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The influence of ternary Cu additions on the nucleation of eutectic grains in a hypoeutectic Al-10 wt.%Si alloy

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Abstract

The Influence of the ternary alloying element Cu on eutectic nucleation in an Al-10 wt.%Si alloy in unmodified and Sr-modified conditions was studied. Cu additions had a relatively minor effect on the unmodified eutectic nucleation frequency. In Sr-modified Al-Si alloys where the nucleation frequency of the eutectic grains is very low compared to the unmodified alloys, the addition of Cu significantly increased the nucleation frequency. Further increases in the Cu concentration resulted in a continuous increase in the number of eutectic grains and an associated decrease in their size. It is proposed that constitutional supercooling plays an important role in promoting the nucleation of eutectic grains ahead of the solidifying interface especially in the case of Sr-modified Al-Si alloys.

Keywords: Eutectic solidification, Aluminium-Silicon alloys, Ternary alloys, Eutectic grain nucleation

1. Introduction

Aluminium dendrites and Al-Si eutectic phases are the major microstructural features of many commercial Al-Si foundry alloys and control of the microstructure of these phases is an important step in achieving quality castings.

The influence of solute on primary grain formation has been extensively studied [1-8] where it has been shown that the final grain size for a particular alloy depends on the alloy chemistry, nuclei potency and their distribution in the melt [5]. The Interdependency Theory links grain formation and nucleant selection of the primary phase and is helpful for revealing the mechanisms controlling the grain size of a broad range of casting alloys [5].

Despite the evidence that the addition of eutectic modifiers such as Sr, Na and Sb influence the eutectic nucleation frequency, macroscopic evolution and hence casting defect formation [9-14], the influence of common alloying elements such as Cu and Mg on eutectic nucleation and the macroscopic evolution of the eutectic phases in Al-Si alloys is unclear.

When Cu is added to the Al-Si alloy, solute is rejected from both of the eutectic constituents. Due to this solute segregation ahead of the eutectic interface the equilibrium melting point (liquidus temperature) changes locally from a low value at the interface towards the higher liquidus temperature for the alloy. When the actual temperature of the melt is less than the equilibrium liquidus temperature, the melt in this boundary layer is constitutionally supercooled [15]. The growth restriction factor of a solute (Q) is the measure of how fast this constitutionally supercooled zone forms ahead of the solid-liquid interface. In addition to changes in the equilibrium liquidus temperature other changes might be expected. These include variations in the surface tension which can influence the wetting angle between the nuclei present in the boundary layer and the melt, and changes to the chemical driving force for nucleation [16]. As such, significant changes can be expected in the nucleation behaviour of the Al-Si eutectic due to ternary solute segregation.

A deeper understanding of how solute additions influence the nucleation pattern of the Al-Si eutectic would allow for the development of higher quality castings. For example, refinement in the eutectic grain size through promoting nucleation either by adding more potent nuclei or by creating more constitutional supercooling to activate nuclei [17] is a potential means of controlling the porosity size and distribution in Sr-modified Al-Si alloys. Easton et al. [1] proposed that the presence of a constitutionally supercooled zone ahead of the primary phase can promote a wave of nucleation events ahead of the interface. However, the underlying theory has not been applied to eutectic solidification. The present work attempts to understand the influence of the ternary alloying element Cu on Al-Si eutectic nucleation in Al-10 wt.% Si alloy. The use of Cu is convenient from a theoretical perspective and is also of practical significance as it is a common alloying element in many commercial casting alloys.

2. Materials and Methods

The experiments were conducted with an Al-10 wt.% Si commercial purity alloy as the high eutectic volume fraction of this alloy assists metallographic observation of individual eutectic grains. Approximately 1 kg of the base alloy (Al-10Si) along with appropriate amounts of commercial purity Si and the Al-33 wt.% Cu master alloy were weighed and melted in a graphite crucible in an electric resistance furnace at 760°C. For Sr-modified alloys, Sr was added to the melt using an Al-10 wt.% Sr master alloy (in rod form) 20 mins before casting. The Cu contents range from 1 wt.% Cu to 6 wt.% Cu.

Two stainless steel cups, coated with boron nitride were preheated at 760°C. Samples were taken simultaneously by dipping these stainless steel cups into the melt. A type N thermocouple covered with a stainless steel sleeve was lowered into one of the samples to record the temperature. Approximately half way through the eutectic reaction the second sample was quenched by lowering the stainless steel cup into a water bath at room temperature.

For each alloy a cooling curve and a derivative curve were plotted. Reaction temperatures were measured using Tamminen’s method [18]. The samples were sectioned parallel to the vertical axis and polished using standard metallographic techniques.

Samples were then etched in Keller’s reagent (2 ml HF, 3ml HCl, 5ml HNO_3, 190 ml H_2O) for 5 seconds to observe the eutectic Si morphology using an Olympus AX70 optical microscope. The area density of polyhedral silicon particles in selected unmodified samples was measured by taking twenty fields (1400µm x 1075µm) of each sample and manually counting the number of polyhedral silicon particles. In Sr-modified alloys the number of eutectic cells was counted manually from a digital macrograph of the quenched sample.

