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Modification and grain refinement of eutectics to improve performance of Al-Si castings

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Abstract

The formulation of alloy compositions for aluminium castings has not changed significantly for decades. Strontium (Sr) modification is commonly used to obtain a refined fibrous morphology of eutectic in Al-Si foundry alloys, and grain refinement can be used to refine the primary Al dendrites. Compared to the coarse plate-like unmodified silicon morphology, the refined fibrous eutectic structure can substantively improve the mechanical properties particularly ductility and fatigue. However, a problem often associated with Sr modification is a change in porosity - distribution and amount. A new alloy technology has been developed to produce castings combining a well-modified eutectic with reduced porosity. This can be achieved by providing effective substrates for the nucleation and growth of eutectic cells. This paper presents the current status in the development and commercialisation of the new eutectic grain refiner and modifier.

Introduction

Strontium is commonly used to refine the eutectic structure of Al-Si alloys. From a coarse plate-like structure in unmodified alloys, a fine fibrous morphology is obtained by only trace additions of Sr. Such a fine structure can potentially increase the ductility and fatigue life of cast specimens [1]. However modified alloys are observed to contain more porosity than unmodified ones, reason why many industrial companies choose not to use modifiers. Several reasons have been raised to explain this increased porosity due to Sr addition, among others: decreased solid-liquid interfacial energy and increased volumetric shrinkage [2], increased susceptibility of the melt to absorb hydrogen [3], influence on oxide bifilms formation [4], and inhibition of interdendritic liquid due to the equiaxed growth of large eutectic grains [5, 6].

This paper reports a new technique to produce castings having (i) a well-modified eutectic and (ii) a reduced porosity. It is based on the key concept of eutectic grain refinement, which is thought to be essential to improve interdendritic feeding, reduce porosity, and enhance mechanical properties in Al-Si alloys.

Background

During the solidification of the Al+Si eutectic, Si is believed to be the leading phase and needs to be nucleated before eutectic growth can occur [7]. Therefore Si nucleation is a key factor for eutectic solidification. The nucleation frequency and spatial distribution of eutectic cells depend on the available nuclants present in the remaining liquid when eutectic temperature is reached. Depending on the alloy composition and solidification conditions, three main eutectic nucleation modes have been distinguished in hypoeutectic Al-Si foundry alloys [5] (see Fig. 1). Figure 1a illustrates the nucleation of the Al+Si eutectic (black on the figure) on primary aluminium dendrites (shown in white here). Figure 1b illustrates the case where nucleation takes place at or adjacent to the wall and the growth is opposite to the thermal gradient (typical of Na modified Al-Si alloys [7]). Figure 1c schematizes heterogeneous nucleation of eutectic on nucleant particles present in

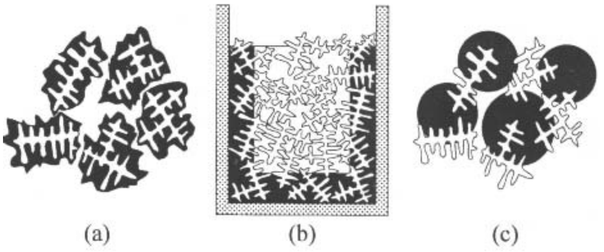


Figure 1: Possible eutectic nucleation modes in the Al-Si system [5]: (a) nucleation on primary aluminium dendrites, (b) front growth opposite to the thermal gradient, and (c) heterogeneous nucleation in interdendritic liquid. The coupled Al+Si eutectic growing side-by-side is illustrated in black, while the dendrites are shown in white.

the interdendritic liquid (typical of Sr modified Al-Si alloys [7]). It is generally believed that Sr additions deactivate AlP particles that can act as nucleants for eutectic Si [8]. Accordingly, Sr containing Al-Si alloys exhibit a larger eutectic undercooling compared to unmodified alloys, resulting in the nucleation and growth of a few but large eutectic grains [5].

