Effect of strontium and solidification rate on eutectic grain structure in an Al-13 wt% Si alloy

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Abstract: The influence of strontium addition and solidification rate on eutectic grain structure in a near-eutectic Al-Si alloy was investigated. The characteristic temperature of eutectic nucleation ($T_N$), minimum temperature prior to recalescence ($T_M$), and the growth temperature ($T_G$) during cooling were determined by quantitative thermal analysis. All characteristic temperatures were found to decrease continuously with increasing Sr content and solidification rate. Microstructural analysis also revealed that the eutectic grain size decreases with increasing Sr content and solidification rate. Such eutectic grain refinement is attributed to the increased actual under-cooling ahead of the liquid/solid interface during solidification.

Key words: Al-Si alloys; microstructure; solidification; eutectic grain; strontium

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I ncreasing demand for fuel economy has a significant influence on the automotive manufacturers’ selection of materials. The use of lightweight materials, such as aluminum alloys, can help reduce vehicle weight and thus improve fuel economy. As a result, aluminum castings have been widely used in automotive industries. As the most widely used aluminum castings, the majority of Al-Si alloys contain 50–90 vol.% eutectic (i.e. the last major transformation during solidification). Thus eutectic structure has a significant effect on casting quality and it dominates the determination of mechanical properties. Further, it has recently been discovered that various spatial distribution patterns in the eutectic can be achieved by controlling eutectic solidification [1,2].

Previous work on the crystallography of eutectic and the mechanisms of eutectic reaction in Al-Si alloys has been reviewed by Makhlof and Guthy [3]. More recently, Shankar et al. [4] investigated the solidification of unmodified Al-Si based alloy, and they concluded that the $\beta$-(Al, Si, Fe) phase nucleates in the solute field ahead of the growing aluminum dendrites (even with the trace amount of Fe in the alloy). Subsequently, the $\beta$-(Al, Si, Fe) phase provides nucleation site for eutectic Si particles. Dahle and co-workers [1,5-8] studied eutectic solidification of hypo-eutectic Al-Si alloys using electron backscatter diffraction (EBSD) and concluded three possible eutectic nucleation and growth modes: (a) nucleation on or adjacent to the mold wall with growth front opposite the thermal gradient (e.g. in Na-modified alloys); (b) nucleation and growth on the primary aluminum dendrites in the unmodified alloy; and (c) independently heterogeneous nucleation of eutectic grains in inter-dendritic regions in the Sr-modified alloys. It was also found that nucleation was prolific in the commercial unmodified alloy while few eutectic grains nucleated in the high-purity unmodified alloy. Further, the addition of strontium to the commercial alloy increased eutectic grain size [9]. Such findings are in contrast to the recent works carried out by the current authors in Al-15.5%Si alloys [10-11], which show that adding Sr to the commercial high-purity alloy resulted in a considerable reduction of eutectic grain size. In this paper, we investigated the influence of Sr on eutectic nucleation and growth in a near eutectic alloy (Al-13%Si). Possible influence from the cooling rate during solidification was also studied.

1 Experimental procedure

1.1 Alloys, melting and casting

The experimental alloys with a nominal composition of Al-13.0%Si were prepared in an electrical resistance furnace, using Al-12.3wt%Si master alloy and crystalline silicon particles (industrial purity, 99.5%Si). An Al-10%Sr master alloy was employed for eutectic modification and added to the
melt at about 730 °C. After holding for 30 minutes, the melt was degassed by adding SW-RJ-1 flux. The melt was then poured into a cylindrical steel mold (with inner diameter of 20 mm and height of 50 mm, preheated to 250 °C producing a cooling rate of about 10 K/s) or a tapered stainless steel cup (with 2 K/s cooling rate) at about 720 °C. The compositions of the experimental alloys were measured using a spectrometer (Switzerland, ARL-3460) and the results are given in Table 1.