A chemical analysis sample was produced by pouring each melt into a chill mould. The composition was analysed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Due to the limitation of ICP analysis in analysing Phosphorous (P) in Al, one sample of the Al-Si-Cu unmodified series and one of the Al-Si-Cu-Sr-modified series were analysed using Glow-Discharge Mass Spectroscopy (GDMS). It was found that the P content in these samples varied between 3-6 ppm. As the base alloy (Al-10Si-commercial purity) was used for all the alloys presented in this work, this range of P contents is expected to be representative. Table 1 provides the analysed chemical compositions of the experimental alloys.

The solidification path of the Al-10Si-Cu alloys was obtained from solidification simulations from *Thermo-calc*® software [19] using the assumption of Schiel conditions and the ThermoTech Al-based Alloys Database (TTAL8 Database version 8.1) [20].

3. Results

For each alloy composition cooling curves, several micrographs and macrographs of the quenched samples were analysed to determine the solidification path and the eutectic grain nucleation density of each sample. However, only an example micrograph or macrograph is provided for each sample depending on which method enables more accurate measurement and observation of the eutectic grain nucleation frequency.

Table 2 presents the nucleation temperatures of the primary Al, Al-Si binary eutectic and Al-Si-$CuAl_2$ ternary eutectic obtained from the cooling curve analysis of Al-10Si-XCu unmodified and Sr-modified alloys. In both cases, the primary Al and eutectic nucleation temperatures decreased as the Cu content increased. The ternary eutectic nucleation temperature remained approximately the same.

Unlike the case of primary phase solidification, quantifying the eutectic nucleation frequency is challenging due to the lack of suitable metallographic techniques. Especially in the case of unmodified alloys in which the eutectic nucleation frequency is very high and the eutectic solidifies with a non-faceted interface led by silicon. In this case, differentiating the individual eutectic cells on metallographic sample sections is difficult even in the samples that were quenched during eutectic solidification.

Research suggests that in the case of unmodified alloys most of the eutectic cells originate from a polyhedral silicon particle which itself nucleates on the AlP particles present as an impurity phase in the melt [21, 22]. Hence, in unmodified alloys the number of polyhedral silicon particles per m^2 of the sample cross-section was used to quantify the eutectic nucleation frequency. Example micrographs of the Al-10Si-XCu (X=1, 2, 4 and 6 wt.%) alloys observed in the samples that were quenched during eutectic solidification are presented in Figure 1. In all the alloy microstructures aluminium dendrites (labelled as 1), eutectic silicon (labelled as 2) and quenched liquid (labelled as 3) can be observed. The morphology of eutectic Si for all of the Cu addition levels is flake-like.

In Sr-modified alloys eutectic grains were relatively large in size and easier to identify after interrupting solidification by quenching the sample. Figure 2 presents the macrographs of the Al-10Si-Sr-modified alloy with increasing Cu concentration from 0 to 6 wt.%. In the Al-10Si-350Sr sample with no Cu added (Figure 2(a)) no eutectic grains are observed in the bulk of the sample throughout the sampled cross-section. Most of the nucleation occurred in a layer adjacent to the mould wall. However, the addition of 1 wt.% Cu to Al-10Si-350Sr alloy promoted nucleation in the bulk of the sample and the eutectic nucleation frequency adjacent to the mould wall decreased.

There is a noticeable increase in the eutectic cell nucleation frequency and a concomitant decrease in the eutectic grain size with further increases in Cu content. By observing the derivative of the thermal analysis curves and the quenched microstructures of all the samples, it appears that in unmodified alloys and Sr-modified alloys aluminium dendrites nucleated as the primary phase followed by Al-Si eutectic formation. The Al-Si-$CuAl_2$ ternary eutectic nucleated after the formation of the Al-Si eutectic at all Cu concentrations for the unmodified and Sr-modified alloys.

The Al-Si eutectic nucleation frequency in unmodified and Sr-modified alloys was measured (in unmodified samples, the total number of polyhedral Si/m^2 of the sample was used to determine the nucleation frequency of eutectic while in the Sr-modified alloys, eutectic grains were counted from the macrographs of the quenched samples) and the area density of eutectic grains in all samples is given in Table 3.

4. Discussion

The results clearly show that the addition of Cu to an Al-Si binary alloy significantly changes the eutectic nucleation frequency. The area density of eutectic grains in unmodified and Sr-modified alloy samples are plotted against the Cu content (in wt.%) and presented in Figure 3, in general it can be observed that the eutectic nucleation frequency increased with an increase in the Cu concentration in both unmodified and Sr-modified alloys.

The ternary Cu segregates ahead of the eutectic-liquid interface during Al-Si eutectic solidification as the partition coefficient of Cu in Si is approximately zero (which indicates that most of the Cu gets rejected as the silicon solidifies) and that of Cu in Al is 0.17.

Easton et al. [1] proposed that the presence of a constitutionally supercooled zone ahead of the primary phase can promote a wave of nucleation events ahead of the interface. The growth restriction factor of a solute (Q) determines how effectively a particular solute can create a constitutionally supercooled zone ahead of the solid-liquid interface which is given by the following equation:

$$Q = mC_o\,(k-1) \quad (1)$$

where m is the gradient of the liquidus line, Co is the concentration of the solute and k is the partition coefficient. The Interdependence theory [5] identified that the final grain size of the primary phase is linearly related to the inverse of the growth restriction factor (Q) of the alloy described by the following equation:

$$d_{gs}=\frac{D\Delta T_n}{vQ}+\frac{4.6D}{v}\left(\frac{C_l^*-C_o}{C_l^*\,(1-k)}\right)+x_{sd} \quad (2)$$