Experimental method

Based on our knowledge of known nucleants and lattice parameters, a number of potential nucleating particles for eutectic Si have been suggested [9]. In this study, CrB particles have been chosen and a CrB-bearing master alloy has been manufactured by LSM. The particles contained in this master alloy are thought to promote eutectic Si nucleation.

To verify this assumption, thermal analysis combined with quenched experiments, as well as porosity and tensile test experiments have been performed on three different alloys: (i) a base alloy consisting of commercial Al-10wt%Si, (ii) the base alloy modified with 300 ppm Sr (called Sr modified) and (iii) the base alloy modified with 300 ppm Sr and CrB particles (called Sr + CrB modified alloy). The base alloy was melted in a resistance furnace held at 640 °C. After skimming, 300 ppm of Sr using Al-10wt%Sr master alloy was added to the melt together with the CrB-bearing master alloy in the case of the Sr + CrB modified alloy. After 10 min, the melt was stirred manually and after further 10 min waiting, the following experiments were performed. It must be noted that degassing of the melt was never performed in this study.

For thermal analysis and quenched experiments, the identical experimental set-up as developed by [6] was used in this study (see Fig. 2a). To sum up, a 640 °C preheated stainless steel cup coated with BN was plunged into the melt of desired composition and then put between two insulating boards. A type N thermocouple connected to an acquisition software recorded the cooling curve of the solidifying sample. A typical cooling rate of 1.5 K/s was achieved just prior to nucleation of the first solid (see Fig. 2b) and the sample was quenched in water at typically halfway through the eutectic arrest (note that the base alloy was not quenched in order to know the extent of the eutectic arrest). The quenched samples were sectioned vertically along the thermocouple line, and after conventional grinding and polishing up to 0.4 micron, they were observed by optical and electron microscopy.

To test the ability of the master alloy to ease interdendritic feeding during eutectic solidification and thus reduce porosity, the previously described alloys were cast in a steel permanent mold that had originally been developed to reproduce the thermal conditions at a spoke-wheel junction of a commercial automotive wheel [10]. The die consisted of three parts, which generated a cast shape with an undifferentiated down sprue and runner feeding perpendicularly into the face of a vertical plate. The junction between the runner and the plate was designed to produce a thermal hot spot as shown in Fig. 3. Large amount of porosity is expected in the plate if interdendritic feeding through the junction is poor and *vice versa.* The mold was coated with BN and preheated at 400 °C and after casting, each sample was photographed to document its external appearance, with particular focus on the surface of the plate.

Finally, in order to investigate the ability of the master alloy to enhance the mechanical properties of cast specimens, ductility in particular, the three considered alloys were cast in a 300 °C preheated stainless steel mold covered with BN. The resulting casting rods (20 mm diameter, 200 mm long) where machined to produce ASTM-E8M standard tensile test specimens. The tensile tests were performed using an Instron 4505 tensile testing machine at a strain rate of 10^{-3}. No thermal treatment was performed and the samples were tested as cast.

