Heterogeneous nucleation of entrained eutectic Si in high purity melt spun Al-Si alloys investigated by entrained droplet technique and DSC

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Abstract. Entrained droplet technique and DSC analyses were employed to investigate the influence of trace elements of Sr, Eu and P on the heterogeneous nucleation of entrained eutectic Si in high purity melt spun Al-5wt.% Si alloys. Sr and Eu addition was found to exert negative effects on the nucleation process, while an increased undercooling was observed. This can be attributed to the formation of phosphide compounds having a lower free energy and hence may preferentially form compared to AlP. Only a trace P addition was found to have a profound effect on the nucleation process. The nucleation kinetics is discussed on the basis of the classical nucleation theory and the free growth model, respectively. The estimated AlP patch size was found to be sufficient for the free growth of Si to occur within the droplets, which strongly indicates that the nucleation of Si on an AlP patch or AlP particle is a limiting step for free growth. The maximum nucleation site density within one droplet is directly related to the size distribution of AlP particles or AlP patches for Si nucleation, but is independent of the cooling rates. Although the nucleation conditions were optimized in entrained droplet experiments, the observed mechanisms are also valid at moderate cooling conditions, such as in shape casting.

1. Introduction
Al-Si based alloys are important casting alloys that constitute ~ 90% of all shape castings [1]. Modification of eutectic Si is of great necessity to improve the mechanical properties [2]. Nevertheless, the modification mechanism, with respect to nucleation and growth of eutectic Si, is still a matter of debate. Generally, not only higher nucleation undercoolings are observed but also growth temperatures are significantly decreased as measured by thermal analysis, suggesting that nucleation is depressed and subsequent growth is also hindered [3].

With respect to the growth, well-accepted twin plane re-entrant edge (TPRE), poisoning of the TPRE [4] or impurity induced twinning (IIT) mechanisms [3] have been reported to be valid under certain conditions. Therefore, the growth of eutectic Si is not a focus of our present investigation. Instead, the main focus is on the nucleation of eutectic Si.
With respect to nucleation, a much more detailed research is required to elucidate the nucleation kinetics of eutectic Si. It is well-known that nucleation is notoriously difficult to be investigated in conventional solidification conditions because of the following facts: (i) the inherent presence of impurities, (ii) the very short nucleation time, and (iii) the very small scale of size. Despite these difficulties, heterogeneous nucleation has been investigated by the novel entrained droplet technique [5], which was first suggested by Wang and Smith [6] to study heterogeneous nucleation. The potential of this technique was recognized and developed further by Cantor and co-workers [5, 7, 8, 9] who employed rapid solidification to produce micrometer to nanometer size droplets, thereby improving the reproducibility of nucleation undercooling by up to 0.2 °C. Ho and Cantor [5] studied high purity Al-Si alloys containing traces of P using the entrained droplet technique and found that just 0.25-2 ppm P is sufficient to form AlP, which could act as a nucleation site for eutectic Si verifying the results by Crosley and Mondolfo [10] and Flood and Hunt [11].

In this paper, the entrained droplet technique and DSC analyses were employed to investigate the influence of trace elements of Sr, Na, Eu and P on the nucleation of entrained eutectic Si in high purity melt spun Al-5wt.% Si based alloys. The nucleation kinetics are discussed on the basis of the classical nucleation theory [12] and the free growth model [13, 14], respectively.

2. Experimental methods

Al-5 Si alloys (wt. %, used through the paper, in case not specified otherwise) with controlled additions of Sr, Eu and P were manufactured. The experimental details about sample preparation and composition measurement and DSC measurement can be found in [15-17].

The DSC results were reproducible within 0.2 °C for several subsequent runs on one sample. In order to elucidate the nucleation kinetics of entrained eutectic Si, a series of DSC experiments with different cooling rates were performed for different Al-5Si based alloys (high purity (5N Al and 5N Si) and medium purity (5N Al and 4N Si)).