where, d_{gs} is the final grain size, D is diffusion coefficient of the solute in liquid, ΔT_n is nucleation undercooling, v is interface velocity, C_l^* is the liquid composition at the interface, C_o is initial solute addition level and k is partition coefficient. The term $\frac{D\Delta T_n}{vQ}$ is the distance that a grain has to grow to generate the minimum consitutional supercooling equal to the nucleation undercooling, ΔT_n, required to trigger nucleation of the next grain. The second term $\frac{4.6D}{v}\left(\frac{C_l^*-C_o}{C_l^*\,(1-k)}\right)$ is the distance between the solid-liquid interface of the previously nucleated grain to the point where the constitutional supercooling generated equals ΔT_n. This term is an indication of the segregation capacity of the solute. The sum of these two terms represents the size of the nucleation-free zone (x_{nfz}) in which nucleation is supressed despite the presence of nuclei. The intercept (x_{sd}) of the grain size versus 1/Q graph is the distance between the end of the nucleation-free zone at x_{nfz} and the location of the most potent nucleant on which the next nucleation event occurs. Assuming the number density of nucleant particles remains constant, x_{sd} (the intercept with the y-axis) will be close to zero in the case of an abundance of potent nuclei such as AlP in the unmodified alloys.

It has been suggested in the literature that the concept of the growth restriction factor can be applied to eutectic growth [11]. This suggestion is reasonable since nucleation of the eutectic occurs independently of the primary Al dendrites. So it is of interest to see in detail if constitutional supercooling play sa role in influencing the nucleation of Al-Si eutectic grains ahead of the eutectic interface.

Traditionally the calculation of a growth restriction factor (Q) is made by considering the behavior of a single solute element with respect to a single primary phase (k and m in Equation 1). In the case of multiple elements segregating with respect to this primary phase, an additive method of calculating Q for primary phase growth can be applied [4]. However, this differs from the case of segregation of a ternary element during solidification of a binary eutectic where each phase will reject the ternary element differently. As a first approximation, the average solid-liquid partition coefficient can be expressed as a weighted arithmetic mean of individual solid-liquid distribution coefficients. In this case we can apply Equation 1 by considering the segregation of Cu during the Al-Si binary eutectic reaction with $k_{Al\text{-}Cu}$ (0.17 [23]) and $k_{Si\text{-}Cu}$ (almost equal to zero) and the volume fractions of the phases V_{Al} (0.87) and V_{Si} (0.13) [24]. This gives a value for the partition coefficient of $k_{(Al,Si)Cu} = 0.148$. The value of m in Equaton 1 is the slope of the binary eutectic valley in the ternary Al-Si-Cu phase diagram, $m_{(Al,Si)Cu} = -1.92$ [11].

To calculate the grain size it is assumed that the eutectic grains are equally distributed in an area of 625 mm^2 of the sample (approximate cross sectional area of the experimental samples), the radius of a eutectic grain at the time of impingement will be $\sqrt{\frac{625*0.52}{n\pi}}$ mm (assuming a simple cubic distribution giving a packing fraction of 0.52 at the time of impingement and n being the number of eutectic grains in the sample cross section). The calculated eutectic grain size in unmodified and Sr-modified Al-10Si-XCu alloys is plotted against 1/Q values for the ternary alloys in Figure 4.

In the case of the unmodified alloy (as observed from Figure 4) the graph shows an approximately straight line with very low intercept (0.28 mm) and gradient (0.44 mm ^{o}C). A low slope of the grain size versus 1/Q implies that the nucleation free zone is small and unmodified eutectic is nucleating from a distribution of very potent nuclei. A low value for the intercept (x_{sd}) indicates that these nuclei exist in relatively large numbers, distributed close to each other. In commercial purity unmodified alloys it is known that there is an abundance of highly potent nuclei which are typically AlP particles, present as an impurity phase [25, 26]. These particles nucleate polyhedral silicon crystals which subsequently grow eutectic grains. Based on the literature and the results of this work there is a relatively high density of AlP particles which have a high nucleant potency. In the presence of these potent nuclei the constitutional supercooling required for nucleation is relatively low, promoting nucleation of the eutectic grains. Thus, nucleation readily occurs ahead of the growing interface of previously nucleated eutectic grains and the new eutectic grains do not have to grow much before triggering more nucleation events ahead of their interface explaining the much smaller grain size in the Al-Si-XCu unmodified alloys. Due to this population of potent nuclei, ternary segregating elements have a relatively small influence on the eutectic grain density in the unmodified alloys.

In the Sr-modified alloys, the eutectic grain size versus 1/Q has a steeper line of best fit with a higher intercept value (slope = 2.35 mm°C and intercept = 2.19 mm). This provides some rationale for the role of available solute in eutectic nucleation, particularly in the Sr-modified alloys where nucleation difficulties are expected. An increase in the gradient and intercept values implies that the addition of Sr to Al-Si alloys decreases the nucleation potency and the nuclei number density in the melt. It is known that the addition of eutectic modifiers to Al-Si alloys significantly decreases the density and potency of the nuclei available for eutectic grains (Figure 3). During the solidification of Al-Si-Sr-modified alloys Al_2Si_2Sr nucleates on the AlP particles well before the nucleation of the Al-Si eutectic grains, leaving fewer and less effective nuclei for the nucleation of the Al-Si eutectic [22, 27].

