EFFECT OF COOLING RATE ON SOLIDIFICATION CHARACTERISTICS OF ALUMINUM ALLOYS A356 AND AA5182

by

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(Department of Metals and Materials Engineering)

We accept this thesis as conforming to the required standard

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**Stephanie Thompson**

Name of Author (please print)

Date: 18 February 2004

Title of Thesis: **EFFECT OF COOLING RATE ON SOLIDIFICATION CHARACTERISTICS OF ALUMINUM ALLOYS A356 AND A95782**

Degree: **Masters of Advanced Science**  Year: **2004**
Microstructural reactions during solidification of aluminum alloys A356 (unmodified and strontium modified) and AA5182 were analyzed using cooling curve analysis to determine the evolution in fraction solid. The experiments involved recording the temperature/time data under different cooling rates so that the various phase changes associated with solidification could be identified. Once collected, the cooling curve data was processed to calculate the first derivative together with a baseline cooling curve (cooling curve in the absence of any transformations). Comparison of the baseline cooling curve to the first derivative data allowed accurate identification of start temperatures of the various liquid to solid transformations and characterization of fraction solid formed during the cooling process.

In A356, strontium modification altered the morphology, decreased the solidification start temperature of new phases (2°C to 11°C) and increased solid fraction of the beginning of eutectic solidification and Mg$_2$Si precipitation (0.01 to 0.05). For the conditions studied, cooling rate appeared to show no effect on fraction solid evolution but an increase in cooling rate reduced solidus temperature (48°C to 75°C), resulting in a larger freezing range.

In AA5182 the main eutectic reaction and subsequent reactions, including Mg$_2$Si formation, occurred at much lower temperatures and higher fraction solids than previously published. The primary eutectic was found to begin solidifying between 575-588°C, which corresponds to a solid fraction between 0.87-0.91 and Mg$_2$Si was found to
precipitate between 551-560°C, which corresponds to a fraction solid between 0.96-0.97. Increasing cooling rate from 0.5°C/s to 2°C/s was observed to result in a slight increase in fraction solid for primary eutectic transformation from 0.87-0.88 at the low cooling rate to 0.89-0.91 at the intermediate cooling rate and 0.91 at the highest cooling rate. The highest cooling rate also resulted in a drop in solidus temperature to 461°C from 500-510°C at the low and intermediate cooling rates. This led to an increase in the solidification interval from 123°C to 151°C.
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CHAPTER 1: BACKGROUND AND INTRODUCTION

1.1 AUTO21

The Network of Centres of Excellence AUTO21 project is focused on the needs and priorities of the automotive sector and on the manufacture and use of vehicles into the 21st century. It is divided into six themes including: Health, Safety and Injury Prevention; Societal Issues; Materials and Manufacturing; Powertrains, Fuels and Emissions; Design Processes and Intelligent Systems and Sensors. The work discussed in this report was an initial investigation into the Advanced Light Metals Casting and Materials Development project as part of the Materials and Manufacturing theme.

Over the past decade[1] aluminum alloys have been increasingly used in the automotive sector due to their high specific strength and stiffness that permit the overall weight of a vehicle to be reduced. Every kilogram of aluminum that replaces traditional higher density materials in a vehicle today saves the equivalent of 20 kilograms of carbon dioxide emissions over the lifetime of the average North American car or light truck[1]. Casting is a widely used method of producing aluminum automotive parts and the ability to simulate the casting process of various products using computer based models allows manufacturers to minimize tool set-up costs as well as helps to minimize rejection of defective products. In order to produce effective models accurate data on the evolution of fraction solid during cooling is required. However, there is a lack of published data on the solidification of aluminum alloys, particularly throughout the mushy or semi-solid region. The current study attempts to address this problem for two commercially important alloys in the automotive sector, A356 and AA5182.
1.2 A356

Due to the ability to produce various combinations of mechanical properties through heat treatment as well as inherent high ductility because of low iron and impurity content, A356 (Al-Si7.5-Mg0.45) is often used in the automotive industry. A variety of components are manufactured including cylinder blocks and heads, manifolds, internal engine parts and die cast wheels\[^{[1]}\]. Die cast aluminum wheels are one of the most difficult automotive castings to produce because of stringent cast surface and mechanical property requirements. In order to meet the mechanical fatigue performance, the alloy is typically modified and heat treated. A356 is heat treatable due to Mg\(_2\)Si hardening of \(\alpha\)-Al dendrites. Mg\(_2\)Si is formed during casting and can be brought into solid solution in \(\alpha\)-Al by solution treating at 500°C-510°C followed by quenching and precipitation treatment at 150-160°C. This allows for chemical homogenization of the \(\alpha\)-Al dendrites\[^{[2]}\]. Heat treating as well as alloy modification is used to alter the morphology of the acicular Al-Si eutectic into a finer, more interconnected fibrous phase improving toughness and ductility\[^{[3-6]}\]. Both sodium and strontium modification have historically been used although the trend in industry is toward the use of strontium, as it has a tendency to fade less, is less toxic and it is also less corrosive to refractories\[^{[3-6]}\]. Typically strontium modified A356 contains approximately 0.01% Sr.

One of the defects found in the casting process that can adversely affect both surface finish and mechanical performance is microporosity. The mechanism of microporosity formation in aluminum alloys is complex owing to its dependence on the interaction of a number of phenomena occurring during solidification, including the decrease in hydrogen
solubility, the decrease in volume and the development of the solidification structure (increase in difficulty in interdendritic feeding)\(^7\).

As a result, the amount, size, and distribution of microporosity is affected by a large number of casting parameters including thermal variables, melt composition, grain structure, modification, and inclusion content, making optimization by trial-and-error methodologies difficult. The current body of work in the literature indicates that alloy modification tends to increase porosity, albeit the exact mechanism is unclear. For example, the increase in microporosity is reported to be due to an increase in hydrogen content, an increase in inclusion content and/or a reduction of the liquid surface tension\(^3\). One other effect, which has also been studied, is the propensity of the modifiers to further under cool the eutectic resulting in a larger freezing range, making interdendritic feeding more difficult and providing more time for hydrogen diffusion and porosity growth\(^3,5\).

1.3 AA5182

AA5182 (Al-Mg5) is a non heat-treatable wrought aluminum alloy that is used in a variety of applications due to its high strength, excellent formability, weldability and corrosion resistance. Applications include automotive components such as lift gate inner-panels, splash guards, heat shields, air cleaner trays and covers, structural and weldable parts and sheet load floors as well as beverage container ends and marine structures\(^1,8\). The predominant casting route for this alloy is the semi-continuous direct chill (DC)
casting process. Figure 1.1 shows a schematic diagram of the process. The process is distinguished by the direct contact of water with the hot surface of the ingot and by its two distinct phases – start-up and steady state. During steady state operation approximately 20% of the heat is removed by the mould and 80% is removed by the water. During the initial stages of the start-up phase the bottom block and mould initially remove the majority of the heat. The deposition of the heat then transitions to the steady state condition over the balance of the start-up phase. The start-up phase typically lasts approximately 1 meter of ingot length and is the most problematic from the standpoint of defect formation. Because of its relatively long freezing range, AA5182 is prone to hot tears during the start-up phase and consequently can be a challenge to recover.

During the start-up phase the base or butt of the ingot is subject to a large deformation known in the industry as ‘butt-curl’ that arises as the sides of the ingot first come into contact with the water. The tensile strains induced in the material can lead to cracks and hot tears\(^9\). The hot-tears that typically form on the broad or rolling face in approximately the middle third of the ingot, are vertically oriented and initiate in proximity to the lip at the base of the ingot. The current body of knowledge indicates that the hot tears arise in the mushy zone as a result of solidification shrinkage coupled with strain in areas subject to inadequate interdendritic feeding during solidification\(^10-15\). Figure 1.2 shows an example of a centre line hot tear in an AA5182 ingot. An examination of the crack surface morphology suggests that the hot tears probably develop at high fraction solid (\(f_s > 0.9\)) in regions where the liquid film is still continuous but is thin enough to limit liquid feeding resulting in embrittlement of the microstructure. The resulting cavitation damage
can then become inter-linked to form interdendritic cracks due to the continued application of thermally induced tensile strains\textsuperscript{[9, 12, 13]}.

Quantification of the conditions that lead to hot tears in AA5182 is challenging because of the many inter-related phenomenon that can influence the evolution of pressure in the interdendritic liquid including, rate of volumetric shrinkage of the alloy, rate of application of mechanically induced strain, temperature gradient and alloy freezing range (as they impact on feeding length), semi-solid permeability, liquid viscosity and presence or absence of sites for heterogeneous nucleation of cavities\textsuperscript{[14, 16]}. In addition the morphology of the solidified structure may also have a bearing on hot tearing susceptibility with the more columnar structures providing a more straightforward path for crack propagation\textsuperscript{[17, 18]}. 
Figure 1.1: Schematic diagram of the semi-continuous DC casting process.
Figure 1.2: Centre line hot tear observed in DC cast aluminum AA5182 ingot.
CHAPTER 2: LITERATURE REVIEW

2.1 A356

Table 2.1 shows the standard composition range for A356. The main phase transformations that occur during the solidification of A356 are: formation of aluminum dendrites (α-Al), a binary eutectic (Al-Si) reaction followed by ternary (Al$_3$FeSi) and quaternary (Al$_3$FeMg$_3$Si$_6$) eutectic formation. The transformation from liquidus to solidus occurs approximately between 615°C and 555°C\cite{19}.