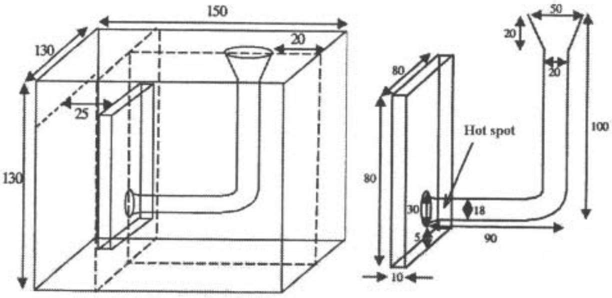
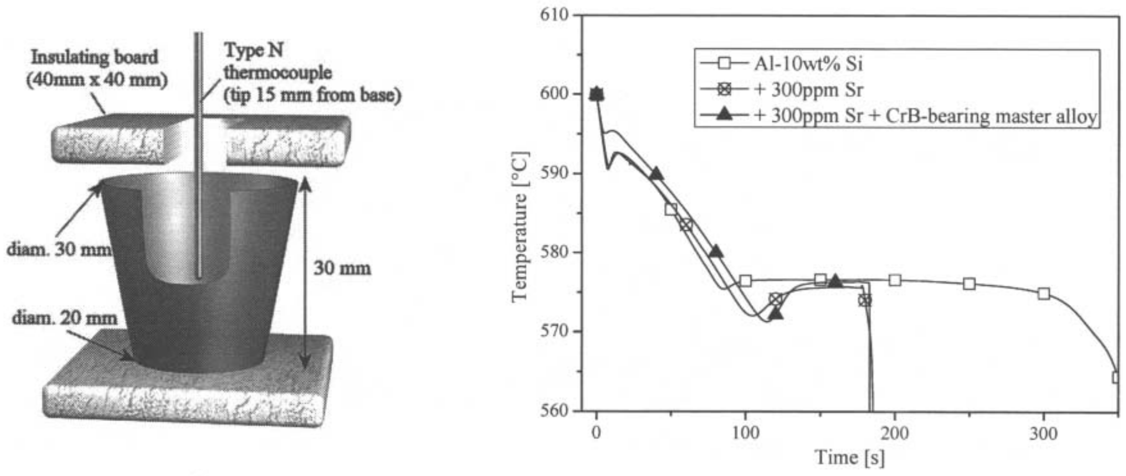


Figure 3: Key dimensions of the assembled "elbow shape" mold in mm, and dimensions of the experimental castings [10].

Results and discussion

It has often been reported that Sr modification is accompanied by a reduced eutectic growth temperature [7]. In this study, the eutectic growth temperature for the base alloy, Sr modified, and Sr + CrB modi-



(a) (b)

Figure 2: (a) A schematic (cut-away and exploded for clarity) of the experimental set-up for thermal analysis and (b) cooling curves of the three considered alloys.

fied alloys was observed to be at 576.6 °C, 575.7 °C, and 576.3 °C, respectively. These small temperature differences (about 1 °C) are within the typical measurement errors and a eutectic growth temperature of 576 ± 1 °C can be considered in each case. However, whereas the base alloy was obviously unmodified, the two other ones were fully modified (see Figs. 4c and d). This shows that a fully modified eutectic structure is not obligatory accompanied with a reduced eutectic growth temperature. Figures 4a and b show the macrographs of the Sr modified and Sr + CrB modified alloys. Whereas the quench was performed approximately at the same time (see Fig. 2b), the alloy containing the CrB-bearing master alloy contains more and smaller eutectic grains, which shows the ability of the CrB-bearing master alloy to promote eutectic Si nucleation.

It has also been often reported that Sr modified alloys exhibit a larger recalescence prior to eutectic growth compared to unmodified alloys. Poisoning of AlP particles by Sr is one of the suggested reasons to explained this increased recalescence. Since the AlP particles are deactivated, a larger undercooling is required so that other particles/nucleants become active. In this study, both Sr and Sr + CrB modified alloys exhibit a much larger recalescence prior to eutectic growth (approximately 4 °C and 5 °C, respectively) than the unmodified one (about 1 °C). This shows that the particles contained in the CrB-bearing master alloys are not as effective for eutectic Si nucleation in Sr modified alloys as AlP particles are in unmodified alloys, even if the number of eutectic grains is larger in the Sr + CrB modified alloy compared to the Sr modified one.

