases the wear resistance of Al–Si hypereutectic alloys\(^3,\,4\). 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 refiners 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.\(^5\) have investigated the microstructure and mechanical properties of hypereutectic Al–Si alloy modified with Cu–P However, Maeng et al.\(^6\) 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.\(^7\) 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.\(^8\) 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.

The Rapid Solidification Process (RSP) of metals and alloys means extraordinarily high rates of cooling during solidification from the molten state\(^9\). 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\(^10\). Jones\(^11\) reviewed the formation of microstructure in rapidly solidified materials and its effect on properties. Trivedi\(^12\) 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.\(^13\) 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, the influence of the combined effect of high cooling rate and phosphor addition on refining the microstructure and modification of primary silicon particles is investigated.
2. Experimental procedures

The base alloy used in this work was A390 alloy with the chemical compositions given in Table 1 for six samples. The alloy was prepared by melting a commercial pure Al and then a commercial pure Si and Cu were added to melt with continuous mixing by graphite mixer. P as Cu₃P was added before pouring the melt in moulds also the Mg as a bulk commercial pure metal. The base alloy was prepared in a graphite crucible using a gas 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 Cu₃P master alloy. The designed addition level of P was fixed to 150 ppm. After holding the melt from 10 min to 40 min, the molten metal poured in a cast iron mould, cooled pure copper mould and sand mould as shown in Fig. 1.

Table 1. Chemical compositions of A390 alloys (wt. %).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element (wt%)</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Fe</th>
<th>Zn</th>
<th>P</th>
<th>Ti</th>
<th>Al</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td></td>
<td>16.330</td>
<td>4.538</td>
<td>0.820</td>
<td>0.095</td>
<td>0.006</td>
<td>0.001</td>
<td>0.003</td>
<td>Bal.</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>16.280</td>
<td>4.507</td>
<td>0.778</td>
<td>0.093</td>
<td>0.005</td>
<td>0.001</td>
<td>0.002</td>
<td>Bal.</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>15.996</td>
<td>4.469</td>
<td>0.829</td>
<td>0.089</td>
<td>0.005</td>
<td>0.001</td>
<td>0.003</td>
<td>Bal.</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>15.998</td>
<td>4.542</td>
<td>0.080</td>
<td>0.092</td>
<td>0.003</td>
<td>0.015</td>
<td>0.003</td>
<td>Bal.</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>16.003</td>
<td>4.404</td>
<td>0.080</td>
<td>0.010</td>
<td>0.007</td>
<td>0.014</td>
<td>0.002</td>
<td>Bal.</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>16.132</td>
<td>4.525</td>
<td>0.083</td>
<td>0.090</td>
<td>0.005</td>
<td>0.015</td>
<td>0.003</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

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. The microstructure was prepared by using an optical microscope (LOM).

3. Results and Discussions

Figure 2 shows the microstructures of three types of A390 alloy without modification by phosphor. As seen in Fig. 2, all the samples A, B and C are composed of three phases: α-Al, eutectic Si and primary Si particles. Meanwhile, it can be obviously found that there are remarkable differences in the microstructures of the three samples.
As shown in Figure 2(A), the primary silicon particles contained in sample A (with a solidification rate of about 10 °C/sec) exhibit starlike primary Si particles to some extent with length of 110 µm. In comparison with sample A, primary Si particles exist a sample B (with a solidification rate of 80 °C/sec) exhibit a massive morphology with length of 80µm. Quite different from those of samples A and B mentioned above, primary Si particles in sample C with the rapidest solidification rate (about 200 °C/sec) take the form of finer grains, about 40µm in size.

Refining and modification tests were carried out to quantify the refining performance of Cu₃P master alloy. Figure 3 shows the typical microstructures of A390 alloys refined and modified by the addition of P in level of 150 ppm. As illustrated in Figure 3 of the primary Si in refined A390 alloys presents more regular morphologies in a comparison with Figure 2, such as fine platelet and star-like As evident in figure (D)–(F), A390 alloys have shown fast grain refinement response to the addition of Cu₃P master alloy, with the average size of primary Si significantly decreasing from 80µm to less than 20µm. Meanwhile, most of primary Si particles are near-spherical in morphology with a homogeneous distribution.