A study on the solidification behaviour of A356 by Arnberg et al.\cite{8} presents the various phase transformations, their start temperature and fraction solid for the unmodified alloy of composition shown in Table 2.2. Bäckerud et al.\cite{20} studied A356.1, a version of A356 with very high Fe content of 0.44. However, since the high Fe content is above the 0.2 maximum set by the ASM standard and causes very different phases to precipitate out, a review of this study has not been included. Another study on unmodified A356.2 by Bäckerud et al.\cite{20} presents slightly different start temperatures and phase transformations than Arnberg et al.’s study and includes the effect of cooling rate. Table 2.3 shows the sample composition from the study by Bäckerud et al.\cite{20}. This study is referenced by Arnberg et al.\cite{8} as the source for their experimental technique. The data was collected using a two-thermocouple technique on 60g cylindrical samples 30mm in length by 35mm in diameter. The samples were held in preheated graphite crucibles seated on 6mm thick Fiberfrax felt mats. One K-type thermocouple was located in the centre of the sample and the other at the wall. Sampling frequency was selected for each experiment to
give 0.1°C resolution during solidification. Cooling rates of 0.3°C/s, 0.7°C/s and 5°C/s were achieved using a full cemented Fiberfrax felt jacket, a cemented Fiberfrax felt lid and compressed air respectively. Cooling curve analysis using filtered data from the central thermocouple allowed first derivative peak identification and phases were identified after full solidification using a combination of metallography, energy dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) measurements. Table 2.4 highlights the results presented by Arnberg et al.[8]. Table 2.5 summarizes the reactions identified by Bäckerud et al.[20]. Comparing Table 2.4 with Table 2.5 highlights that Bäckerud et al.[20] include the precipitation of Al₈Mg₃FeSi₆ before Mg₂Si precipitates. This could be due to the fact that they claim Al₃FeSi can start precipitating before the main eutectic reaction which can either remain in the microstructure as Al₅FeSi needle forms or transform into Al₈Mg₃FeSi₆ on cooling[20]. However, Arnberg et al.[8] comment on the fact that no pre-eutectic phase precipitations occur due to low Fe contents even though their samples contained 0.08% Fe as did Bäckerud’s. The solidification sequence, temperatures and fraction solids were reported as follows:

- Formation of α-Al dendrites: 610°C[8] and 608°C-615°C[20].
- Start of main eutectic reaction (Liq→Al+Si+Al₅FeSi): 568°C/0.51 fraction solid[8] and 554°C-564°C/0.58-0.72 fraction solid[20].
- Precipitation of Mg₂Si: 557°C/0.96 fraction solid[8] and 534-561°C/0.90-0.93 fraction solid[20].
- Final precipitation of the complex eutectic Al₈Mg₃FeSi₆: 550°C/0.99 fraction solid[8] and 519-553°C/0.96-0.98 fraction solid[20].
- Solidus: 543°C[8] and 544°C[20].


Arnberg et al.'s study included analysis of different compositions and, although their results were only reported as a summary for all their samples together, they do comment that strontium modification suppressed the eutectic reaction.

A study by Wang et al.\cite{21} characterizes the solidification sequence of an Australian designated alloy 601 (which is comparable to A356) with and without strontium modification at various cooling rates. The compositions of their samples are shown in Table 2.6. Samples were cast at 745°C in 50mm diameter sand and metal moulds. Cooling curves were obtained from two K-type thermocouples (one placed at the centre and one at the wall, 25mm from the bottom of the sample) using a data acquisition system. However, the large diameter of this cast would have set up a significant temperature gradient from the centre to the wall of the casting. Differential scanning calorimetry (DSC) was carried out on discs of approximately 4mm in diameter and 10-25mg. To study phase transformation during solidification the DSC was run at 10°C/min between 500°C and 650°C. A note to regard their recorded start temperatures and ranges with caution was included since no direct measurement of sample temperature was taken. Due to the setup of DSC equipment where the sample sits in one pan on a heating element containing a Pt resistance thermometer and a reference sample is sat in a pan on a different heating element containing another thermometer, only readings from the two heating elements can be taken which always leads to a temperature lag between sample temperature and temperature sensor. This lag would increase to several degrees with high values of heat flux in the sample (such as at the start of precipitation of a new phase). Optical microstructural analysis was carried out on sample surfaces polished to a 1μm
diamond finish. EDX equipment was used for qualitative analysis and wavelength dispersive spectrometry for quantitative analysis. Wang et al.\cite{21} reference the study by Bäckerud et al.\cite{20} and their DSC results agree with Bäckerud et al.'s solidification reaction: Nucleation and growth of $\alpha$-Al dendrites followed by an Al-Si binary eutectic reaction (at around 570°C for the 601Sr [0.3Mg] sample) where Fe is enriching the liquid phase as the fraction of liquid decreases and the ternary eutectic is reached (solidifying Al, Si and Al$_5$FeSi). Further cooling produces Al, Si and Mg$_2$Si and then finally Al$_8$FeMg$_3$Si$_6$ (at around 554°C for the 601Sr [0.3Mg] sample). However, they do point out that reaction 3a (Liquid $\rightarrow$ Al + Si + Al$_5$FeSi) and 3b (Liquid + Al$_5$FeSi $\rightarrow$ Al + Si + Al$_8$FeMg$_3$Si$_6$) can only be identified using SEM images as they do not produce a thermal signature in Bäckerud et al.'s\cite{20} cooling curves or their own DSC traces. An explanation for this is given as the Al-Si and AlFeSi reactions overlap so much that they are merged in thermal traces. Wang et al. found that increasing cooling rate lowered the liquidus and binary eutectic temperature but stated that neither dendrite arm spacing nor strontium modification had any effect on precipitation behaviour.

A study by Mackay et al.\cite{2} of A356 (along with A357), whose composition is shown in Table 2.7, also characterized the solidification sequence using thermal analysis. They used a stainless steel crucible with Zirtex 25 refractory wash and one inch of Fiberfrax insulation around the sides and bottom. The crucible held a 200g sample of molten metal with a K-type thermocouple immersed in the centre. A personal computer recorded the time/temperature data via a 16 bit analog to digital converter. The results agree with those shown in Table 2.4 even though the samples contained a very high copper content (0.61)
which is out of the standard range for A356. They suggest that formation and growth of primary \(\alpha\)-Al dendrites begins at 612°C. Cooling allows these dendrites to grow, enriching the remaining liquid in silicon, iron and magnesium and at around 577°C Al-Si eutectic precipitation alters cooling rate to almost zero while latent heat of fusion is evolved. They claim that \(\text{Al}_3\text{FeSi}\) cannot be seen in the first derivative due to it being submerged behind the Al-Si plateau. \(\text{Mg}_2\text{Si}\) is reported to form at 555°C. \(\text{Al}_8\text{Mg}_3\text{FeSi}_6\) is reported to precipitate at 562-567°C but is also said not to be detectable in the first derivative at low Mg levels as the phase volume is too small.

All the previously published data on solidification of A356 reviewed above has been summarized in Table 2.8.

2.2 AA5182

Table 2.9 shows the standard composition range for aluminum alloy AA5182. There are four main phase transformations that occur during the solidification of AA5182: formation of aluminum dendrites (\(\alpha\)-Al), a ternary eutectic reaction \([\text{Al}_6(\text{FeMn})]\)] followed by \(\text{Mg}_2\text{Si}\) precipitation and a complex eutectic \((\text{Al}_8\text{Mg}_3)\). The transformation from liquidus to solidus occurs approximately between 638°C and 577°C\(^{[19]}\).

Two previously published sets of results from studies of the solidification behaviour of AA5182 by Arnberg et al.\(^{[8]}\) and Bäckerud et al.\(^{[22]}\) were carried out on AA5182 samples of compositions shown in Tables 2.10 and 2.11. The experimental technique used was
identical for both studies where the data was collected using a two-thermocouple technique on 60g cylindrical samples 30mm in length by 35mm in diameter. The samples were held in preheated graphite crucibles seated on 6mm thick Fiberfrax felt mats. One K-type thermocouple was located in the centre of the sample and the other at the wall. Sampling frequency was selected for each experiment to give 0.1°C resolution during solidification. Cooling rates of 0.3°C/s, 0.9°C/s, 2.8°C/s and 11°C/s were achieved using a full cemented Fiberfrax felt jacket, a cemented Fiberfrax felt lid, compressed air and water mist respectively. Cooling curve analysis using filtered data from the central thermocouple allowed first derivative peak identification. Phases were identified by Bäckerud et al.\textsuperscript{[22]} after full solidification using a combination of metallography, EDX and the Al-Fe-Si phase diagram. Arnberg et al.\textsuperscript{[8]} give fraction solid values at the beginning of solidification of each new phase. The results of these studies are summarized in Tables 2.12 and 2.13. The solidification sequence proposed by each study is essentially the same except that in the latest publication Arnberg et al.\textsuperscript{[8]} do not mention the precipitation of Al\textsubscript{3}Fe with the main eutectic reaction, presumably because it is not revealed by the cooling curve or first derivative, only by metallography and EDX. They both report that the first phase to nucleate and grow at the start of solidification consists of equiaxed dendrites of α-Al (at 637°C\textsuperscript{[8]} and 623-632°C\textsuperscript{[22]}) followed by the main eutectic reaction, Liq→Al+ Al\textsubscript{6}(FeMn), (at 623°C and 0.40 fraction solid\textsuperscript{[8]} and 617°C-621°C\textsuperscript{[22]}). Bäckerud et al.\textsuperscript{[22]} also report concurrent precipitation of Al\textsubscript{3}Fe [or Al\textsubscript{3}(FeMn)] due to ‘local inhomogeneties in the interdendritic liquid’. This is reported to be followed by Mg\textsubscript{2}Si precipitation (at 582°C and 0.93 fraction solid\textsuperscript{[8]} and 571°C-586°C\textsuperscript{[22]}) and a complex eutectic, Liq→Al+Mg\textsubscript{2}Si+Al\textsubscript{3}Fe+Al\textsubscript{8}Mg\textsubscript{5}, (at 560°C and 0.98 fraction
solid \[^8\] and 470-557°C \[^{22}\]. The end of solidification is stated to occur at 536°C by Arnberg et al.\[^8\] and 470°C by Bäckerud et al.\[^{22}\], however, Bäckerud et al.\[^{22}\] have not calculated fraction solid but simply used the Al-Fe-Si diagram to provide an estimate. Arnberg et al.\[^8\] also note that the addition of titanium to one of their samples does not affect precipitation of intermetallic phases, it only serves to make them finer.