Table 1: Composition of experimental alloys (wt%)

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Si</th>
<th>Sr</th>
<th>Cooling condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.12</td>
<td>-</td>
<td>Stainless steel cup mold or cylindrical steel mold</td>
</tr>
<tr>
<td>2</td>
<td>13.16</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>13.29</td>
<td>0.030</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>13.07</td>
<td>0.041</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>13.34</td>
<td>0.064</td>
<td></td>
</tr>
</tbody>
</table>

1.2 Thermal analysis

Analysis of cooling curves during solidification was performed in accordance with the method proposed by McDonald.[6,7] As shown in Fig. 1, a tapered stainless steel cup was used for this test. The steel cup was coated with a thin layer of ZnO and preheated to the same temperature as the melt prior to sampling. Samples for thermal analysis were taken by submerging the preheated stainless steel cups into the melt at 720 °C. Two samples (with and without a (type-K) thermocouple) were taken simultaneously from each heating. During solidification the temperature of the sample with the thermocouple (hereafter termed the instrumented sample) was real-time monitored and the sample without the thermocouple was quenched when the eutectic reaction was approximately 40 % completed (referring to the solidification information obtained from the instrumented sample). For both samples, the average cooling rate of the liquid prior to solidification was about 2.0 K/s. Three characteristic temperatures for the eutectic reaction were determined from the cooling curves, after Tamminen.[12] These temperatures are the nucleation temperature, \( T_N \) (defined as the first noticeable change on the derivative of the cooling curve); the minimum temperature prior to recalescence, \( T_M \); and the growth temperature, \( T_G \) (defined as the maximum reaction temperature reached after recalescence).

1.3 Metallographic analysis

As-quenched samples were sectioned along the central axis, while the fully solidified samples were sectioned radially 9 mm from the bottom of the tapered samples and 20 mm from the base of the cylindrical samples. All metallographic samples were made following the standard metallographic preparation technique. To reveal the eutectic microstructure detail, all samples were etched for 20 s in a solution of 10 g of sodium hydroxide and 10 g of potassium ferricyanide in 100 mL of water (modified Murakami’s reagent) at room temperature. Micrographs were taken using an optical microscope (OLYMPUS, BX-60M). For statistical quantification of eutectic cells/grains, a total of fifteen micrographs were taken randomly from each sample at various locations. Due to the irregular morphology of eutectic grains, equivalent circular diameter (Eq. 1) was employed in this work to quantify the eutectic grain size.

\[
D = 2 \cdot \sqrt{A} \tag{1}
\]

Where, \( D \) is the equivalent circular diameter and \( A \) is the area of each eutectic grain.

2 Results

2.1 Characteristic temperatures of Al-13.0%Si alloys during solidification

Figure 2 shows the cooling curves of the unmodified and Sr (0.041%)-modified alloys. It can be seen clearly that an obvious recalescence is present in both samples; and that the addition of Sr results in a considerable drop of eutectic arrest. These observations are consistent with results reported previously.[13-15] Changes of the characteristic temperatures (\( T_N, T_M \) and \( T_G \)) with Sr content in the alloys are shown in Fig. 3. All of the characteristic temperatures are continuously decreased with increasing Sr content. \( T_N \) decreased from 575.0 °C for the unmodified alloy to 567.7 °C for the Sr (0.064 %) modified alloy, which indicates that the nucleation of eutectic requires greater undercooling in the modified alloy than in the unmodified alloy. McDonald et al. [9] and Wang et al. [2] reported similar findings. \( T_M \), representing the temperature when large numbers of nucleating events occur, decreases from 572.9 °C for the unmodified alloy to 565.6 °C for the Sr (0.064%) modified alloy. Meanwhile, the eutectic undercooling \( \Delta T_E \) (\( = T_E - T_G \)), where \( T_E \) is the equilibrium temperature of eutectic reaction, usually 577 °C) increases remarkably from –1.1 °C to 8.6 °C.
Fig. 2: Cooling curves of the unmodified (a) and the Sr (0.041%) modified (b) Al-13.0%Si alloys (the dotted lines denoting the derivatives of the cooling curves).

Fig. 3: Effect of Sr content on the characteristic temperatures of Al-13.0%Si alloys during solidification.

2.2 As-quenched macro/micro structures

Figure 4 shows the macrostructures of the as-quenched samples cast in a tapered stainless steel cup mold. The dark gray color in the macrostructure represents as-quenched liquid and the light gray color is the solidified solid. Samples shown in Figs. 4(b)–(f) were quenched when the eutectic solidification was approximately 40% completed. In contrast to the Sr-modified alloy, it is hard to differentiate the liquid region from the solid in the macrostructure of the unmodified alloy (Fig. 4b). To further understand eutectic solidification in the unmodified alloy, another sample was quenched immediately after the melt temperature reached the temperature plateau. It is seen from the macrostructure (Fig. 4a) that nucleation of eutectic did occur in a relatively large-scale area near the mold wall, but not throughout the whole section. This indicates that the nucleation of the unmodified alloy is limited by the thermal undercooling of the melt. For the unmodified alloy, a certain degree of undercooling is required for nucleation \( \Delta T_n = 2.0 \) °C, \( \Delta T_n \) the nucleation undercooling is defined as the difference between \( T_E \) and \( T_N \), which is consistent with the thermal analytical data (Fig. 3). However, this finding is in opposition