Figure 3 (D), (E) and (F) are LOM micrographs of as-cast A390 alloys which cast in different mould materials and modified by phosphor addition. Primary silicon and eutectic silicon in as-cast A390 alloy at the cooling rate of 10 °C/s exhibit coarse irregular and long needle-like morphologies, respectively, as shown in Fig. 3(D). Figure. 3(F) shows the effect of rapid solidification as well as the phosphor addition on the primary silicon and eutectic silicon, respectively. When the cooling rate is up to 200 °C/s, the morphologies of primary silicon where drastically changed to a fine block-shape (Average size of 18µm). Some researchers have suggested that there are silicon atom clusters [14, 15] and silicon tetrahedron (pre-existent) [16] in the melt of Al–Si alloys. These silicon atom clusters and silicon tetrahedron can serve as nuclei and grow into observable silicon particles during rapid solidification [15]. In the experiment, the diffusion of silicon atoms can be limited to a great extent due to the rapid solidification. Therefore, the growth of primary silicon in sample F is inadequate because the action of high cooling rate and the presence of P in A390 alloy. Uzun et al [17] have investigated the micro structural characteristics of a rapidly solidified Al–16 wt.% Si alloy by melt-spinning technique and concluded that the structure of the melt-spun ribbon was completely composed of finely dispersed α-Al and eutectic silicon. According to the present experiment, the smaller eutectic silicon can be obtained by using high cooling and phosphorus modification technique, as shown in Figure. 3(F). The phenomenon can be interpreted as indication that (a) the solidification rate for A390 is high enough to retain most of the added silicon in
solid solution and (b) the growth of eutectic silicon is also inadequate due to addition of P and the rapid solidification. These results revealed that the combined action of the cooling rate and adding phosphor played an important role in determining the morphologies of primary silicon and eutectic silicon.

The variation of average size of primary Si refined by three kinds of casting moulds is illustrated in Table 2 and Fig.4. It is clear that the refining performance of addition of 150 ppm of P with the fastest solidification rate (i.e., casting in copper mould) is much better than those of two other samples, especially in shorter holding time. The primary Si in A390 alloy refined by P and cast in copper mould (sample F) is very small with average size of 18 µm even holding for only 10 min, compared with those in alloys refined by P and cast in sand mould and cast iron mould. This indicates that the rapid solidification has a significant improvement on the refining performance of phosphor refined alloy.

4. Conclusion
(1) The rapid solidification has significant impact on the microstructure of A390 alloy and improves obviously the refining and modification performance of phosphor.
(2) With rapidly solidified A390 Al-Si alloy treated by Cu₃P master alloy, the primary Si of the A390 alloy can be remarkably refined to 18 µm on average even holding for only 10 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 and modification performance of Cu₃P master alloy.
Fig. 1: (A, B) cast iron mould

Fig. 1: (C, D) copper mould

Fig. 2: As cast A390 alloys without modification (A) cast into sand mould, (B) cast into cast iron mould, (C) cast into cooled copper mould, all micrographs are at x200
Samples | Mean particle size of primary Si (µm)  
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td></td>
<td>10 min</td>
<td>20 min</td>
<td>30 min</td>
<td>40 min</td>
</tr>
<tr>
<td>Sand mould</td>
<td>40</td>
<td>27</td>
<td>20</td>
<td>16.8</td>
</tr>
<tr>
<td>Cast iron mould</td>
<td>28</td>
<td>22</td>
<td>17</td>
<td>15.2</td>
</tr>
<tr>
<td>Copper mould</td>
<td>18</td>
<td>16</td>
<td>15</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Table 2. Influence of holding time after the phosphor addition.
Fig 4. Influence of holding time on the size of primary Si- particles.
5. References


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