**Table 2.1: ASM Standard Composition (wt%) of Aluminum Alloy A356\[^{19}\]**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A356</td>
<td>6.5-7.5</td>
<td>0.25-0.45</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

**Table 2.2: Composition (wt%) of Arnberg et al.'s A356 samples\[^8\]**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti (or B)</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>7.26</td>
<td>0.38</td>
<td>0.08</td>
<td>0.039</td>
<td>0.002</td>
<td>0.006</td>
<td>0.016</td>
<td>0.0012Na</td>
</tr>
<tr>
<td>Sample 2</td>
<td>7.26</td>
<td>0.38</td>
<td>0.08</td>
<td>0.039</td>
<td>0.002</td>
<td>0.006</td>
<td>0.016</td>
<td>0.0012Na</td>
</tr>
<tr>
<td>Sample 3</td>
<td>7.26</td>
<td>0.38</td>
<td>0.08</td>
<td>0.039+0.1Ti</td>
<td>0.002</td>
<td>0.006</td>
<td>0.016</td>
<td>0.0012Na</td>
</tr>
<tr>
<td>Sample 4</td>
<td>7.26</td>
<td>0.38</td>
<td>0.08</td>
<td>0.039+0.1B</td>
<td>0.002</td>
<td>0.006</td>
<td>0.016</td>
<td>0.0012Na +0.02Sr</td>
</tr>
<tr>
<td>Sample 5</td>
<td>7.26</td>
<td>0.38</td>
<td>0.08</td>
<td>0.039</td>
<td>0.002</td>
<td>0.006</td>
<td>0.016</td>
<td>0.0012Na +0.02Sr</td>
</tr>
</tbody>
</table>

**Table 2.3: Composition (wt%) of Bäckerud et al.'s A356 samples\[^{20}\]**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti (or B)</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A356.2</td>
<td>6.8</td>
<td>0.35</td>
<td>0.08</td>
<td>0.15</td>
<td>0</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Summary of Reactions</td>
<td>Temperature</td>
<td>( f_s (%) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>-------------------</td>
<td>----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of solidification and formation of ( \alpha )-Al</td>
<td>610°C (1130°F)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of main eutectic reaction</td>
<td>568°C (1119°F)</td>
<td>51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq( \rightarrow )Al+Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq( \rightarrow )Al+Si+Al(_2)FeSi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation of Mg(_2)Si</td>
<td>557°C (1035°F)</td>
<td>96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq( \rightarrow )Al+Si+Mg(_2)Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation of complex eutectic</td>
<td>550°C (1022°F)</td>
<td>99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq( \rightarrow )Al+Si+Mg(_2)Si+Al(_3)Mg(_3)FeSi(_6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>End of solidification</td>
<td>543°C (1009°F)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling Rate (°C/s)</td>
<td>Reaction*</td>
<td>Temperature (°C)</td>
<td>( f_s ) (%)</td>
<td>Accumulated ( f_s ) (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------</td>
<td>------------------</td>
<td>----------------</td>
<td>-------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>1</td>
<td>615-609</td>
<td>18</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2+3</td>
<td>563-564</td>
<td>23</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>561-553</td>
<td>7</td>
<td>97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>553-544</td>
<td>3</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>1</td>
<td>615-610</td>
<td>21</td>
<td>21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2+3</td>
<td>564-562</td>
<td>23</td>
<td>81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>558-549</td>
<td>8</td>
<td>93</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>5</td>
<td>546-541</td>
<td>4</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>614-608</td>
<td>27</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2+3</td>
<td>556-554</td>
<td>16</td>
<td>88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>548-534</td>
<td>7</td>
<td>98</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>5</td>
<td>534-519</td>
<td>2</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reactions:*

1. Development of dendritic network
2a. Liq → Al + Si
2b. Liq → Al + Al₅FeSi
3a. Liq → Al + Si + Al₅FeSi
3b. Liq + Al₅FeSi → Al + Si + Al₈Mg₃FeSi₆
4. Liq → Al + Mg₂Si + Si
5. Liq → Al + Si + Mg₂Si + Al₈Mg₃FeSi₆
### Table 2.6: Composition (wt%) of Wang et al’s samples\(^{[21]}\)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti (or B)</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>601Sr (0.3Mg)</td>
<td>7.0</td>
<td>0.3</td>
<td>0.13</td>
<td>0.13</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.019</td>
</tr>
<tr>
<td>601um (0.4Mg)</td>
<td>6.8</td>
<td>0.39</td>
<td>0.13</td>
<td>0.13</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>601Sr (0.4Mg)</td>
<td>7.0</td>
<td>0.41</td>
<td>0.14</td>
<td>0.13</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.019</td>
</tr>
</tbody>
</table>

### Table 2.7: Compositions (wt%) of Mackay et al’s samples\(^{[2]}\)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ni</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>A356 (as-received)</td>
<td>7.21</td>
<td>0.36</td>
<td>0.082</td>
<td>0.023</td>
<td>0.059</td>
<td>0.61</td>
<td>&lt;0.016</td>
<td>0.009</td>
</tr>
</tbody>
</table>

### Table 2.8: Summary of Reported Temperatures of Reactions Occurring During Solidification of A356

<table>
<thead>
<tr>
<th>Study</th>
<th>Primary Al (°C)</th>
<th>Al-Si Eutectic (°C)</th>
<th>Mg$_2$Si (°C)</th>
<th>Complex Eutectic (°C)</th>
<th>Solidus (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arnberg et al.(^{[8]})</td>
<td>610</td>
<td>568</td>
<td>557</td>
<td>550</td>
<td>543</td>
</tr>
<tr>
<td>Bäckerud et al.(^{[20]})</td>
<td>608-615</td>
<td>554-564</td>
<td>534-561</td>
<td>519-553</td>
<td>544</td>
</tr>
<tr>
<td>Wang et al.(^{[21]})</td>
<td>-</td>
<td>570</td>
<td>-</td>
<td>554</td>
<td>-</td>
</tr>
<tr>
<td>Mackay et al.(^{[2]})</td>
<td>612</td>
<td>577</td>
<td>555</td>
<td>562-567</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 2.9: ASM Standard Composition (wt%) of Aluminum Alloy AA5182\(^{[19]}\)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti</th>
<th>Mn</th>
<th>Cu</th>
<th>Cr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA5182</td>
<td>&lt;0.2</td>
<td>4.0-5.0</td>
<td>&lt;0.35</td>
<td>&lt;0.10</td>
<td>0.20-0.50</td>
<td>&lt;0.15</td>
<td>&lt;0.10</td>
<td>&lt;0.25</td>
</tr>
</tbody>
</table>
Table 2.10: Composition (wt%) of Arnberg et al.’s AA5182 Samples[^8]

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti</th>
<th>Mn</th>
<th>Cu</th>
<th>Cr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample (1)</td>
<td>0.10</td>
<td>4.69</td>
<td>0.21</td>
<td>0.005</td>
<td>0.37</td>
<td>0.05</td>
<td>0.001</td>
<td>0.008</td>
</tr>
<tr>
<td>Sample (2)</td>
<td>0.10</td>
<td>4.69</td>
<td>0.21</td>
<td>0.005+0.02</td>
<td>0.37</td>
<td>0.05</td>
<td>0.001</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Table 2.11: Composition (wt%) of Bäckerud et al.’s AA5182 Samples[^22]

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti</th>
<th>Mn</th>
<th>Cu</th>
<th>Cr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>0.10</td>
<td>4.74</td>
<td>0.28</td>
<td>-</td>
<td>0.34</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.12: Metallurgical Reactions Occurring During Solidification of AA5182[^22]

<table>
<thead>
<tr>
<th>Summary of Reactions</th>
<th>0.3°C/s</th>
<th>0.9°C/s</th>
<th>2.8°C/s</th>
<th>11°C/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liq→Al, dendritic network</td>
<td>632</td>
<td>632-630</td>
<td>631-628</td>
<td>632-623</td>
</tr>
<tr>
<td>Liq→Al+ Al₆(FeMn)</td>
<td>621-617</td>
<td>621-617</td>
<td>620</td>
<td>620</td>
</tr>
<tr>
<td>or: Liq→Al+ Al₃Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq→Al+Mg₂Si</td>
<td>586</td>
<td>584-581</td>
<td>576-571</td>
<td>583</td>
</tr>
<tr>
<td>Liq→Al+Al₃Fe +Mg₂Si +Al₅Mg₅</td>
<td>557-470*</td>
<td>556-470*</td>
<td>553-470*</td>
<td>543-470*</td>
</tr>
<tr>
<td>End of solidification</td>
<td>470*</td>
<td>470*</td>
<td>470*</td>
<td>470*</td>
</tr>
</tbody>
</table>