However, the increased number of eutectic grains in the Sr + CrB modified alloy compared to the Sr modified alloy seems to have a significant influence on interdendritic feeding. Figure 5 shows the surface of the castings performed using the "elbow shape" mold described in Fig. 3. The amount of surface porosity of the Sr modified alloy (Fig. 5a) is clearly much larger than that of the Sr + CrB modified alloy (Fig. 5b). Such a large porosity difference is very unlikely due to (i) a difference in solid-liquid interfacial energy or (ii) an increased susceptibility of the melt to absorb hydrogen due to Sr modification, since both alloys have the same Sr content. Also, since both samples were cast following the same procedure (and quite roughly moreover), it is believed that the amount of entrapped oxide bifilms is more or less similar in both samples. However, it must be noted that the CrB-bearing master alloy acts as inoculant for primary Al as well (TiB_2 particles are likely to be formed, since both Ti and B are present in the master alloy). This can also be seen on the cooling curves (see Fig. 2b), where nucleation of primary Al happens at a lower undercooling for the Sr + CrB modified alloy compared to the other alloys. However even if it is well known that primary Al grain refinement is standard practice to get (among others) uniformly distributed microporosity in castings [11], it cannot explain such a large difference in the amount

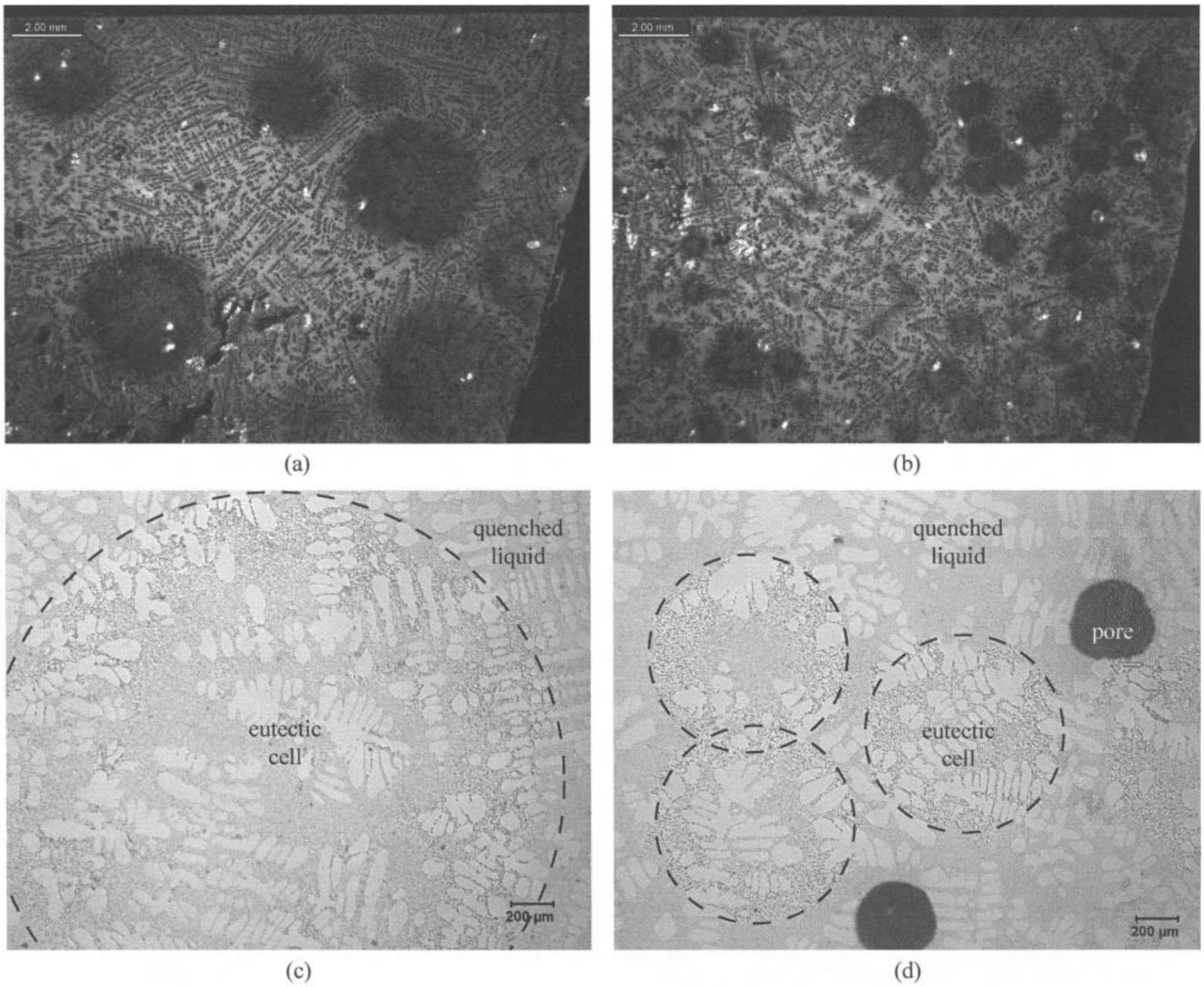
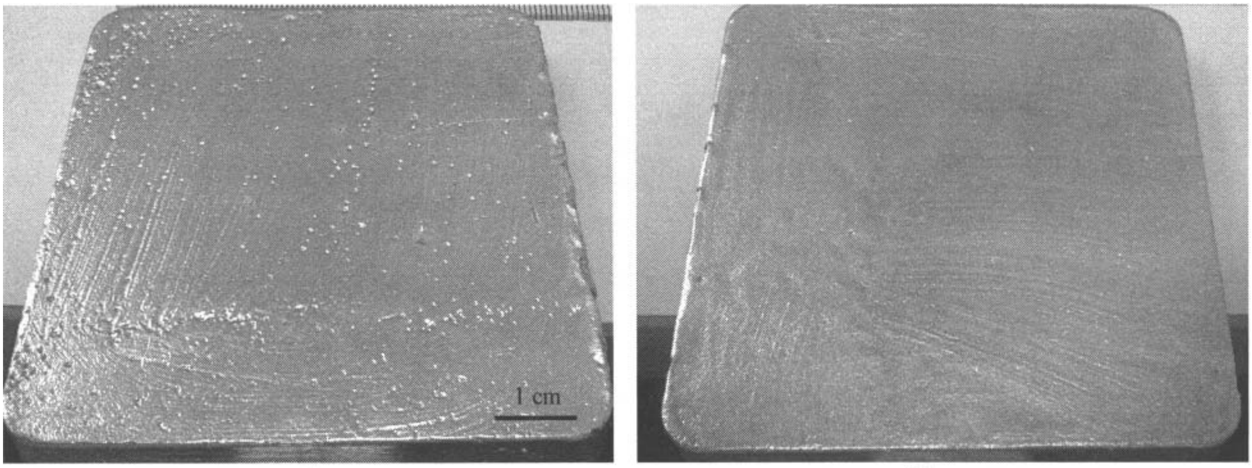