In this case, the minimum constitutional supercooling required to trigger nucleation on the most potent nucleant will be much higher compared to unmodified alloys and the difference is supported by observations from the cooling curve analysis of Al-Si-X unmodified and Sr-modified alloys. These differences will result in a nucleation-free zone (the sum of first two terms in Equation 2) that is larger when compared to the unmodified alloy. The larger values of x_{nfz} suppress nucleation ahead of the interface irrespective of the presence of nuclei. As the potential nuclei are also distributed further from each other (the average distance between the centre of eutectic grains is 708µm in the unmodified Al-10Si-1Cu alloy and 5097µm in the Al-10Si-1Cu-350Sr alloy) x_{sd} (from Equation 2) will be high resulting in a much larger eutectic grain size as observed in the Al-Si-X-Sr-modified alloys.

The above analysis indicates that even though the Q value of Cu with respect to Al-Si eutectic is lower compared with similar calculations in primary phase solidification Cu still acts to grain refine the Sr-modified eutectic. However, the direct application of the Interdependence model to predict the eutectic grain size may be limited due to the reason that in the case of unmodified eutectic, the eutectic nucleates as discrete grains with a higher nucleation frequency and growth of these grains proceeds with a convoluted interface, led by silicon. The Interdependence model is based on the planar interface assumption which in the case of unmodified Al-Si eutectic is not applicable. However, in the case of Sr-modified eutectic the interface growth characteristics in terms of interface morphology and the growth velocity, have some similarities with aluminium dendrites. Hence, it is of interest to examine further the applicability of the Interdependency model to predict the eutectic grain size in the case of Sr-modified eutectic.

The value of ΔT_n (the minimum constitutional supercooling required to initiate nucleation) was calculated using the difference between nucleation temperatures of Al-Si eutectic obtained from the cooling curve analysis and the eutectic temperature of Al-Si-XCu-350Sr alloys as predicted by *Thermo-calc*® and presented in Table 2.

The interface velocity of the Sr-modified eutectic grain just after nucleation was calculated using the equation $V = 0.33\ (\Delta T)^2$ [28, 29]. By using the values of the parameters listed in Table 4, the size of the nucleation-free zone x_{nfz} was calculated using Equation 2.

From Table 4 it can be observed that an increase in the addition of Cu decreased the size of the nucleation-free zone. Due to the increase in constitutional supercooling, as defined by Q, ahead of the eutectic grain-liquid interface the size of the nucleation-free zone around growing grains decreased allowing more nucleation events to occur and therefore, the number of eutectic grains increased resulting in a continued decrease in the eutectic grain size. The slope of the x_{nfz} versus 1/Q curve (Figure 4) was calculated as 2.88 mm^{o}C for Al-Si-Cu-Sr modified alloys which is a good approximation when compared to the experimental slope value of 2.35 for these alloys (as shown in Figure 4). The similarity of the slopes of the predicted x_{nfz} plot and the measured eutectic grain size indicates that the number density of eutectic nulceant particles that are able to be activated does not change significantly with Cu concentration [30]. This observation may support the earlier suggestion that the AlP particles are poisoned by Sr forming a layer of Al_2Si_2Sr on the AlP particles implies the addition of Cu does not affect the potency or number density of the available nucleant particles.

5. Conclusions

- The addition of the ternary alloying element Cu to an Al-10Si alloy influences the Al-Si eutectic nucleation frequency. The constitutionally supercooled zone that is created due to Cu segregation in front of the eutectic interface plays an important role in promoting further nucleation ahead of the interface.

- As has been established for primary α-Al grains, it is proposed that the Al-Si eutectic grain size is related to the inverse of the alloy growth restriction factor by the empirical relationship $d_{gs} = a+b/Q$ in both unmodified and Sr-modified conditions.

- The linear relationship in the case of unmodified alloys revealed that in commercial purity unmodified alloys there is an abundance of potent nuclei particles (small value of grain size 0.28 mm at the intercept of the 1/Q plot) and the undercooling required for nucleation, ΔTn, is relatively low (low slope of the 1/Q plot of 0.44 mm^{o}C) promoting nucleation of the eutectic grains. Hence, the presence of ternary segregating Cu has a relatively minor effect on the (already high) eutectic grain density in unmodified alloys

- On the other hand, the addition of Sr to Al-Si alloys significantly decreases the density (large intercept value of 2.19 mm) and potency of the nuclei (steeper slope of 2.35 mm^{o}C) available for nucleating the eutectic grains. Thus, more constitutional supercooling is needed to activate these nuclei resulting in the formation of a much larger nucleation-free zone which prevents nucleation on many of the nuclei. In this case, the presence of ternary Cu provides constitutional supercooling ahead of the eutectic grain-liquid interface that decreases the size of the nucleation-free zone around growing grains allowing more nucleation events to occur and therefore, there is an increase in the number of eutectic grains with an increase in the level of Cu.