* Estimated from the Al-Fe-Si diagram
Table 2.13: Summary of Metallurgical Reactions Occurring During Solidification of AA5182[^8]

<table>
<thead>
<tr>
<th>Summary of Reactions</th>
<th>Temperature</th>
<th>( f_s (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start of solidification and formation of ( \alpha )-Al</td>
<td>637°C (1179°F)</td>
<td>0</td>
</tr>
<tr>
<td>Start of main eutectic reaction</td>
<td>623°C (1153°F)</td>
<td>40</td>
</tr>
<tr>
<td>( \text{Liq} \rightarrow \alpha \text{-Al} + \text{Al}_6(\text{FeMn}) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation of ( \text{Mg}_2\text{Si} )</td>
<td>582°C (1080°F)</td>
<td>93</td>
</tr>
<tr>
<td>( \text{Liq} \rightarrow \text{Al} + \text{Mg}_2\text{Si} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation of complex eutectic</td>
<td>560°C (1040°F)</td>
<td>98</td>
</tr>
<tr>
<td>( \text{Liq} \rightarrow \text{Al} + \text{Mg}_2\text{Si} + \text{Al}_3\text{Fe} + \text{Al}_8\text{Mg}_5 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>End of solidification</td>
<td>536°C (997°F)</td>
<td>100</td>
</tr>
</tbody>
</table>
CHAPTER 3: SCOPE AND OBJECTIVES

The current models under development to predict micropore formation and hot tearing require an understanding of the evolution in fraction solid in the alloys systems to which they are being applied. These models require a detailed understanding of the evolution in fraction solid with temperature and ideally cooling rate. Two example alloys have been selected for study owing to their industrial significance – A356 a commercial foundry alloy prone to microporosity formation and AA5182 a commercial sheet alloy prone to hot tearing during ingot casting.

In the case of A356, a summary of reported transformation temperatures occurring during solidification is given in Table 2.8. This table shows the extent to which there is variability in the reported start temperatures for the various phase transformations that occur in this alloy. There is also disagreement on the effect of strontium modification on precipitation behaviour as Arnberg et al.\cite{Arnberg} claim that it suppresses the eutectic reaction whereas Wang et al.\cite{Wang} claim there is no effect. To this end, one of objectives of this study was to characterize the evolution in fraction solid in modified and unmodified A356 under a range of cooling rates. Ultimately, incorporation of this data into a comprehensive microporosity model should shed light on how microporosity is influenced by strontium modification and lead to the development of better more accurate mathematical process models for the prediction of casting related defects.
It is also clear from comparing previously published that there is poor agreement in the temperature and fraction solid data relating to the solidification sequence of AA5182 particularly at high fraction solids (solidus: 536°C[18], 470°C[22], 577°C[19]). As a second objective the evolution in fraction solid in AA5182 has been quantified under a range of cooling rates. Incorporation of this data into DC casting models should ultimately help to provide more accurate predictions of hot tear incidents that could lead to the reduction of waste material from the ingot base.

A cooling curve analysis technique similar to that used by Bäckerud et al.[20] was used to characterize the temperature of samples during transformation from a liquid to solid state. Analysis of this data allowed accurate identification of the temperature and fraction solid that the liquidus, solidus and several phase transformations in between occurred.
CHAPTER 4: EXPERIMENTAL TECHNIQUES

4.1 Material

The experimental work was performed on two commercially significant alloys: A356, supplied by Canadian Autoparts Toyota Inc. and AA5182, supplied by Alcan International. The chemical compositions of the samples are given in Table 4.1. Three versions of A356 were tested: unmodified, strontium modified and sodium modified. However, microstructural analysis and inductively coupled plasma (ICP) atomic emission spectroscopy indicated that sodium almost completely faded from the sodium modified samples during melting and therefore these results have not been included. The ICP atomic emission spectroscopy results found the sodium content was reduced by 75% from 69mg/kg initially to 24mg/kg after two melting and solidifying cycles.

4.2 Cooling Curve Analysis

The experiments were carried out using the Universal Metallurgical Simulator and Analyzer (UMSA), shown in Figure 4.1. The instrument, designed for analysis of the thermal processes of metal samples, was located in the Department of Mechanical, Automotive and Materials Engineering at the University of Windsor in Windsor, Ontario. The UMSA consisted of a computer controlled heat induction coil that was used to melt and solidify each sample inside a sintered Al₂O₃ cup made up of a very thin sleeve and insulating end caps (see Figure 4.2). Once the samples were at liquid state (above 750°C for at least two minutes) the power was switched off and the metal air-cooled. PC-based thermal analysis apparatus concurrently recorded the temperature/time data (energy...
signature) of the sample via a ceramic-coated K-type thermocouple in order to identify the transformations that occurred during solidification.

A variety of cooling rates were investigated ranging from 0.3-1.4°C/s for the A356 samples and 0.52-1.99°C/s for the AA5182 samples as shown in Table 4.2. In Table 4.2, the samples designated 3UN were unmodified A356, those designated 3SR were A356 modified with strontium and those designated 518 were AA5182. The different cooling rates for each alloy were due to the cooling rate control methods available, namely air cooling with and without insulation and forced air-cooling.

Samples were 14mm in diameter and 18mm in length to allow for conditions approaching isothermal cooling over the range of cooling conditions examined. The thermocouple was placed in a central cavity within the sample as shown in Figure 4.2. For each experiment two heating/cooling cycles were carried out in order to first melt the metal to ensure good contact between the insulated thermocouple and the sample and second measure the temperature under different cooling conditions. The resulting two cooling curves served to assess the repeatability of the tests, however, the reproducibility was not considered.

4.3 Microstructural Analysis

After testing, the samples were horizontally sectioned through the centerline shown as A-A in Figure 4.2 and polished to a 1µm finish using commercial diamond slurry. The resulting surface was sufficient for metallographic observation of the A356 samples, however, the AA5182 samples were further polished to a 0.5µm finish with colloidal
silica slurry and etched using Kroll’s reagent (920ml distilled water, 60ml nitric acid, 20ml hydrofluoric acid).

Optical micrographs (x10) were taken of the surfaces under polarized light using a Nikon Epiphot 300. Elemental mapping of the 1μm polished surfaces using the Back Scattered Electron (BSE) mode of a Hitachi S-3000N Scanning Electron Microscope (SEM) provided qualitative maps of silicon, magnesium and iron content throughout the microstructure (x500). Pixera Viewfinder and Quartz PCI Image Management software packages were also used to produce micrographs.

4.4 Volume Fraction Analysis

A Leitz Orthoplane Microscope together with CIMAGEING Incorporated’s Simple™ image analysis software were used following the ASTM E1245-89 standard (Determining Inclusion Content of Steel and Other Metals by Automatic Image Analysis). Fifty fields at 8x magnification were analyzed on through-sectioned surfaces polished to 1μm in the case of A356 samples and 0.5μm in the case of AA5182 samples. The software calculated volume fractions based on greyscale images of the microstructure and the operator defined greyscale limits of each phase as well as select the size of small anomalies to ignore.
### Table 4.1: Composition of A356 and AA5182 Samples (wt%)

<table>
<thead>
<tr>
<th>Composition</th>
<th>A356 (Unmodified)</th>
<th>A356 (Strontium Modified)</th>
<th>AA5182</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>7.28</td>
<td>7.25</td>
<td>0.006</td>
</tr>
<tr>
<td>Mg</td>
<td>0.3</td>
<td>0.34</td>
<td>4.66</td>
</tr>
<tr>
<td>Fe</td>
<td>0.14</td>
<td>0.12</td>
<td>0.21</td>
</tr>
<tr>
<td>Ti</td>
<td>0.11</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.0011</td>
<td>0.0012</td>
<td>-</td>
</tr>
<tr>
<td>Sr</td>
<td>0.0032</td>
<td>0.0119</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>0.011</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>0.002</td>
<td>0.002</td>
<td>0.31</td>
</tr>
<tr>
<td>Cu</td>
<td>0.001</td>
<td>0.001</td>
<td>0.057</td>
</tr>
<tr>
<td>Zn</td>
<td>0.003</td>
<td>0.006</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>0.002</td>
<td>0.002</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>0.002</td>
<td>0.0042</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
</tr>
</tbody>
</table>

### Table 4.2: Sample Codes and Cooling Rates

<table>
<thead>
<tr>
<th>Insulation Type</th>
<th>Sample Code</th>
<th>(Cooling Rate [°C/s])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic + Jacket</td>
<td>SR-B (0.3)</td>
<td>UN-B (0.3)</td>
</tr>
<tr>
<td>Ceramic</td>
<td>SR-A (0.5)</td>
<td>UN-A (0.5)</td>
</tr>
<tr>
<td>Ceramic + Forced External Air Flow</td>
<td>SR-C (1.3)</td>
<td>UN-C (1.4)</td>
</tr>
</tbody>
</table>
Figure 4.1: UMSA equipment (Courtesy of J Sokolowski, Windsor University).
Figure 4.2: Sample construction.
5.1 Cooling Curve Analysis and Results

Solidifying each sample using the UMSA equipment provided temperature/time data that could be plotted into a cooling curve. This data was processed to provide first derivative data so that it could be plotted against temperature \((dT/\text{dt} \text{ Vs } T)\) in order to identify peaks in the first derivative. These peaks allowed identification of the start temperature of new phases since they represented alterations in cooling rate, initiated by latent heat evolved due to phase changes. After identification of these phase changes, particularly the solidus and liquidus, fraction solid values could be estimated at any time throughout the mushy zone using the method described below.