(a) (b) (c) (d)

Figure 4: Optical macrograph of a quenched (a) Sr modified and (b) Sr + CrB modified Al-10wt%Si alloy. The quenched liquid is in light grey, whereas the dark grey circles represent the solidified eutectic cells. The bottom pictures show a magnified view of (c) the Sr modified and (d) the Sr + CrB modified alloys. Adding the CrB-bearing master alloy clearly increases the number of eutectic cells and reduces their size.

of porosity, since the eutectic fraction in these alloys can reach 55% (using a Scheil approximation). Hence, since only the amount of eutectic grains is significantly changed between both experiments, these results show that the influence of a eutectic grain refiner is critical for interdendritic feeding, and hence for porosity as well.

A reduced porosity should lead to an increased ductility in a cast specimen. Figure 6 shows the true stress-strain curves of the samples cast using the base alloy (open squares), the Sr modified alloy (crossed-open circles), and the Sr + CrB modified alloy (black triangles). It is clear from these preliminary results that the Sr modified alloy is more ductile than the base alloy, whereas the Sr + CrB modified alloy is even more ductile with a maximum strain of about 3.5% (which is fairly high for an as-cast Al alloy). Each of the stress strain-curve exhibits a round shape, which is characteristic of a composite. This is no surprise since the eutectic fraction in these alloys approaches 55%. It was checked that the secondary dendrite arm spacing, λ_2, was similar between all three alloys ($\lambda_2 \approx 22 \pm 2\,\mu$m). However, the characteristic length of the coarse plate-like eutectic microstructure of the unmodified alloy was at least 3 times larger than the refined fibrous eutectic



(a)

(b)

Figure 5: Photographs of the external planar surface of the castings produced with the "elbow shape" mold (see Fig. 3) using (a) the Sr modified alloy and (b) the Sr + CrB modified alloy. A better surface finish and a reduced porosity is clearly obtained using the latter.

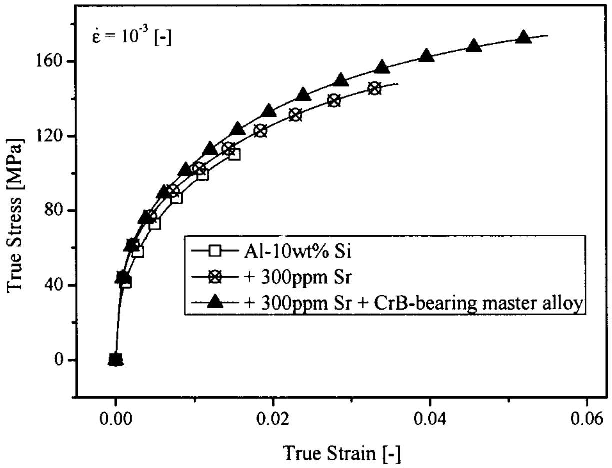


Figure 6: Influence of Sr and CrB-bearing master alloy additions on mechanical properties of Al-10wt%Si alloys.

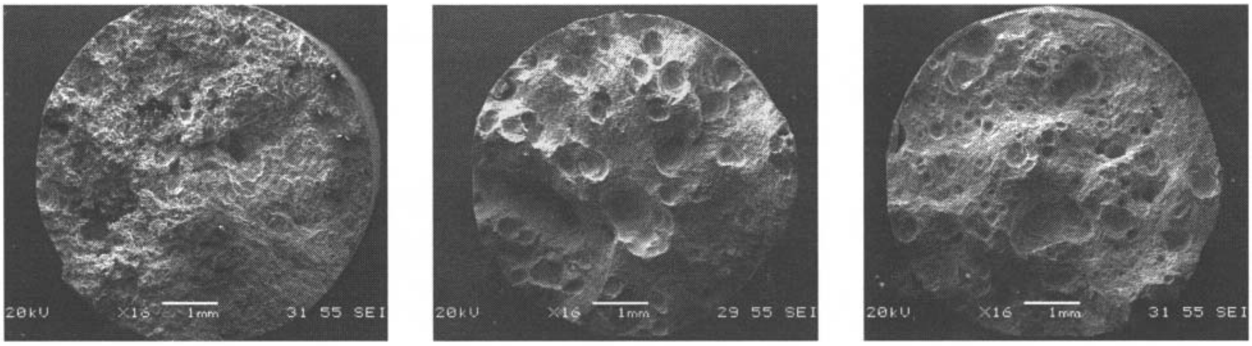
structure of the modified alloys (which had both a eutectic spacing of about 1 μm). Accordingly, the increase in ductility between the base alloy and the Sr modified alloy is most probably due to the refinement of the eutectic structure, despite of the huge porosity increase in the Sr modified alloy (see Figs. 7a and b). On the other hand, the increase in ductility between the Sr modified and Sr + CrB modified alloy is most likely due to the difference in porosity between both alloys (more distributed and finer pores are found in Fig. 7c than in Fig. 7b), and not due to primary Al grain refinement since (i) the eutectic fraction is about 55% and (ii) the load at high strain is supported almost only by the strong percolated Al+Si eutectic.