3. Results

Figure 1a shows the DSC thermogram of high purity Al-5Si alloy without any addition (Sr, Eu) but with a low concentration of 0.4 ppm P only (5N Al + 5N Si), resulting from the intrinsic remaining P content of the high purity Al (5N). The first sharp exotherm A (grain boundary eutectic peak) occurred with an onset temperature of 575.5 °C, which is 1.5 °C less than the equilibrium eutectic solidification temperature, whilst the small exotherm B (entrained droplet peak) occurred with an onset temperature of 544.5 °C. Undercooling is defined here as the difference between the onset temperatures of the grain boundary eutectic peak and the entrained droplet peak. The undercooling (ΔT) was measured to be ~31.0 °C (for 5N Al + 5N Si) and ~20.5 °C (for 5N Al + 4N Si), respectively. The undercooling decreases significantly from 31.0 °C to 20.5 °C when a lower grade Si (4N) is used, which has been associated by Ho and Cantor [5] and Li and Schumacher [15] as an effect of P contamination of the Si used. During reheating four times in DSC, exotherm B becomes less significant, as shown in figure 2, indicating that no significant P is available for the nucleation of eutectic Si after reheating.

Figure 1b shows the DSC solidification exotherms of high purity Al-5Si alloy with 3 ppm P addition. With the presence of 3 ppm P, the formation of a shoulder in the eutectic droplet peak (exotherm B) was observed to be just after the solidification of the grain boundary eutectic exotherm A. Deconvolution of the peak gives a rough estimated onset temperature of the entrained droplet peak of ~357 °C [15], which is approximately identical to the grain boundary eutectic onset temperature, strongly indicating that the presence of P, even with a trace level, can significantly enhance the nucleation of eutectic Si and thereby reduce the undercooling of eutectic Si.

Figure 1c shows the DSC solidification exotherms of high purity Al-5Si alloy with 100 ppm Sr addition. Exotherm B occurred with an onset temperature of 526 °C with a measured undercooling of about 49.5 °C, indicating that the nucleation of the entrained droplets started at a very high undercooling. Furthermore, a new peak emerged on the DSC trace with the onset temperature of 566.5 °C, which may represent the precipitation of the highly undercooled Al2Si2Sr phase. It should be
noted here that the presence of Al$_2$Si$_2$Sr phase is expected above the eutectic reaction in equilibrium conditions. However, because of the high purity elements used here, no significant nucleation sites for the Al$_2$Si$_2$Sr phase appear to be present and thereby delay the formation of Al$_2$Si$_2$Sr phase.

Figure 1d shows the DSC solidification exotherms of high purity Al-5Si alloy with 50 ppm Sr and 1 ppm P addition. A decreased undercooling of 38 °C was observed, which can be attributed to the presence of 1 ppm P, again indicating that P concentrations and thereby AlP nucleation site are extremely vital to the nucleation of eutectic Si.

**Figure 1.** DSC solidification exotherms of Al-5Si alloys without (a) and with 3 ppm P (b), 100 ppm Sr (c), 50 ppm Sr and 1 ppm P (d), at a cooling rate of 10 °C / min.

**Figure 2.** DSC solidification exotherms of Al-5Si alloys at a cooling rate of 10 °C / min. During reheating four times in DSC, exotherm B becomes less significant; indicating that less P is available for the nucleation of eutectic Si.
Figure 3. DSC solidification exotherms of Al-5Si alloys without (a) and with 50 ppm Eu and 0.5 ppm P (b), 100 ppm Eu and 0.5 ppm P (c), 200 ppm Eu and 0.5 ppm P (d), at a cooling rate of 10 °C / min.

Similar to the Sr addition (figure 1c), an increased undercooling was also observed in the case of Eu addition, which can be related to modification caused by Eu [19]. Figure 3 shows the DSC solidification exotherms of high purity Al-5Si alloys with 50 ppm, 100 ppm, 200 ppm Eu addition together with 0.5 ppm P. With increasing Eu contents from 50 ppm, 100 ppm to 200 ppm, the onset temperature of exotherm B decreases from 544 °C, 532 °C to 517 °C, respectively. The measured undercooling of entrained eutectic droplet is about 31.5 °C, 43.5 °C, and 58.5 °C. Indeed, an increased undercooling, even compared with 100 ppm Sr, was observed. However, the presence of 3 ppm P, even with 200 ppm Eu addition, results in an absence of exotherm B, as shown in figure 4b, highlighting the importance of AlP for the nucleation of eutectic Si.

Figure 4. DSC solidification exotherms of Al-5Si alloys with 200 ppm Eu and 0.5 ppm P (a), 200 ppm Eu and 3 ppm P (b) at a cooling rate of 10 °C / min. The presence of 3 ppm P results into an absence of exotherm B.

Only a trace P addition (i.e. 3 ppm) has a profound effect on the nucleation of entrained eutectic droplets (figure 1d, figure 4). Either/or a decreased undercooling was observed with the presence of P. However, Sr and Eu addition depletes or consumes the available AlP nucleation site. An increased undercooling was observed, which can be attributed to the formation of phosphide compounds having a lower free energy and hence form preferentially compared to AlP [15].

In order to understand the observed undercooling of Al-Si entrained droplets and thereby the nucleation kinetics, classic nucleation theory [20], as described by Kim et al [21], was firstly used. As reported in our previous research [15], a wetting angle of about 16° for the nucleation of Si was
evaluated for high purity Al-5Si alloy, indicating that the acting substrate for Si is still highly effective. However, the resulting number of nucleation sites (-12.44 for high purity Al-5Si alloy) is far smaller than 1 nucleation site [15], indicating that the physical description of the classical nucleation theory based on a continuum approach does not hold for a small contact angle below 30°. Clearly, a better model is required to elucidate the nucleation kinetic of Si.

Free growth model is subsequently used to describe the nucleation kinetics of entrained eutectic Si in Al-Si based alloys. Similar to the nucleation and free growth of Al on active TiB₂ particles, the size of AlP patches or AlP particles and their size distribution is proposed to become a rate limiting step [22, 23]. Free growth away from the AlP patches or AlP particles occurs when the critical size of Si nucleation sites is identical to the equivalent size of the AlP patches or AlP particles [15]. Furthermore, the free growth model does not imply a constant nucleation rate. At a given temperature interval, a number of AlP patches or AlP particles will fulfil the free growth criterion from which free growth of Si can occur. Applying the approach by Kim et al [21] for droplet nucleation kinetics and using the free growth criterion, yields

\[ \ln\left(\frac{\Delta T - \Delta T_0}{\Delta T_g}\right) + \frac{1}{2} \left(\frac{\Delta T - \Delta T_0}{\Delta T_g}\right)^2 = \ln\left(\frac{n_{\text{max}}}{\sqrt{2\pi}}\right) \]  

From equation (1), it is clear that the maximum number density of nucleation sites \( n_{\text{max}} \) within one droplet is directly related to the size distribution of AlP particles or AIP patches for Si nucleation, but it is independently of the cooling rates. On the other hand, the size distribution of AIP particles or AIP patches depends on the available P content in a given droplet. Thus, the limiting step for the growth of Si on AIP patches can be regarded as the free growth criterion. The maximum number density of nucleation sites \( n_{\text{max}} \) is dependent on the size distribution of droplets and P content. In the case of high purity Al-5Si alloy, the calculated maximum nucleation site value \( n_{\text{max}} \) is about \( 6.77 \times 10^2 \).

4. Conclusions

Entrained droplet technique and DSC analyses were employed to investigate the heterogeneous nucleation of entrained eutectic Si in high purity melt spun Al-5wt.% Si alloys. Sr and Eu addition exerts negative effects on the nucleation process, while an increased undercooling was observed. This can be attributed to the formation of phosphide compounds having a lower free energy, which preferentially formed compared to AIP. Only a trace P addition has a profound effect on the Si nucleation.

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