5.1.1 Cooling Curves

During each heating and cooling cycle raw time/temperature data was recorded and plotted as shown in Figure 5.1 which shows the cooling curve of unmodified A356 cooled at a rate of 0.52°C/s. The expanded region in Figure 5.1 shows the time period when the sample cooled and transformed from liquid to solid (mushy zone). Two major features can readily be seen from the data presented in this form: (A) a temperature recalescence associated with nucleation and growth of equiaxed primary \(\alpha\)-Al phase and (B) a temperature plateau associated with growth of a primary eutectic phase. The reason the temperature ceases to drop at these points is due to large amounts of latent heat being released at the start of primary phase precipitation. Secondary reactions only release small amounts of latent heat and tend to take place over a narrow temperature interval.
and therefore can only be identified using the first derivative of temperature with respect to time \((dT/dt)\) where they are revealed as sharp peaks\(^{22}\).

### 5.1.2 First Derivative

**Figures 5.2** and **5.3** show first derivative plots for the unmodified A356 sample cast at 0.52°C/s and the AA5182 sample cast at 0.97°C/s respectively. The data encompassing the solid to liquid phase transformation has been smoothed (using a proprietary technique based on an interpolation matrix from the University of Windsor) and the section of the plot expanded. The three main peaks seen in each plot can be associated with the start of three dominant phase transformations occurring during solidification - primary \(\alpha\)-aluminum, primary eutectic (Al-Si for A356, \(\text{Al}_6(\text{FeMn})\) for AA5182) and \(\text{Mg}_2\text{Si}\) precipitation - according to data published on A356 and AA5182\(^{8, 20, 22}\).

### 5.1.3 Baseline and Fraction Solid

Apart from the start temperatures, the solid fraction at the start of each transformation can also be obtained from the cooling curve data using the method originally described by Stefanescu et al\(^{23}\) and extensively used by others\(^{24-26}\). The method hinges on the following 4 main assumptions:

1. Internal conduction within the sample can be ignored and the cooling behaviour of the molten metal can be considered to be isothermal – e.g. Biot number less than 0.1. The Biot number \((hL/k)\) is a measure of internal heat resistance \((L/k)\) over
external heat resistance \((1/h)\) where \(l\) is the sample length, \(k\) is the thermal conductivity and \(h\) is the heat transfer coefficient of the sample.

2. During solidification the volumic specific heat of the metal remains constant and does not vary significantly with temperature.

3. The rate of release of latent heat for each of the transformations occurring during the solidification sequence is the same per unit amount transformed.

4. The rate of heat extraction from the sample can be described by a Cauchy type boundary condition in which the heat transfer coefficient and sink temperature are constant over the solidification temperature range.

Assumption 1 is reasonable given the relatively small size of the sample, the relatively low external cooling conditions and the relatively high conductivity of the alloys. Latent heat evolved throughout the mushy zone region also helps to maintain isothermal conditions since it reduces temperature gradients within the sample. Estimates for the Biot number for the experiments place it in the range of \(1 \times 10^{-3}\) to \(2.9 \times 10^{-3}\) for A356 at the low and high cooling rate cases respectively, and \(1.5 \times 10^{-3}\) to \(3.9 \times 10^{-3}\) for AA5182 at the low and high cooling rate cases respectively, all of which are well below the 0.1 limit for isothermal type behaviour. The material properties and boundary conditions used in the above analysis are given in Table 5.1.

Assumption 2 is probably not unreasonable since the difference between specific heat in the solid and liquid phase of a metal is generally very small\(^{[22]}\), although a value for the volumic specific heat of the A356 liquid could not be found. The volumic specific heat of
the A356 solid is reported to be $2.59 \times 10^6 \text{ Jm}^{-3}\text{K}^{-1}$ at 100°C\cite{19}. For AA5182 the volumic specific heat is reported to be $2.40 \times 10^6 \text{ Jm}^{-3}\text{K}^{-1}$ at 20°C\cite{27} and $2.91 \times 10^6 \text{ Jm}^{-3}\text{K}^{-1}$ at 640°C\cite{28}.

As far as assumption 3 is concerned a review of the literature indicates that the latent heat for A356 is $10.43 \times 10^8 \text{ Jm}^{-3}$\cite{19,27}, the latent heat of a Al-Si eutectic alloy is $8.1 \times 10^8 \text{ Jm}^{-3}$\cite{29}, the latent heat of pure Al is between $10.72 \times 10^8 \text{ Jm}^{-3}$\cite{30,31} and $10.45 \times 10^8$\cite{27,32} and the latent heat for AA5182 is $10.52 \times 10^8 \text{ Jm}^{-3}$\cite{28} (based on a rule of mixtures). This data shows that there is around a 24% difference between the latent heat of pure aluminum and that of Al-Si eutectic hence assumption 3 is likely to introduce a small error in the A356 fraction solid data calculated, however, the phase transformation temperatures will be unaffected.

Finally, assumption 4 is felt to be reasonable because radiation effects are likely to be small over the temperature range examined and convective heat transfer to air is expected to have only a small dependence on temperature over the range examined in the study.

Based on assumptions 1 through 4 and on energy conservation, the following simplified expressions can be developed to describe the rate of change of temperature in the sample within the solid-liquid (S/L) phase transformation temperature range, Equation [1], and outside the transformation temperature range, Equation [2].

\[
\left( \frac{dT}{dt} \right)_{pt} = -\frac{hA(T - T_m)}{C_p V} + \left( \frac{L}{C_p} \right) \left( \frac{df}{dt} \right) \tag{1}
\]
\[
( dT / dt )_{npt} = - \frac{hA(T - T_\infty)}{C_pV}
\]  \[2\]

where: 

- \( h \) = heat transfer coefficient (Jm\(^{-2}\)K\(^{-1}\))
- \( A \) = surface area of the crucible (m\(^2\))
- \( T_\infty \) = surrounding temperature (°C)
- \( t \) = time (sec)
- \( L \) = latent heat (Jm\(^{-3}\))
- \( V \) = volume of sample (m\(^3\))
- \( C_p \) = volumic specific heat (Jm\(^{-3}\)K\(^{-1}\))
- \( f_s \) = fraction solid


\[
L(df_s / dt) = C_p[(dT / dt)_{pt} - (dT / dt)_{npt}]
\]  \[3\]

where the subscripts on the differentials \( pt \) and \( npt \) refer to phase transformation and no phase transformation respectively. Integrating Equation [3] with the limits given below yields the total latent heat.

\[
L \int_{0}^{t} df_s = C_p \int_{0}^{t} [(dT/dt)_{pt} - (dT/dt)_{npt}] dt
\]  \[4\]
where \( t_l \) is the time at liquidus temperature and \( t_s \) is the time at solidus temperature.

The ratio of the fractional latent heat (latent heat at any fraction solid \( f_s \) or time \( t \)) to the total latent heat is given as follows:

\[
\begin{align*}
\int_{t_l}^{t_s} \left[ (dT/dt)_{pt} - (dT/dt)_{npt} \right] dt \\
\int_{t_l}^{t_s} \left[ (dT/dt)_{pt} - (dT/dt)_{npt} \right] dt
\end{align*}
\]

\[ f_s = \frac{\int_{t_l}^{t} [(dT/dt)_{pt} - (dT/dt)_{npt}] dt}{\int_{t_l}^{t_s} [(dT/dt)_{pt} - (dT/dt)_{npt}] dt} \tag{5} \]

and may be set equal to the fraction solid \( f_s \) at any time \( t \) residing between \( t_l \) and \( t_s \). This allows the specific heat term to be dropped out.

With this technique the fraction solid at any time/temperature can be estimated providing the variation in the derivative of the temperature in the absence of the phase transformation can be estimated. This so-called base line curve has been estimated in this work by simply curve fitting the base line data below the solidus and above the liquidus using a third order polynomial\(^{[33]}\). This relationship is assumed to hold in the S-L phase change temperature region. Other studies\(^{[24-26]}\) have adopted a slightly different approach whereby the form of the extrapolating function is based on an analytical solution of Equation 1, which is then fitted to the data below the solidus and above the liquidus using a least squares approach. The result is virtually identical. Figure 5.4 shows the base line curve added to the unmodified A356 diagram using the polynomial approach, solidus and
liquidus temperatures are also identified. The 3\textsuperscript{rd} order polynomial yielded a correlation coefficient of greater than 0.999 and an example is given below in Equation [6].

\[
\frac{dT}{dt}_{\text{npt}} = AT^3 + BT^2 + CT + D \tag{6}
\]

where A is $7.25 \times 10^9$, B is $1.05 \times 10^6$, C is $-1.75 \times 10^3$ and D is -0.44 for unmodified A356 cooled at a rate of 0.52°C/s.

Equation 5 was calculated in practice using simple numerical integration (quadrature method). The area between the first derivative and baseline curves was divided into equal sized rectangular segments where the height was measured using values of the first derivative minus the baseline and the width was determined by the time-step used during UMSA data acquisition (0.2 seconds). An example of the data obtained from the analysis is presented in Figure 5.5 which shows the variation in fraction solid with temperature for the unmodified A356 sample cast at a cooling rate of 0.52°C/s.

Cooling rate was calculated using the change in temperature over the change in time from the start ($f_s=0$) to the end ($f_s=1$) of the mushy zone. From this data the fraction solid at the start of primary eutectic growth, Mg$_2$Si precipitation and the solidus temperature can be established using values corresponding to the first derivative peaks as shown in Figure 5.6.