We have then shown that ductility of Al-Si cast alloys can be improved with small additions of Sr and the help of a eutectic grain refiner. The latter allows a finer and more distributed porosity in Sr modified alloys, because the interdendritic liquid can flow more easily to compensate for solidification shrinkage if the eutectic cells are smaller.

This brings a new aspect for the simulation of porosity formation in aluminium alloys. This is of course beyond the scope of this paper but in addition to the conventional phenomena that need to be modeled (see [12] for the details), our results show that the fluid flow calculations should be coupled with microstructure simulations, since the interdendritic liquid flow depends on the density/type of eutectic cells.

Conclusion

Modification of Al-Si alloys with Sr causes a dramatic reduction of the nucleation frequency compared to unmodified alloys. This, in turn, increases drastically the amount of porosity because of the inhibition of interdendritic liquid due to the equiaxed growth of large eutectic grains, i.e. both feeding and permeability are reduced. In this study, we have shown that by increasing the number of eutectic cells using a eutectic grain refiner, it is possible to reduce poros-



(a) (b) (c)

Figure 7: SEM images showing the fracture surface of (a) the base alloy, (b) the Sr modified alloy, and (c) the Sr + CrB modified alloy.

ity and improve significantly the ductility of Sr modified commercial Al-10wt%Si alloy. Although more experiments and characterisation are needed to verify these promising preliminary results, the key concept of eutectic grain refinement is thought to be a major advance in the development of Al-Si alloys.

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References

[1] Q.G. Wang, "Microstructural Effects on the Tensile and Fracture Behavior of Aluminum Casting Alloys A356/357," *Metallurgical Materials Transactions A*, 34 (2003), 2887–2899.

[2] D. Emadi, J.E. Gruzleski, and J.M. Toguri, "The Effect of Na and Sr Modification on Surface Tension and Volumetric Shrinkage of A356 Alloy and their Influence on Porosity Formation," *Metallurgical Materials Transactions B*, 24 (1993), 1055–1063.

[3] John Campbell, *Castings*, (Oxford, United Kingdom: Elsevier Butterworth-Heinemann, 2003), 17–31.

[4] J. Campbell and M. Tiryakioglu, "Review of Effect of P and Sr on Modification and Porosity Development in Al-Si Alloys," *Materials Science and Technology*, 26 (2010), 262–268.

[5] A.K. Dahle et al., "Eutectic Nucleation and Growth in Hypoeutectic Al-Si Alloys at Different Strontium Levels," *Metallurgical Materials Transactions A*, 32 (2001), 949–960.

[6] S.D. McDonald, K. Nogita, and A.K. Dahle, "Eutectic Nucleation in Al-Si Alloys," *Acta Materialia*, 52 (2004), 4273–4280.

[7] A.K. Dahle et al., "Eutectic Modification and Microstructure Development in Al-Si Alloys," *Materials Science and Engineering A*, 413-414 (2005), 243–248.

[8] Y.H. Cho et al., "Effect of Sr and P on Eutectic Al-Si Nucleation and Formation of β-Al5FeSi in Hypoeutectic Al-Si Foundry Alloys," *Metallurgical Materials Transactions A*, 39A (2008), 2435–2448.

[9] A.K. Dahle et al., US patent 2009/0297394 A1, 2009.

[10] M. Easton, "Grain Refinement Mechanisms in Aluminium and its Alloys and the Effect of Grain Refinement on Castability," (Ph.D. thesis, The University of Queensland, 1999), 174.

[11] L. Lu and A.K. Dahle, "Effects of Combined Additions of Sr and AlTiB grain refiners in Hypoeutectic Al-Si Foundry Alloys," *Materials Science and Engineering A*, 435 (2006), 288–296.

[12] J.A. Dantzig and M. Rappaz, *Solidification* (Lausanne, Switzerland: EPFL Press, 2009), 479–514.