Fig. 4: Macrographs of samples with 0 %Sr (a) and (b), 0.015 %Sr (c), 0.030 %Sr (d), 0.041 %Sr (e), and 0.064 % Sr (f) in the Al-13% Si alloys, cast in a stainless steel cup. Sample shown in (a) was quenched immediately after the melt temperature reaches the temperature plateau and samples shown in (b)-(f) were quenched when the eutectic reaction time was approximately 40% completed.
to that reported by McDonald et al. \[9\], where nucleation was found to be very prolific after \(\sim 50\) \% completion of eutectic reaction in a commercial Al-10\%Si unmodified alloy.

Sr has a significant impact on eutectic solidification in Al-Si alloys. In the Sr-modified alloys, the eutectic phases nucleate either at the mold wall or in liquid in the vicinity of the mold wall, and grow toward the mold center with a definite and approximately planar liquid-solid interface. Increasing the Sr content appears to increase the fraction of solid for a given period of solidification time, as shown in Figs. 4(c)-(f). This is attributed to the increased interface undercooling. It can also be seen from Fig. 4 that eutectic grains continuously nucleate in front of the liquid-solid interface during solidification, and that Sr tends to reduce eutectic grain sizes, although a few eutectic grains are also favored. Figure 5 illustrates typical microstructures of regions near the liquid-solid interface at the bottom of the as-quenched modified samples. It is seen that the coupled-growth front of the eutectic material is almost isothermally planar. The formation of both unequiaxed and equiaxed eutectic grains in the high Sr-containing alloy further indicates continuous nucleation of eutectic material in the modified alloy.

![Micrographs showing eutectic grain structures near the liquid-solid interface at the bottom of the as-quenched samples with 0.015 % Sr (a), 0.030 % Sr (b), 0.040 % Sr (c) and 0.065 % Sr content (d) in Al-13% Si alloys, cast in a stainless steel cup](image)

Fig. 5: Micrographs showing eutectic grain structures near the liquid-solid interface at the bottom of the as-quenched samples with 0.015 % Sr (a), 0.030 % Sr (b), 0.040 % Sr (c) and 0.065 % Sr content (d) in Al-13% Si alloys, cast in a stainless steel cup

### 2.3 Eutectic grain size of Al-13.0%Si alloys

It is generally accepted that the growth of the eutectic aluminum phase is coupled with the eutectic Si phase in Al-Si system to form eutectic grains. In the unmodified alloys, the liquid-solid interface of eutectic growth is non-isothermal and eutectic Si flakes protrude into the liquid ahead of the eutectic Al phase \[16,17\]. The interlacement of eutectic Si flakes at the final stage of solidification makes it difficult to observe the eutectic grain boundaries. Hence, no observation of eutectic grain boundaries has been reported in the literature for the unmodified Al-Si alloys. In the Na- or Sr-modified alloys, however, silicon is no longer the leading phase during eutectic growth and the coupled-growth front of eutectic material is almost isothermally planar. In this case, trace elements and impurities accumulate in the final solidification region delineating the boundaries of eutectic cells after being etched for 20 seconds in the modified Murakami’s reagent.

The micrographs in Fig. 6 show the influence of the Sr content and the cooling rate during solidification on morphology and size of eutectic grains in Al-13.0wt%Si alloys. Quantitative relationships between eutectic grain size and Sr content and cooling rate are plotted in Fig. 7. It is seen that increasing the Sr content and the cooling rate significantly reduces the eutectic grain sizes. In the case of a slow cooling rate (2 K/s), increasing the Sr content from 0.015 % to 0.064 % decreases the eutectic grain size by more than 20 % (from 476 \(\mu\)m to 367 \(\mu\)m). This is different from the results reported by McDonald et al. \[9\].

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Fig. 6: Micrographs showing the influence of Sr content and cooling rate on morphology and size of eutectic grains in Al-13.0wt% Si alloys (a) & (b) cast in a tapered cup mold with a cooling rate of about 2 K/s, (c) & (d) cast in a cylindrical mold with a cooling rate of about 10 K/s. (a) and (c) containing 0.030 %Sr, (b) and (d) containing 0.064 %Sr.

Fig. 7: Eutectic grain size as a function of Sr content and cooling rate in Al-13.0%Si alloy.

For a given Sr content, the cooling rate also plays an important role in refining eutectic grains. In the alloy containing 0.030 % Sr, the average eutectic grain size of the rapidly solidified microstructure (10 K/s) is only about half that of the microstructure solidified slowly (2 K/s).

3 Discussions

It is well known that Al-Si binary eutectic material is a typical faceted/non-faceted structure and that the non-metallic silicon phase (faceted phase) is the leading one during the coupled-growth of the two phases. However, it has not yet been well established which phase nucleates first. Therefore, the factors determining nucleation and growth of the two eutectic phases would dominate the refinement of eutectic grains. Based on classical solidification theory, the grain size depends on both the number of potentially efficient nuclei in the melt and the nucleation rate. A high density of efficient nuclei favors finer grain structure. The nucleation rate has a close relationship with the actual undercooling ahead of the solid/liquid interface. A larger undercooling results in a higher solidification rate, and thus a larger number of nuclei form in a unit volume of the melt.

In the unmodified alloy, aluminium phosphide (AIP), present naturally in aluminum ingots, has been considered as an efficient site for nucleation of the eutectic silicon phase. Under this circumstance, the nucleation of the eutectic phase only requires about 2 °C of $\Delta T_N$. Therefore, in the unmodified alloy the nucleation events are limited by the thermal undercooling of the melt and this favors nucleation in a relatively large-scale area near the mold wall, but not throughout the whole section of the sample. Increasing Sr content results in a drop of eutectic arrest and hence an increase in $\Delta T_N$. As shown in Fig. 3, $T_N$, $T_M$, and $T_G$ decrease with the addition of Sr in the Al-13.0%Si alloy. It is generally accepted that the decreased $T_N$ is attributed to the potential nucleation sites (AIP) poisoned by Sr. However, the decreased $T_N$ also suggests that
the required nucleation undercooling is increased. This implies that some nucleation sites, which can operate at a relatively high temperature in the unmodified alloy, are suppressed by Sr. This also means that the addition of Sr makes the nucleation of the eutectic phase more difficult at high temperature. As a result, the melt has to be undercooled to a lower temperature. The nucleation of eutectic material in the Sr-modified alloys to a great extent originates either at the mold wall or in the liquid in the vicinity of the mold wall. The decrease in $T_a$ indicates the actual undercooling of the melt is increased when a great number of nucleation events occur. In this case, the driving force for the nucleation of the eutectic phase increases with Sr content in the alloys. In addition, other potential nucleation sites are also activated although they cannot operate at a high temperature. A strong driving force and frequent operations of other activated nucleation sites lead to an increase in the nucleation rate of the eutectic phase. It makes it possible for nucleation events of eutectic material to continuously operate in the liquid in front of the liquid-solid interface during solidification. Addition of Sr does not reduce the number of eutectic nuclei. In contrast, it favors the nucleation event of eutectic material. As a result, the eutectic grain size decreases with adding Sr content in the alloys.

The influence of the cooling rate on eutectic refinement is also attributed to the change of actual undercooling of the melt. When liquid melt is solidified at a high cooling rate, the actual undercooling of the melt is large and thus the nucleation rate of eutectic material is increased.

4 Conclusions

The characteristic temperatures ($T_N$, $T_a$ and $T_d$) of Al-13%Si alloy during solidification are continuously decreased with increasing Sr content. Quantification of the eutectic grain size in the near-eutectic Al-Si alloys solidified at different cooling rates indicates that the addition of Sr effectively refines the eutectic grains. The cooling rate during solidification also plays a very important role in eutectic refinement. A higher cooling rate yielded finer eutectic grains.

Actual undercooling of the melt for eutectic nucleation is increased with Sr addition. The increased driving force for eutectic nucleation and possible operations of other activated nucleation sites, due to greater undercooling, lead to an increase in the eutectic nucleation rate and make it possible for nucleation events of eutectic material to continuously operate ahead of the liquid-solid interface during solidification. The eutectic grain structure is consequently refined with Sr addition. Similarly, a higher cooling rate caused larger actual undercooling of the melt, which results in a higher eutectic nucleation rate and finer eutectic grains.

References


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