5.1.4 Cooling Curve Data

The data for all three cooling rates (low, intermediate and high), for unmodified and strontium modified A356 have been summarized and are presented in Tables 5.2 and 5.3.
The AA5182 data have been summarized and presented in Tables 5.4 and 5.5. Some of the peaks were impossible to identify using this approach and therefore corresponding sections of Tables 5.4 and 5.5 have been left blank.

Plots have been generated to display the effects of cooling rate on first derivative as well as fraction solid evolution: Figures 5.7, 5.8 and 5.9 show these results for unmodified A356, strontium modified A356 and AA5182 respectively. Further plots have been generated showing the start temperatures and fraction solids as a function of cooling rate for all materials and are shown in Figures 5.10 and 5.11 for modified and unmodified A356 and Figures 5.12 and 5.13 for AA5182. In most of the tests the reproducibility in the measured start temperature was quite good and was found to be within approximately 1°C for A356 and 3°C for AA5182. Exceptions to this trend found in the A356 data include: 1) in two cases (primary eutectic start temperature at 0.3°C/s and primary eutectic start temperature at 1.4°C/s in the unmodified sample) the reproducibility was found to be poorer but still within 4°C; 2) the repeatability of the solidus temperature at the highest cooling rates was poor for the modified alloy and for the unmodified alloys - within 15°C and 19°C, respectively. Exceptions found in the AA5182 data include: 1) the start temperature for primary α-Al at the lowest cooling, which was poorer (within 9°C); 2) the start temperature for primary eutectic and solidus at the intermediate cooling rate (between 5 and 9°C); 3) the start temperature of Mg2Si at the highest cooling rate (8°C); and 4) the solidus temperature at the highest cooling rate (21°C).
5.2 Structure Evaluation

5.2.1Metallographic Analysis and Results

A356

Figures 5.14 and 5.15 show the microstructures of both unmodified (a) and strontium modified (b) A356 samples under polarized light and as back scattered electron images, respectively. The dark areas in Figure 5.14 are the eutectic features and it can clearly be seen that they are acicular plates in the unmodified sample and a more fibrous phase in the modified sample. Bäckerud et al.\textsuperscript{[20]} identify grey Si particles, brown ‘script’ regions of Al\(_8\)Mg\(_3\)FeSi\(_6\) and black localized regions of Mg\(_2\)Si within the eutectic region. Arnberg et al.\textsuperscript{[8]} recognize the same features and in addition identify Al\(_5\)FeSi needles with brown colouring.

Figure 5.15 displays quantitative maps of silicon levels throughout the microstructures. The higher the intensity of the light phase, the higher the concentration of that element. There are definite regions in Figures 5.15a and 5.15b where Si, Fe and Mg are intense which may signify the presence of Al\(_8\)Mg\(_3\)FeSi\(_6\). Figure 5.15b illustrates areas where Si and Fe intensity is high but no Mg appears, these can be seen as long thin sections on the backscattered image and probably signify Al\(_5\)FeSi needles. The silicon images also illustrate the effect of strontium modification on breaking down Al-Si eutectic into a more interconnected fibrous phase.
Figures 5.16 and 5.17 show the microstructure of AA5182 under polarized light and as back scattered electron images, respectively. Figure 5.16a is a micrograph of the sample cooled at 0.52°C/s, Figure 5.16b was cooled at 0.97°C/s and Figure 5.16c at 1.99°C/s. The light phase clearly shows the primary α-Al dendrites which occupy approximately 80-90% of the microstructure. The eutectic features have been preferentially attacked during etching. There appears to be a slight reduction in the size of the secondary dendrites arm spacing with increased cooling rates. However, it is difficult to analyze this accurately since the sample cooled at 1.99°C/s etched very quickly and it was therefore difficult to prevent over-etching. It can be seen that AA5182 possesses an equiaxed dendritic structure.

Arnberg et al. and Bäckerud et al. studied AA5182 unetched samples polished to a 1μm finish and reported finding Mg₂Si regions that appear black under an optical microscope, (Arnberg et al. locate them along grain boundaries). Arnberg et al. also describe finding long small needles of Al-Mg-Fe-Mn. Bäckerud et al. report needles of Al₃Fe and large angular particles of Al₆FeMn.

Figure 5.17 displays qualitative maps of silicon, magnesium and iron levels throughout the microstructure (the top left quarter is a backscattered electron image of the same region). It appears that iron is concentrated in the interdendritic eutectic region, indicating the possible presence of Al₆(FeMn) or Al₃Fe in these areas. Magnesium has very high concentrations in selected areas where silicon is also found, indicating areas of Mg₂Si.
The presence of Mg in the eutectic region where there appears to be a low concentration of silicon could signify Al₃Mg₅.

5.2.2 Volume Fraction Analysis and Results

Quantification of the volume fraction of primary-α phase present in the fully solidified structure was attempted in order to validate fraction solid evolution calculations. The results displayed in Table 5.6 show the results measured using the ‘Simple’ Image analysis technique. The numbers in brackets were calculated by assuming that the only phase measured during unmodified A356 analysis was silicon due to its final microstructure. The A356 eutectic is Al-Si so a 50:50 content of Al to Si was assumed, producing a eutectic content twice that of the one originally measured. Published results[8] state the primary-α volume fraction in A356 to be 51% and the AA5182 primary-α content to be 40%. The measured results were deemed inconclusive due to the inability to accurately define the boundaries of primary-α regions.

5.3 Discussion

5.3.1 A356

Comparison with Published Data

Tables 5.2 and 5.3 indicate that the unmodified samples cooled at 0.52°C/s, 0.3°C/s and 1.5°C/s show very similar findings to those reproduced in Tables 2.4[8] and 2.5[20] as well as those published by Wang et al.[21] and Mackay et al.[2]. Primary α-Al was found to start solidifying at 608°C-619°C c.f. 610°C[8] and 604°C-615°C[20], primary eutectic solidification began at slightly higher temperatures: 569°C-575°C c.f. to 568°C[8] and
554°C-564°C\textsuperscript{[20]}. Mg\textsubscript{2}Si precipitation was found to begin at 554°C-557°C in \textbf{Table 5.2} c.f. 557°C\textsuperscript{[8]} and 534°C-561°C\textsuperscript{[20]}. The solidus was reached at 468-543°C c.f. 543°C\textsuperscript{[8]} and 554°C\textsuperscript{[20]}. The low solidus temperatures in the current study were from the highest cooling rates studied. It is not clear what cooling rate Arnberg \textit{et al.}\textsuperscript{[8]} used and Bäckerud \textit{et al.}\textsuperscript{[20]} only give one solidus value for the whole study even though they assessed A356 at three different cooling rates. The fraction solids that have been reported in the current study for unmodified A356 cooled at 0.52°C/s and by Arnberg \textit{et al.}\textsuperscript{[8]} for the start of solidification of each phase were exceptionally close and within 0.01.

\textit{Modification Effects}

The overall trend in the data shown in \textbf{Figure 5.10} is that alloy modification tends to decrease transformation start temperature. Specifically, the results for the primary eutectic and Mg\textsubscript{2}Si start temperatures show a consistent decrease with strontium addition for all three of the cooling rates examined. The magnitude of the drop in the primary eutectic ranged from 3 to 9°C and in Mg\textsubscript{2}Si from 5 to 11°C. The observed drop in the primary eutectic start temperature is consistent with the findings of previous studies\textsuperscript{[3, 5, 8]}. The notable exceptions to this trend are in the case of the primary $\alpha$-Al start temperature at the high cooling rate, which exhibits an increase of approximately 3°C with modification, and in the solidus temperature at the high cooling rate, which exhibits an increase of around 22°C. These results, however, are questionable owing to the poor reproducibility in the high cooling rate tests.
**Cooling Rate Effects**

The general trend in the data shown in Figure 5.10 for cooling rate is that an increase tends to slightly decrease transformation start temperatures. In the unmodified samples the primary $\alpha$-Al start temperature drops from 619°C to 608°C and the solidus temperature falls from 542°C to 468°C. In the modified samples the start of primary eutectic solidification drops from 569°C to 565°C; Mg$_2$Si precipitation falls from 552°C to 544°C and the solidus drops from 538°C to 490°C. The exceptions are the start temperatures of the unmodified primary eutectic solidification which rises from 572°C to 576°C (at cooling rates of 0.29°C/s and 0.52°C/s respectively); Mg$_2$Si precipitation in the unmodified samples which rises from 554°C to 555°C (at cooling rates of 0.52°C/s to 1.5°C/s) and primary $\alpha$-Al solidification in the modified samples which maintains a start temperature of 611°C at cooling rates of 0.53°C/s and 1.34°C/s.

**Freezing Range**

Figure 5.10 also illustrates how the overall freezing range varied with cooling rate. In the unmodified samples, the freezing range was 76°C at the lowest cooling rate compared to 140°C at the highest. In the modified samples the range varied from 78°C to 121°C from the lowest to the highest cooling rate. There appears to be minimal difference between the freezing ranges for the low and intermediate cooling rate samples. The effect of strontium modification does not appear to alter the freezing range except for reducing it from 140°C to 121°C at the highest cooling rate. However, it should be noted that the repeatability at the highest cooling rates was poor and these results are questionable. Arnberg *et al.*[8] reported a freezing range of 67°C for unmodified A356 and 70°C for
0.02 strontium modified A356. Bäckerud et al.\textsuperscript{[20]} reported a freezing range of 71°C for unmodified A356 cooled at a rate of 0.3°C/s and 95°C for unmodified A356 cooled at a rate of 5°C/s. This data supports the findings of the current study that increasing cooling rate can increase the freezing range of A356.