6. References

1. Easton, M. and D. StJohn, *Grain refinement of aluminum alloys: Part II. Confirmation of, and a mechanism for, the solute paradigm.* Metallurgical and Materials Transactions A, 1999. **30**(6): p. 1625-1633.
2. Easton, M. and D. StJohn, *Grain refinement of aluminum alloys: Part I. the nucleant and solute paradigms—a review of the literature.* Metallurgical and Materials Transactions A, 1999. **30**(6): p. 1613-1623.
3. Easton, M.A. and D.H. StJohn, *A model of grain refinement incorporating alloy constitution and potency of heterogeneous nucleant particles.* Acta Materialia, 2001. **49**(10): p. 1867-1878.
4. Qian, M., et al., *An analytical model for constitutional supercooling-driven grain formation and grain size prediction.* Acta Materialia, 2010. **58**(9): p. 3262-3270.
5. StJohn, D.H., et al., *The Interdependence Theory: The relationship between grain formation and nucleant selection.* Acta Materialia, 2011. **59**(12): p. 4907-4921.
6. Hutt, J.E.C., et al. *Effects of growth restriction and effective nucleant potency on grain size and morphology in Al-Si and Al-Cu alloys*. 1999.
7. Greer, A.L., et al., *Grain refinement of alloys by inoculation of melts.* Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 2003. **361**(1804): p. 479-495.
8. Quested, T.E. and A.L. Greer, *Grain refinement of Al alloys: Mechanisms determining as-cast grain size in directional solidification.* Acta Materialia, 2005. **53**(17): p. 4643-4653.
9. Knuutinen, A., et al., *Porosity formation in aluminium alloy A356 modified with Ba, Ca, Y and Yb*. Journal of Light Metals, 2001. **1**(4): p. 241-249.
10. Nogita, K., et al., *Mechanisms of eutectic solidification in Al-Si alloys modified with Ba, Ca, Y and Yb*. Journal of Light Metals, 2001. **1**(4): p. 219-228.
11. McDonald , S., *Eutectic solidification and porosity formation in unmodified and modified hypoeutectic aluminium-silicon alloys*, 2002, The University of Queensland: Brisbane.
12. Lu, L., et al., *Eutectic solidification and its role in casting porosity formation.* JOM Journal of the Minerals, Metals and Materials Society, 2004. **56**(11): p. 52-58.
13. Dahle, A., et al., *Eutectic nucleation and growth in hypoeutectic Al-Si alloys at different strontium levels.* Metallurgical and Materials Transactions A, 2001. **32**(4): p. 949-960.
14. McDonald, S., et al., *Modification-related porosity formation in hypoeutectic aluminum-silicon alloys.* Metallurgical and Materials Transactions B, 2004. **35**(6): p. 1097-1106.
15. Kurz, W. and D.J. Fisher, *Fundamentals of Solidification*. 4th ed. 1998: Trans Tech Publications
16. Yao, X., et al., *Effect of solute on the growth rate and the constitutional undercooling ahead of the advancing interface during solidification of an alloy and the implications for nucleation.* Journal of Materials Research,, 2006. **21**: p. 2470-2479.

17. Mc Donald , S., *Eutectic solidification and porosity formation in unmodified and Modified hypoeutectic Aliminium-Silicon alloys*, 2002, University of Queensland.
18. Tamminen, J., *Thermal Analysis for Investigation of Solidification Mechanisms in Metals and Alloys: Doctoral dissertation*, 1988, Stockholm University: Stockholm, Sweeden.
19. http://www.thermocalc.com/products-services/software/thermo-calc
20. http://www.thermocalc.com/media/5985/dbd_ttal8.pdf
21. Nogita, K., et al., *Aluminium phosphide as a eutectic grain nucleus in hypoeutectic Al-Si alloys.* J Electron Microsc, 2004. **53**(4): p. 361-9.
22. Dinnis, C.M., *Porosity formation in unmodified Al-Si-Mg-(Cu) foundry alloys: The role of iron and manganese: Doctoral dissertation*, 2004, The University of Queensland.
23. Bäckerud, L. and M. Johnsson, *The Relative Importance of Nucleation and Growth Mechanisms to Control Grain Size in Various Aluminium Alloys.* Light Metals 1996: p. 679-685.
24. Day, M.G. and A. Hellawell, *The lamellar-Fibre Transition in the Aluminium-Zinc Eutecti*c,Journal of The Australian Institute of Metals, 1964. **9**: p. 213-218.
25. Liang, S.-M. and R. Schmid-Fetzer, *Phosphorus in Al–Si cast alloys: Thermodynamic prediction of the AlP and eutectic (Si) solidification sequence validated by microstructure and nucleation undercooling data.* Acta Materialia, 2014. **72**(0): p. 41-56.
26. Crosley, P.B. and L.F. Mondolfo, *The modification of aluminium-silicon alloys.* AFS Transactions, 1966. **74**: p. 53-64.
27. Cho, Y.H., et al., *Effect of Strontium and Phosphorus on Eutectic Al-Si Nucleation and Formation of β-Al5FeSi in Hypoeutectic Al-Si Foundry Alloys.* Metallurgical and Materials Transactions A, 2008. **39**(10): p. 2435-2448.
28. Hogan, L. and H. Song, *Interparticle spacings and undercoolings in Al-Si eutectic microstructures.* Metallurgical and Materials Transactions A, 1987. **18**(5): p. 707-713.
29. Glenister, S.M.D. and R. Elliott, *Strontium modification of Al-12.7 wt%Si alloys.* Metal Science, 1981. **15**(4): p. 181-184.
30. Easton, M. and D. St John, *An analysis of the relationship between grain size, solute content, and the potency and number density of nucleant particles.* Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 2005. **36**(7): p. 1911-1920.

Figure 1 Micrographs of quenched unmodified samples: Al-10Si-(a) 1Cu, (b) 2Cu, (c) 4 Cu and (d) 6Cu. Aluminium dendrites are labelled as 1, eutectic Si is labelled as 2 and quenched liquid is labelled as 3.

Figure 2 Macrographs of quenched Sr-modified samples: Al-10Si-(a) 0Cu, (b) 1Cu, (c) 2Cu, (d) 4Cu, and (e) 6Cu.

Figure 3 Change in the number of nucleation events in the (a) unmodified and (b) Sr-modified alloys.

Figure 4 Eutectic grain size versus 1/Q for the addition of Cu to the unmodified and Sr modified Al-10%Si alloy (solid lines). The dashed line is the values of the nucleation-free zone, x_{nfz}, predicted by the sum of the first two terms in equation 2.

Table 1 Chemical compositions of the experimental alloys (weight percent) measured by ICP-AES.

Alloy nominal composition	Si	Cu	Mg	Ni	Fe	Sr
Al-10Si	9.89	<0.01	<0.01	0.01	0.12	<0.001
Al-10Si-1Cu	9.80	0.92	<0.01	0.01	0.11	<0.001
Al-10Si-2Cu	9.43	1.98	<0.01	0.01	0.11	<0.001
Al-10Si-4Cu	9.76	3.93	<0.01	0.01	0.10	<0.001
Al-10Si-6Cu	9.46	5.85	<0.01	0.01	0.11	<0.001
Al-10Si-350Sr	10.0	<0.01	<0.01	0.01	0.12	0.032
Al-10Si-1Cu-350Sr	9.89	0.95	<0.01	0.01	0.12	0.030
Al-10Si-2Cu-350Sr	9.68	1.90	<0.01	0.01	0.11	0.030
Al-10Si-4Cu-350Sr	10.20	3.78	<0.01	0.01	0.10	0.037
Al-10Si-6Cu-350Sr	9.78	5.90	<0.01	0.01	0.10	0.036

Table 2 Nucleation temperatures of primary Al, binary and ternary eutectics. $T_{n\text{-}\alpha\text{-}Al}$ is the nucleation temperature of the primary Al, $T_{n\text{-}Al\text{-}Si}$ is the nucleation temperature of the Al-Si eutectic, and $T_{n\text{-}Al\text{-}Si\text{-}CuAl2}$ is the nucleation temperature of ternary eutectic. Subscript TC indicates the nucleation temperature of each phase as indicated by *Thermo-calc*®.

Alloy nominal composition	$T_{n\text{-}Al}$ (°C)	$T_{n\text{-}Al\text{-}TC}$ (°C)	$T_{n\text{-}Al\text{-}Si}$ (°C)	$T_{n\text{-}Al\text{-}Si\text{-}TC}$ (°C)	$T_{n\text{-}Al\text{-}Si\text{-}CuAl2}$ (°C)	$T_{n\text{-}Al\text{-}Si\text{-}CuAl2\text{-}TC}$ (°C)
Al-10Si-1Cu	590	591	576	577	515	525
Al-10Si-2Cu	587	587	566	574	517	525
Al-10Si-4Cu	587	580	570	570	518	525
Al-10Si-6Cu	573	573	566	568	517	525
Al-10Si-1Cu-350Sr	595	591	570	577	519	525
Al-10Si-2Cu-350Sr	586	587	565	574	518	525
Al-10Si-4Cu-350Sr	583	580	562	570	519	525
Al-10Si-6 Cu-350Sr	575	573	556	568	519	525

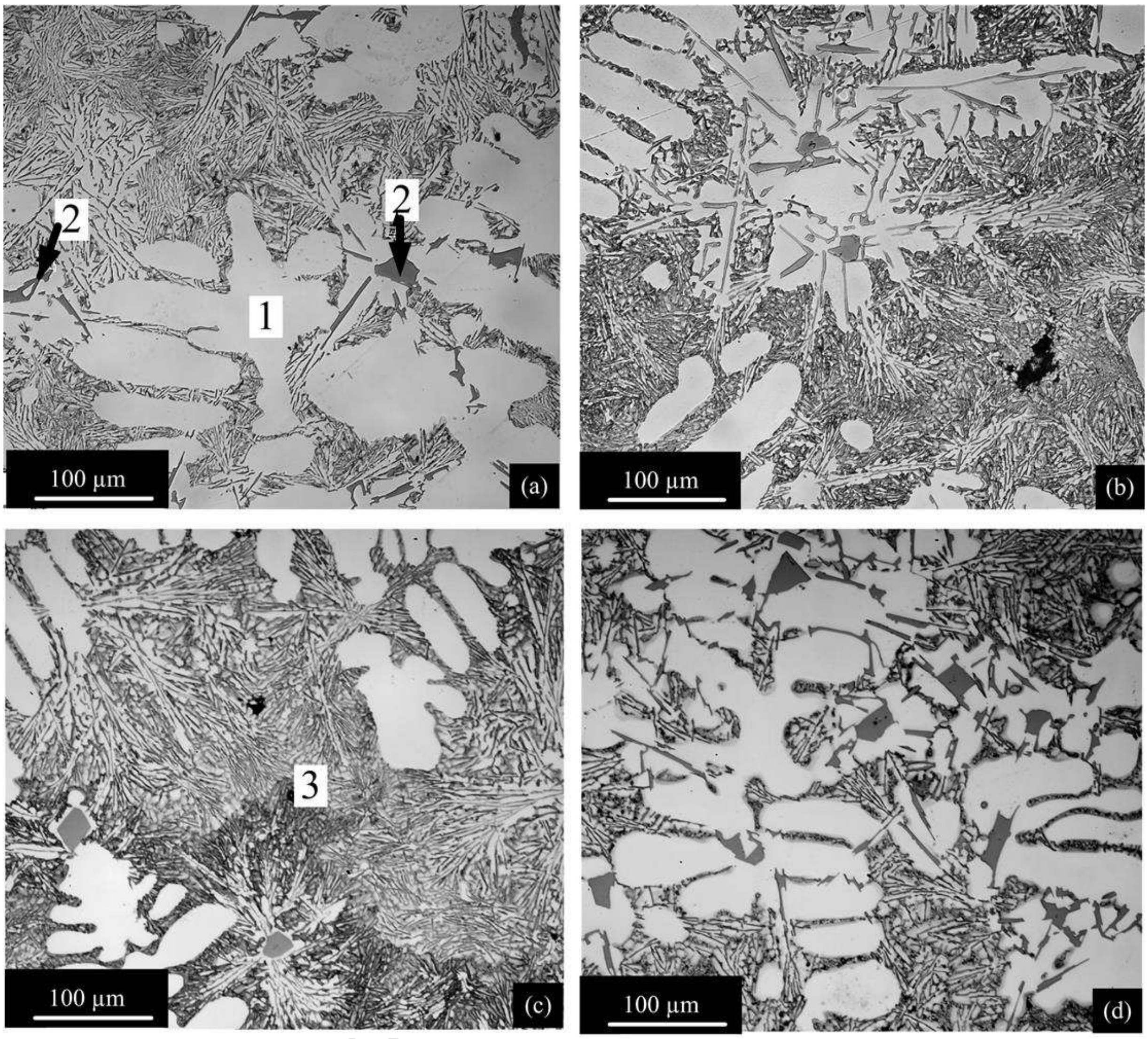
Table 3 The number of eutectic grains per unit area (n_A) in Al-10Si-X (X = Cu) unmodified and Sr-modified alloys.

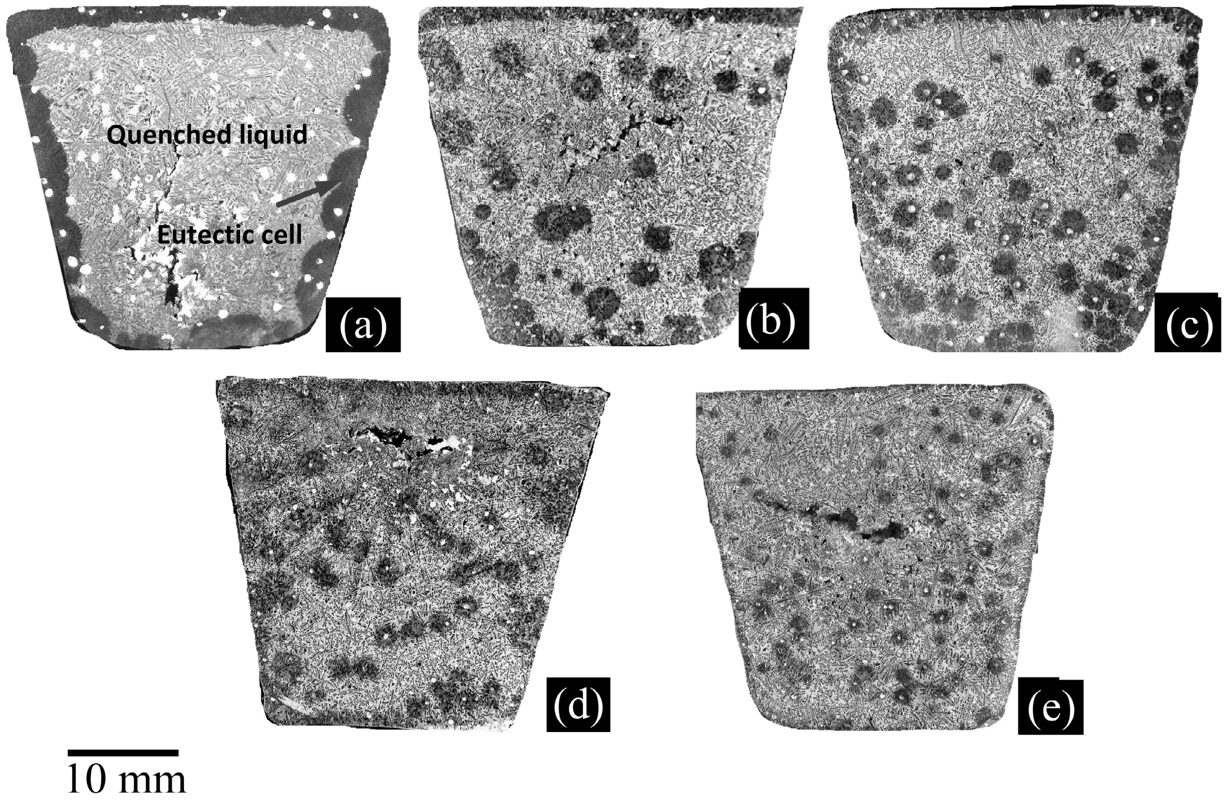
Nominal alloy composition	Number of eutectic grains per unit area (n_A mm^{-2})	Nominal alloy composition	Number of eutectic grains per unit area (n_A mm^{-2})
Al-10Si	2.51	Al-10Si-350Sr	0.012
Al-10Si-1Cu	2.54	Al-10Si-1Cu-350Sr	0.048
Al-10Si-2Cu	2.18	Al-10Si-2Cu-350Sr	0.096
Al-10Si-4Cu	5.73	Al-10Si-4Cu-350Sr	0.081
Al-10Si-6Cu	9.10	Al-10Si-6Cu-350Sr	0.121