\textit{Fraction Solid}

The fraction solid data is presented in Figure 5.11. The results show that strontium modification causes a slight increase in the fraction solid that primary eutectic begins to form at (increasing the amount of primary \(\alpha\)-Al present) and a slight increase in the fraction solid that \(\text{Mg}_2\text{Si}\) begins to form at. Cooling rate appears to have little overall effect on the fraction solid that primary eutectic and \(\text{Mg}_2\text{Si}\) begin to precipitate.

\textbf{5.3.2 AA5182}

\textit{Comparison with Published Data}

Comparing the data from the current study with that from work previously published by Arnberg \textit{et al.}\textsuperscript{[8]} and Bäckerud \textit{et al.}\textsuperscript{[22]} the following observations can be made: Firstly, Table 5.4 shows a slightly lower start temperature for primary \(\alpha\)-Al solidification compared to Table 2.13 (624-633°C c.f. 637°C) but is consistent with Bäckerud \textit{et al.}'s findings in Table 2.12: 628-632°C. However, Arnberg \textit{et al.}\textsuperscript{[8]} and Bäckerud \textit{et al.}\textsuperscript{[22]} describe the start of solidification temperature as the point where the derivative suddenly deviates from the baseline, which is slightly different than the method used by the authors of the current work who chose to use the tip of the first peak in the derivative. Secondly, the start of primary eutectic precipitation is different. In Table 5.4 the primary eutectic
was found to begin solidifying between 575-588°C which corresponds to a solid fraction of 0.87-0.91. Whereas, in Table 2.13 it is reported to begin solidifying at 623°C and 0.4 fraction solid and in Table 2.12 it is reported to begin solidifying between 617°C and 621°C. Thirdly, the start temperature of Mg₂Si precipitation is reported to be at a much lower temperature and corresponding higher fraction solid in Tables 5.4 and 5.5: 551-560°C and 0.96-0.97 fraction solid compared to Table 2.13: 582°C and 0.93 fraction solid and Table 2.12: 571-586°C. Another discrepancy appears to be the solidus temperature which is reported to be much lower in Table 5.4 compared to Table 2.13 (461-510°C c.f. 536°C). However the solidus temperature in the current work corresponds more closely to the report by Bäckerud et al.²² that suggests the solidus temperature could be 470°C based on the Al-Si-Fe phase diagram. Both Arnberg et al.⁸ and Bäckerud et al.²² define the end of solidification point as shown in Figure 5.18 whereas the current study used the temperature corresponding to where fraction solid equals one according to the data analysis.

From the above comparison, it appears that the data from the two studies may have been interpreted differently. For example, in this study the peaks identified as the primary eutectic and Mg₂Si appear to correspond to those identified by Arnberg et al.⁸ and Bäckerud et al.²² as the Mg₂Si and complex eutectic peaks respectively. It can be seen from their first derivative and cooling data plots, Figure 5.19, that the peak they have identified as the main eutectic reaction is very close to the primary-α peak. This could mean that it is being confused with the strong temperature recalesence and subsequent plateau due to nucleation and growth of primary-α, which is clearly shown by the cooling
curve. Turning to the photomicrographs, Figure 5.16, it can be seen that primary $\alpha$-Al dendrites occupy ~80-90% of the microstructure, which would appear to support the findings of this study. Furthermore, the back scattered electron images of the microstructure appearing in Figure 5.17, do not show any appreciable evidence of Fe present in the primary structure consistent with the transformation of Liq→$\alpha$-Al+$\text{Al}_6(\text{FeMn})$ at solid fractions around 0.4. It is only present in the eutectic structure formed in the later stages of solidification at fraction solids greater than 0.8. The Al-Fe-Mn phase diagram shown in Figure 5.20 was also studied for further clarification, however, the ternary eutectic occurs just below 660°C which is still above the liquidus temperature of A356. Finally, studies on the solidification of A356 indicted Mg$_2$Si precipitation in the range from 557 to 534°C depending on alloy modification and cooling rate, which is also in better agreement with the findings of this study.

Cooling Rate

Figure 5.12 illustrates the overall trend of increasing cooling rate on the start temperatures of phase precipitation. Generally the start temperatures either show no effect or a slight decrease with increasing cooling rate. The primary $\alpha$-Al start temperature hardly varies with cooling rate (632-633°C); primary eutectic precipitation temperature slightly decreases with increasing cooling rate (587°C to 578°C to 575°C); Mg$_2$Si precipitation does not appear to be affected by cooling rate (557-560°C). The exception is solidus temperature which occurs at approximately the same temperature at the low and intermediate cooling rates (500°C-510°C) but drops quite dramatically at the highest cooling rate to 461°C.
Freezing Range

**Figure 5.12** also illustrates the effect of cooling rate on the freezing range of AA5182. Focusing on the second cooling cycle for each sample shows that there is no difference in freezing range between the lower cooling rate compared with the intermediate cooling rate (123°C), however, at the highest cooling rate the freezing range is increased to 151°C. A previous study by Bäckerud *et al.* \(^{22}\) suggests that cooling rate has no effect on solidification interval, however, they chose a fixed value from the Al-Fe-Si phase diagram of 470°C as the end of solidification for each cooling rate studied.

**Fraction Solid**

The fraction solid data presented in **Figure 5.13** illustrates that increasing cooling rate appears to have very little effect on fraction solid evolution. Increasing cooling rate appears to slightly increase the fraction solid that primary eutectic precipitates at (0.87-0.88 at the low cooling rate, 0.89-0.91 at the intermediate cooling rate and 0.91 at the highest) but has little or no overall effect on the fraction solid that Mg₂Si precipitates at.
Table 5.1: Material Properties and Boundary Conditions Used for Biot Number Analysis

<table>
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<th>Material</th>
<th>Heat Transfer Coefficient, h Js⁻¹ m⁻² K⁻¹</th>
<th>Thermal Conductivity¹⁹⁾, k Js⁻¹ m⁻¹ K⁻¹</th>
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<tr>
<td>A356 (Low Cooling Rate)</td>
<td>28</td>
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<tr>
<td>A356 (High Cooling Rate)</td>
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<td>151-161</td>
<td>0.007</td>
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<td>AA5182 (Low Cooling Rate)</td>
<td>26.5</td>
<td>127</td>
<td>0.007</td>
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<tr>
<td>AA5182 (High Cooling Rate)</td>
<td>7</td>
<td>127</td>
<td>0.007</td>
</tr>
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Table 5.2: A356 Temperatures for Start of Primary α-Al, Primary Eutectic, Mg₂Si and Solidus

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling Rate (°C/s)</th>
<th>Primary α-Al Unmodified</th>
<th>Primary Eutectic Unmodified</th>
<th>Mg₂Si Unmodified</th>
<th>Solidus Unmodified</th>
</tr>
</thead>
<tbody>
<tr>
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<td>537</td>
</tr>
<tr>
<td>3UNCC 1</td>
<td>1.5</td>
<td>608</td>
<td>569</td>
<td>555</td>
<td>468</td>
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<tr>
<td>3UNCC 2</td>
<td>1.43</td>
<td>608</td>
<td>573</td>
<td>555</td>
<td>487</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling Rate (°C/s)</th>
<th>Primary α-Al Modified</th>
<th>Primary Eutectic Modified</th>
<th>Mg₂Si Modified</th>
<th>Solidus Modified</th>
</tr>
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<tbody>
<tr>
<td>3SRB 1</td>
<td>0.29</td>
<td>616</td>
<td>569</td>
<td>552</td>
<td>538</td>
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<td>3SRB 2</td>
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<td>568</td>
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<tr>
<td>3SRA 1</td>
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<td>611</td>
<td>567</td>
<td>548</td>
<td>532</td>
</tr>
<tr>
<td>3SRA 2</td>
<td>0.53</td>
<td>611</td>
<td>567</td>
<td>550</td>
<td>533</td>
</tr>
<tr>
<td>3SRC 1</td>
<td>1.34</td>
<td>611</td>
<td>566</td>
<td>545</td>
<td>490</td>
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<tr>
<td>3SRC 2</td>
<td>1.27</td>
<td>611</td>
<td>565</td>
<td>544</td>
<td>505</td>
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</table>


Table 5.3: Fraction Solid for Start of Primary α-Al, Primary Eutectic, Mg₂Si and Solidus of A356

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling Rate (°C/s)</th>
<th>Primary α-Al Unmodified</th>
<th>Primary Eutectic Unmodified</th>
<th>Mg₂Si Unmodified</th>
<th>Solidus Unmodified</th>
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<tr>
<td>3UNB 3</td>
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<td>0.52</td>
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<td>0.52</td>
<td>0.96</td>
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<tr>
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<td>0.96</td>
<td>1</td>
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<td>1.5</td>
<td>0</td>
<td>0.52</td>
<td>0.96</td>
<td>1</td>
</tr>
<tr>
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<td>1.43</td>
<td>0</td>
<td>0.49</td>
<td>0.95</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling Rate (°C/s)</th>
<th>Primary α-Al Modified</th>
<th>Primary Eutectic Modified</th>
<th>Mg₂Si Modified</th>
<th>Solidus Modified</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.29</td>
<td>0</td>
<td>0.52</td>
<td>0.98</td>
<td>1</td>
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<tr>
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<td>0.3</td>
<td>0</td>
<td>0.52</td>
<td>0.98</td>
<td>1</td>
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<tr>
<td>3SRA 1</td>
<td>0.54</td>
<td>0</td>
<td>0.52</td>
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<td>1</td>
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<tr>
<td>3SRA 2</td>
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<td>0</td>
<td>0.53</td>
<td>0.98</td>
<td>1</td>
</tr>
<tr>
<td>3SRC 1</td>
<td>1.34</td>
<td>0</td>
<td>0.53</td>
<td>0.99</td>
<td>1</td>
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<tr>
<td>3SRC 2</td>
<td>1.27</td>
<td>0</td>
<td>0.54</td>
<td>0.99</td>
<td>1</td>
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</tbody>
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Table 5.4: AA5182 Temperatures for Start of Primary α-Al, Primary Eutectic, Mg$_2$Si and Solidus