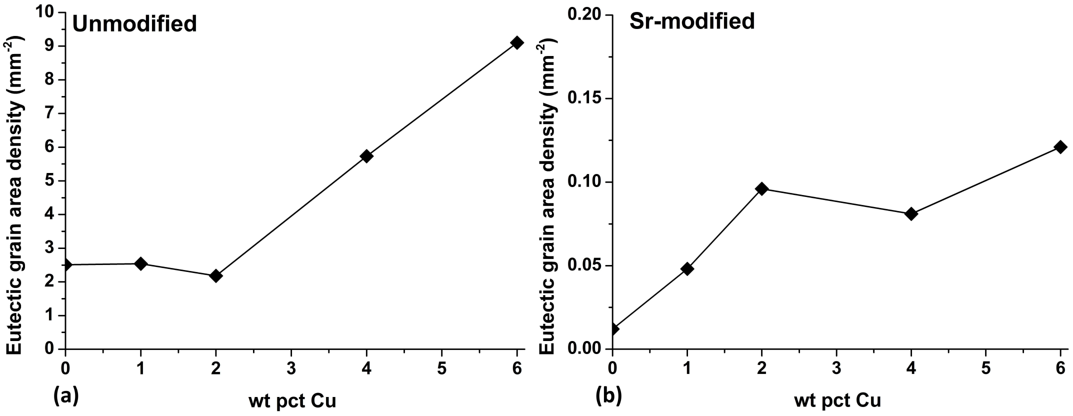
Table 4 Parameters of the Al-Si-XCu-350 Sr alloys that are used in nucleation free zone calculation.

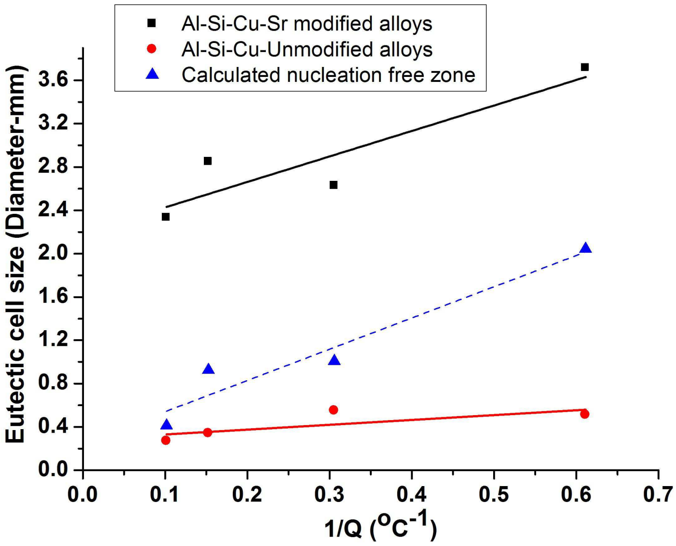
Alloy nominal composition	C_0 (wt%)	C_l^* (wt%)	k	m	Q	ΔTn (°C)	V (µm/sec)	D*$10^{-9}$$m^2$/sec [1]	NFZ (µm)
Al-10Si-1Cu	1	10.6	0.148	-1.92	1.63	7	8.2	3.55	2042
Al-10Si-2Cu	2	13.5	0.148	-1.92	3.27	9	11.8	3.55	1008
Al-10Si-4Cu	4	17.4	0.148	-1.92	6.54	8	16.1	3.55	925
Al-10Si-6Cu	6	23.3	0.148	-1.92	9.81	12	26.7	3.55	411

1. Du, Y., et al., *Diffusion coefficients of some solutes in fcc and liquid Al: critical evaluation and correlation.* Materials Science and Engineering: A, 2003. **363**(1–2): p. 140-151.


2
2
1
100 µm
(a)
100 µm
(b)
3
100 µm
(c)
100 µm
(d)


Quenched liquid
Eutectic cell
(a)
(b)
(c)
(d)
(e)
10 mm


Unmodified
Eutectic grain area density (mm^{-2})
0
1
2
3
4
5
6
7
8
9
10
0
1
2
3
4
5
6
(a)
wt pct Cu
Sr-modified
Eutectic grain area density (mm^{-2})
0.00
0.05
0.10
0.15
0.20
0
1
2
3
4
5
6
(b)
wt pct Cu


Al-Si-Cu-Sr modified alloys
Al-Si-Cu-Unmodified alloys
Calculated nucleation free zone
Eutectic cell size (Diameter-mm)
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
1/Q ($^{o}C^{-1}$)

The influence of the ternary alloying element Cu on the Al-Si eutectic nucleation is investigated in unmodified and Sr-modified conditions. The highlights from the research are:

- Addition of Cu to an Al-10Si alloy influences eutectic nucleation frequency.
- The number of eutectic grains increases with an increase in the level of Cu.
- Al-Si eutectic grain size is related to the inverse of the ternary alloy Q value.
- Constitutional supercooling promotes the nucleation of eutectic grains.