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling Rate (°C/s)</th>
<th>Primary α-Al</th>
<th>Primary Eutectic</th>
<th>Mg$_2$Si</th>
<th>Solidus</th>
</tr>
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<tbody>
<tr>
<td>518B1</td>
<td>0.49</td>
<td>624</td>
<td>587</td>
<td>557</td>
<td>508</td>
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<td>518B2</td>
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<td>588</td>
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<td>510</td>
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<tr>
<td>518A1</td>
<td>0.99</td>
<td>632</td>
<td>578</td>
<td>553</td>
<td>500</td>
</tr>
<tr>
<td>518A2</td>
<td>0.97</td>
<td>632</td>
<td>585</td>
<td>558</td>
<td>509</td>
</tr>
<tr>
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<td>575</td>
<td>551</td>
<td>461</td>
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<td>1.99</td>
<td>633</td>
<td>-</td>
<td>559</td>
<td>482</td>
</tr>
</tbody>
</table>

Table 5.5: Fraction Solid for Start of Primary α-Al, Primary Eutectic, Mg$_2$Si and Solidus of AA5182

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling Rate (°C/s)</th>
<th>Primary α-Al</th>
<th>Primary Eutectic</th>
<th>Mg$_2$Si</th>
<th>Solidus</th>
</tr>
</thead>
<tbody>
<tr>
<td>518B1</td>
<td>0.49</td>
<td>0</td>
<td>0.87</td>
<td>0.97</td>
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<td>2.09</td>
<td>0</td>
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<td>0.97</td>
<td>1</td>
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<tr>
<td>518C2</td>
<td>1.99</td>
<td>0</td>
<td>-</td>
<td>0.96</td>
<td>1</td>
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Table 5.6: Measured Volume Fraction from ‘Simple’ Image Analysis Results

<table>
<thead>
<tr>
<th></th>
<th>Primary α Vf (%)</th>
<th>Eutectic Vf (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3UNA</td>
<td>79.52 (59.04)</td>
<td>20.48 (40.96)</td>
</tr>
<tr>
<td>3SRA</td>
<td>66.74</td>
<td>33.26</td>
</tr>
<tr>
<td>518A</td>
<td>84.39</td>
<td>15.61</td>
</tr>
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</table>

Figure 5.1: Cooling curve of unmodified A356 at 0.52°C/s.
Figure 5.2: First derivative plot of unmodified A356 cooled at 0.52°C/s.

Figure 5.3: First derivative plot of AA5182 cooled at 0.97°C/s.
Figure 5.4: Baseline added to unmodified A356 at 0.52°C/s first derivative plot.

Figure 5.5: Fraction solid plot of unmodified A356 at 0.52°C/s.
Figure 5.6: Fraction solid and first derivative plot of unmodified A356 at 0.52°C/s.

Figure 5.7: First derivative and fraction solid profiles of unmodified A356 at three different cooling rates.
Figure 5.8: First derivative and fraction solid profiles of Strontium Modified A356 at three different cooling rates.

Figure 5.9: First derivative and fraction solid profiles of AA5182 at three different cooling rates.
Figure 5.10: Plot of primary α-Al, primary eutectic, Mg$_2$Si and solidus temperatures in modified and unmodified A356 at three different cooling rates.

Figure 5.11: Plot of primary eutectic and Mg$_2$Si fraction solid in modified and unmodified A356 at low, intermediate and high cooling rates.
Figure 5.12: Plot of primary $\alpha$-Al, primary eutectic, $\text{Mg}_2\text{Si}$ and solidus temperatures in AA5182 at low, intermediate and high cooling rates.

Figure 5.13: Plot of primary eutectic and $\text{Mg}_2\text{Si}$ fraction solid in AA5182 at low, intermediate and high cooling rates.
Figure 5.14a: Micrograph of unmodified A356 under polarized light (cooled at 0.5°C/s).

Figure 5.14b: Micrograph of strontium modified A356 under polarized light (cooled at 0.5°C/s).
Figure 5.15a: Backscattered electron images of unmodified A356 (Cooled at 0.5°C/s) highlighting Si, Fe and Mg regions.

Figure 5.15b: Backscattered electron images of strontium modified A356 (Cooled at 0.5°C/s) highlighting Si, Fe and Mg regions.
Figure 5.16a: Micrograph of AA5182 under polarized light (cooled at 0.5°C/s).

Figure 5.16b: Micrograph of AA5182 under polarized light (cooled at 1°C/s).
Figure 5.16c: Micrograph of AA5182 under polarized light (cooled at 2°C/s).

Figure 5.17: Backscattered electron images of AA5182 (cooled at 1°C/s) highlighting Si, Fe and Mg regions.
Figure 5.18: Determination of end of solidification as determined by Bäckerud et al.\textsuperscript{[22]}

Figure 5.19: First derivative and cooling data for AA5182 after Bäckerud et al.\textsuperscript{[22]}
Figure 5.20: Al-Fe-Mn Ternary Phase Diagram\textsuperscript{[34]}
CHAPTER 6: CONCLUSIONS

The following main conclusions can be drawn from this work:

1. Strontium clearly modified the A356 Al-Si primary eutectic to a much finer, more fibrous phase.

2. Strontium generally retarded the transformation of new phases during solidification of A356 to lower temperatures. The drop in temperature ranged from 2°C to 11°C. There was an increase of 3°C for the nucleation of primary α-Al at the fastest cooling rate, which is suspect owing to poor reproducibility in the high cooling rate tests.

3. Strontium modification increased fraction solid for the start of primary eutectic transformation and Mg$_2$Si precipitation in A356. The increase in fraction solid ranged from 0.01 to 0.05.

4. Cooling rate appeared to have little or no influence on fraction solid evolution in A356.

5. Faster cooling rates appeared to lower the solidus temperature of A356. The decrease in solidus temperature ranged from 48°C to 75°C at the highest cooling rate examined.

6. The freezing range of A356 was increased substantially at the highest cooling rate from approximately 76°C to 140°C in unmodified A356 and from 78°C to 121°C in strontium modified A356.

7. In AA5182, the solidification of primary eutectic and subsequent phases was identified from cooling curve analysis to occur at a lower temperature and fraction solid than has been previously reported$^{[11,12]}$. 

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8. Increasing cooling rate of AA5182 was observed to result in a slight increase in fraction solid for primary eutectic transformation (0.87 at the low cooling rate to 0.91 at the highest). The highest cooling rate also resulted in a drop in solidus temperature to 461°C from 500-510°C (at the low and intermediate cooling rates) which led to an increase in the freezing range from 123°C to 151°C.

Overall the results of this study indicate that the effects of cooling rate and alloy modification on the evolution in fraction solid in A356 are significant and should not be ignored in the context of trying to predict microporosity. Firstly, it is important to correctly quantify the rate of change in fraction solid with time as it impacts on the overall heat balance (through latent heat evolution) and the development of thermal gradients. The latter in turn influences interdendritic feeding lengths. Secondly, the correct evolution in fraction solid is needed to predict the evolution in the local shrinkage pressure – i.e. the rate of evolution in fraction solid is linked directly to the local pressure differential needed to supply liquid. Thirdly and finally, the correct freezing range is needed as it impacts on the overall feeding length and evolution in the local shrinkage pressure. It remains to be determined if these effects are sufficient to give rise to the higher microporosity amounts observed with strontium modification.

The temperature and solidification sequence of AA5182 was found to be slightly different than those reported in other studies\[^{8,22}\]. It is suggested that primary eutectic does not begin to solidify until lower temperature and higher fraction solid. This has been based on the knowledge of Mg\(_2\)Si precipitation in other systems (such as aluminum alloy
A356) as well as analysis of the microstructure of completely solidified AA5182 which shows over 80% primary \(\alpha\)-Al dendrites present. These dendrites do not show any appreciable content of Fe which is consistent with primary eutectic \([\text{Al}_6(\text{FeMn})]\) solidifying at a fraction solid higher than 0.8. Increasing cooling rate lowers solidus temperature and expands the solidification interval of AA5182. This is reported to increase susceptibility to hot tearing due to an increased time available for stress build-up.
CHAPTER 7: FUTURE WORK

Since this work identifies such different start temperatures and fraction solid for the solidification of phases during AA5182 casting it would be prudent to design tests to accurately identify these phases as they occur. For example, it may be possible to quench samples from specific temperatures when it is predicted that new phases begin to solidify. This would enable the microstructure to be accurately analyzed before the final eutectics have been given time to solidify.

Due to the nature of the UMSA equipment the cooling rates studied during this work were the fastest possible in order to maintain isothermal cooling conditions. It would be useful to adapt the equipment to conduct tests at faster cooling rates in order to simulate actual conditions occurring during casting (e.g. up to 3°C/s for die casting of wheels and up to 10°C/s to simulate the surface of a DC cast ingot). Maintaining a low biot number to achieve isothermal conditions would be the crux of the design.
References:


