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Development of Thermal Analysis and Analytical Techniques for the Assessment of Porosity and Metallurgical Characteristics in 3XX Aluminum Alloys

by

Aleksandar Mitrasinovic

A Thesis
Submitted to the Faculty of Graduate Studies and Research Through the Engineering Materials in Partial Fulfillment of the Requirements for the Degree of Master of Applied Science at the University of Windsor

Windsor, Ontario, Canada

2004

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Abstract

One of the major problems associated with cast aluminum components is the formation of porosity. Porosity is associated with a reduction in mechanical properties, loss of pressure tightness and poor surface integrity in cast components. Porosity formation is usually attributed to the following factors: the shrinkage process, a lack of interdendritic feeding during the mushy zone solidification and the evolution of hydrogen bubbles during the solidification process.

This thesis presents the results of studies aimed at developing a new methodology for on-line assessment of the porosity level in 319 aluminum melts using the Environmental Aluminum Thermal Analysis Platform (Enviro-AITAP). The results suggest that the level of dissolved hydrogen in the melt and the resulting porosity can be predicted on the basis of cooling curve characteristics, with a relatively high degree of accuracy up to $R^2 = 0.91$.

The second goal of this thesis is the utilization of the algorithms proposed by the NSERC/NEMAK/University of Windsor Industrial Research Chair in Light Metals Casting Technology team that have been derived from binary equilibrium phase diagrams.
in order to update the data necessary to improve the Silicon Equivalency (SiEQ) method. The chemical compositions of present major and minor alloying elements in the aluminum melt will be expressed through the value of SiEQ. In this thesis, this algorithm will be used to calculate the characteristic temperatures of equilibrium solidification of the multi-component 3XX series of aluminum alloys such as: the liquidus temperature, as well as both \( T^{\text{AlSi}} \), \( T^{\text{AlSiCu}} \) eutectic temperatures. Potentially, the Silicon Equivalency algorithm could be used to estimate the latent heat of an aluminum alloy (\( L_H \)) as well as the Multi Component Aluminum Alloys Grain Growth Restriction Factor (MCGGRF). The above mentioned algorithms can be implemented on the foundry floor for quality control of cast components.
I dedicate this thesis to my parents for their support, encouragement, patience and understanding.

I would like to thank my supervisor, Dr. J. Sokolowski, and the other members of the NSERC\NEMAK\University of Windsor Industrial Research Chair team for their support during the completion of this thesis.

I would particularly like to thank Dr. Mile Djurdjevic, Dr. Witold Kierkus and Wojciech Kasprzak for their guidance and advice.

Many thanks to Dr. Glenn Byczynski for his help and thanks to the Networks of Centres of Excellence (AUTO21) and the NEMAK of Canada Corporation for their sponsorship of the IRC program.

I would also like to thanks my Thesis Committee members and the Office of Graduate Studies and Research for their effort and for their assistance with the completition of this work.

Special thanks to Francisco Robles Hernandez for numerous conversations about metallurgy as well as his great support and help during my studies.
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The metal casting industry is one of the largest suppliers of automotive components. In order to satisfy the increasing demand for more good quality components with less labour, energy and scrap, the casting industry has been forced to increase the quality of its products.

To achieve this goal the automotive industry requires a method to monitor and control the quality of incoming ingots, melts and cast components, in order to recognize potential quality problems before the casting operation takes place.

At the present time there is no universal technique on the market that can satisfy all of the above-mentioned requirements. Therefore, the NSERC/NEMAK/University of Windsor Industrial Research Chair (IRC) in Light Metals Casting Technology developed the Novel Analytical Platform (NAP), the Aluminum Thermal Analysis Platform (A1TAP) and the Enviro-A1TAP techniques that should be able to monitor the quality of incoming ingots, melts and cast components, both off and on-line.

One of the major problems in the casting industry is porosity. The amount of hydrogen dissolved in the liquid melt is one of the factors that affect the porosity in as cast products. There are several apparatuses and experimental techniques on the market that can determine the amount of dissolved hydrogen in the liquid aluminum melt. Unfortunately, there are no techniques or methods that can predict the porosity in cast components. A novel experimental technique called the Enviro-A1TAP has been
developed as a part of this Master's thesis and the obtained laboratory results, show that this technique can be used to predict the amount of porosity in cast products [1].

A detailed description of the experimental technique will be outlined in Chapter 3, and the laboratory results will be described in Chapter 4. Chapter 5 emphasizes the possibility of using the AITAP to predict melt cleanliness in cast components.

This research is a part of the long term program. One of the goals of this thesis is to develop further the NAP for assessment of main thermal properties (characteristic solidification temperatures [2] such as liquidus temperature, Dendrite Coherency Point, AlSi eutectic nucleation temperature, AlSiCu nucleation temperature and Latent Heat [3]), structural properties (Fraction Solid, Grain Size, Secondary Dendrite Arm Spacing [4]) and mechanical properties, based on the bulk chemistry. This novel platform uses the Silicon Eqivalency (SiEQ) algorithm. This algorithm expresses the effect of major and minor alloying elements in the 3XX aluminum alloys through an equivalent amount of silicon [1,2,3]. Therefore, any multicomponent 3XX aluminum system can be modeled by, using SiEQ, a pseudobinary Al-SiEQ system. Application of this novel platform will be demonstrated in Chapter 6. Also, analysis of the obtained results will be compared with already published data in available literature. Chapter 7 summarizes the main achievements in this work.
Research Objectives

- To develop and implement an experimental and analytical procedure for thermal quality control of ingots and melts in the light metal casting industry.

1. To develop Thermal Analysis testing procedures for quantifying the level of dissolved hydrogen and related porosity in the W319 aluminum melt.
   1.1. To obtain thermal parameter(s) from the cooling curve for on-line prediction of the level of dissolved hydrogen.
   1.2. To implement the Enviro-AITAP into the NEMAK Windsor Aluminum Plant (WAP) quality control system.

2. To develop a novel analytical procedure for the quality control of incoming ingots, melts and cast components.
   2.1. To utilize the Silicon Equivalency (SiEQ) algorithm to predict solidification characteristics such as: Liquidus Temperature ($T^{\text{LDeN}}_{\text{E,NUC}}$), $T^{\text{AlSi}}_{\text{E,NUC}}$ and $T^{\text{AlSiCu}}_{\text{E,NUC}}$ Eutectic Temperatures for 3XX aluminum alloys.
   2.2. To provide recommendations for implementation of the hardware and software, developed by the IRC team, into NEMAK's quality control system.
Chapter Two

Literature Review

2.1 Chemical Composition of the 319 and W319 Aluminum Alloys

Due to good casting characteristics, reasonable mechanical properties, good machinability and the ability to be heat-treated, the 319 alloy is one of the most frequently used aluminum alloys in the industry. In the last few decades, many automotive iron castings have been replaced by the 319 aluminum alloy. This alloy provides an excellent stress carrying ability, close mechanical flatness tolerances, close machined microfinishes and an excellent natural age hardening ability. At the same time, due to its large solidification range, this alloy is susceptible to porosity formation. The variability of the chemistry of the basic 319 aluminum alloy is shown in Table 2.1.

Table 2.1: Chemical composition of the 319 aluminum alloy [5] and the W319 aluminum alloy [6], wt.%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>319.0</td>
<td>5.5-6.5</td>
<td>3.0-4.0</td>
<td>1.0</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>319.1</td>
<td>5.5-6.5</td>
<td>3.0-4.0</td>
<td>0.8</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>319.2</td>
<td>5.5-6.5</td>
<td>3.0-4.0</td>
<td>0.6</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>A319.0</td>
<td>5.5-6.5</td>
<td>3.0-4.0</td>
<td>1.0</td>
<td>0.1</td>
<td>0.5</td>
<td>3.0</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>A319.1</td>
<td>5.5-6.5</td>
<td>3.0-4.0</td>
<td>0.8</td>
<td>&gt;0.1</td>
<td>0.5</td>
<td>3.0</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>B319.1</td>
<td>5.5-6.5</td>
<td>3.0-4.0</td>
<td>1.2</td>
<td>&gt;0.1</td>
<td>0.8</td>
<td>1.0</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>B319.2</td>
<td>5.5-6.5</td>
<td>3.0-4.0</td>
<td>0.9</td>
<td>&gt;0.1</td>
<td>0.8</td>
<td>1.0</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>W319</td>
<td>6.5-8.0</td>
<td>3.0-4.0</td>
<td>0.4</td>
<td>0.05-0.5</td>
<td>0.2-0.3</td>
<td>1.0</td>
<td>0.25</td>
<td>0.30</td>
</tr>
</tbody>
</table>

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The W319 alloy consists primarily of aluminum with a higher amount of silicon than the commonly used 319 aluminum alloy, with 6.5-8.0 wt% Si, 3.0-4.0 wt% Cu and a maximum of 0.4 wt% Fe [7].

Properties of 319 aluminum cast components considerably depend on the amount of alloying elements and impurities. The most important alloying elements and impurities are briefly described below.

2.1.1 Silicon

The major alloying element in 319 alloys is Silicon. Silicon improves the fluidity of the metal during casting and minimizes shrinkage during solidification. In the solidified component, silicon increases the strength and improves the wear resistance. Increasing the amount of silicon tends to decrease the ductility. However, despite the ability for the aluminum to be supersaturated by silicon upon rapid cooling to room temperatures, no improvement in the mechanical properties is seen in aluminum-silicon alloys. Therefore, additional alloying elements need to be added to obtain property improvements.

2.1.2 Copper

Copper is the most important alloying element in aluminum alloys after silicon. It increases the strength and hardness of the alloy and improves the elevated temperature properties. This is accomplished through heat-treating, where the development of a Cu-based precipitate (such as Al$_2$Cu and others) occurs; the final properties are dependent upon the precipitates developed. However, copper can decrease the corrosion resistance.
2.1.3 Iron

Iron is an unwanted element in aluminum alloys. Iron has no significant solid solubility in Al below 655°C, which leads to a decrease in the feeding ability and can considerably reduce the ductility and toughness of the cast component through the formation of brittle intermetallics that act as severe stress inducers. Often, deliberate additions of manganese are specified to change the morphology of these intermetallics and improve the ductility.

2.1.4 Magnesium

Significant increases in the strength of an aluminum alloy with similar ductility levels can be accomplished by alloying with magnesium. This refinement is possible through the heat-treating process, where the formation of Mg containing precipitates, such as Mg₂Si or Al₂CuMg, occurs.

2.1.5 Manganese

Manganese has very low solubility in aluminum and as a consequence manganese in the remaining liquid will combine with iron, silicon and aluminum to produce various intermetallics. It has been found that the ratio 1 to 2 between manganese and iron is the least detrimental to the mechanical properties [8].

2.1.6 Zinc

Mackay et al. [9] investigated the role of zinc in the 356 based aluminum alloy with residual levels up to 1.5wt.% Zn. Thermal Analysis (TA) was used by the authors to better understand the solidification kinetics of an Al-7wt.% Si-0.3wt.% Mg alloy having incremental zinc levels between approximately 0 wt.% and 1.5 wt.%.

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The findings of this work indicate that the behaviour of Al-Si-Zn alloys is similar to that of 3XX.X alloys. That is, they solidify as primary dendritic structures with Al-Si eutectic phases. Other secondary phase reactions are script and needle phases. These phases grow more numerous after the Al-Si eutectic reaction when zinc levels increase.

2.1.7 Nickel

The main purpose of nickel in aluminum alloys is to increase tensile strength, yield strength and reduce elongation at room temperature. The detrimental factor for the wider use of nickel in Al-Si alloys is its cost.

2.1.8 Strontium

Strontium is added to refine the silicon morphology in hypoeutectic Al-Si alloys. Prior to the addition of strontium, the silicon structure in the 319 alloys is composed of coarse needles and/or flake-like plates. The addition of strontium (typically 50-500ppm) will change the silicon morphology from acicular to lamellar or fibrous. Aside from changing the morphology of silicon, strontium also modifies the copper phases, by leading to an increase of Al2Cu blocky type. Several analytical and testing techniques were developed in order to quantify the effect of strontium additions on the silicon morphology. M. Djurdjevic, T. Stockwell and J. H. Sokolowski [10] showed that the AITAP thermal analysis technique can be used to determine the aluminum-silicon eutectic morphology before and after the addition of strontium.
2.1.9 Titanium

The effect of elevated titanium in the ingot material affects the grain refining potency of grain refiners [11, 12]. Recent work by the IRC team proved that the Thermal Analysis Technique is capable of quantifying primary undercooling, $\Delta T$, and solidification time $\Delta t$, that are directly related to the grain size.

![Figure 2.1: Correlation between the addition of master alloy (2g, 1g and 0.5g) into the 319 aluminum alloy and the undercooling parameters taken from the cooling curve (A1-B3 – different titanium based master alloys) [13].](image)

Thermal Analysis samples used in the experiments reported in Figure 2.1 were always 300g±10g. Using an coded composition of master alloy (known only to the company); TA technique shows the difference between the master alloy’s efficiency and the amount of master alloy that should be added for a given undercooling.
2.2 Microstructure of the 319 Alloy

Beside primary aluminum, two eutectic microconstituents, Al-Si and Al-Cu rich, are mainly responsible for structural composition in 3XX series alloys (Figure 2.2). These microconstituents can be detected by analysis of the cooling curve(s), or more precisely its first derivative(s). M. Djurdjevic et al. [14] demonstrated that it is possible to quantify and to characterize development of a microstructure in the 3XX series of aluminum alloys using the AITAP.

The sequence of solidification and the formation of microconstituents in Al-Si-Cu casting components during solidification can be described as follows [15]:

1. A primary $\alpha$-aluminum dendritic network forms between 580 - 610°C. The exact temperature depends mainly on the amount of Si and Cu in the alloy. Formation of an $\alpha$-aluminum leads to the increase of the concentration of Si and Cu in the remaining liquid.

2. Between 570 - 555°C (the Al-Si eutectic temperature) the eutectic mixture of Si and $\alpha$-Al forms, leading to a further localized increase in the Cu content of the remaining liquid.

3. At approximately 540°C, the $\mathrm{Mg}_2\mathrm{Si}$ and $\mathrm{Al}_3\mathrm{Mg}_2\mathrm{FeSi}_6$ phases begin to precipitate.

4. Close to 525°C, the "massive" or "blocky" $\mathrm{Al}_2\mathrm{Cu}$ phase (containing approximately 40wt% Cu) forms together with $\beta$-Al$_5$FeSi platelets.

5. Around 507°C, a fine Al-Al$_2$Cu eutectic phase forms (containing approximately 24wt% Cu). If the melt contains more than 0.5wt% Mg, an ultra fine Al$_5$Mg$_6$Cu$_2$Si$_6$ eutectic phase also forms at a similar temperature. This phase grows from any of the two previously mentioned Al$_2$Cu phases.

The amount of each microconstituent depends on the alloy composition and on the solidification conditions [15].
2.2.1 Eutectic Silicon

The eutectic silicon is not uniformly distributed, but tends to be concentrated at the interdendritic boundaries. The natural morphology for the eutectic silicon is acicular or plate-like. Using chemical additions or solution treatment can transform it to a fine fibrous morphology (Figure 2.3). The heat treatment mechanism is a solid state diffusion driven process where the eutectic silicon is fragmented and spheroidized. In general, the addition of silicon in this family of alloys improves metal fluidity, castability and reduces metal shrinkage during solidification.

Figure 2.3: Unmodified and thermally modified eutectic silicon [16]
2.2.2 Copper Rich Phases

Alloys with copper rich phases show higher hardness and strength. The as-cast hardness of copper rich alloys is usually acceptable. Precipitation heat treatment is used to develop the maximum hardness and strength. Depending on the service conditions, the peak-aged condition may not be optimum. Often castings are over-aged to provide a compromise between strength and dimensional stability in service. Copper-rich eutectic phases may take several forms depending on the alloy composition, solidification conditions and heat treatment. The most common phases found in the 319 alloy are described in Figure 2.4:

Figure 2.4: Photomicrographs showing the Cu-rich phases formed during the solidification process; 1) $\text{Al}_3\text{Mg}_6\text{Cu}_2\text{Si}_6$; 2) interdendritic (blocky) $\text{CuAl}_2$; 3) eutectic Al-$\text{CuAl}_2$ pocket [15].

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2.2.3 Iron Rich Intermetallics

Aluminum alloys produced from recycled materials have more iron than those commonly found in primary alloys. Depending on the level of iron, and elements (Mn, Mg, Cr) known to form phases with iron, a large number of different types of iron rich intermetallics can be found. The formation of these phases is also largely dependent on the local solidification rates [17] and the melt’s holding temperature [18]. The two most common phases found in the 319 alloy are listed in Table 2.2:

<table>
<thead>
<tr>
<th>Phase Description</th>
<th>Composition</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-phase or “Chinese script”, multi-armed or semi-symmetrical in shape</td>
<td>Al_{15}(FeMn)<em>{3}Si</em>{2}</td>
<td>Preferred form, seen as less harmful to ductility, stable during heat treatment.</td>
</tr>
<tr>
<td>β-phase, thin plates</td>
<td>Al_{5}FeSi</td>
<td>Undesirable due to its morphology. These are known to reduce casting ductility and increase shrinkage porosity by blocking feed paths.</td>
</tr>
</tbody>
</table>

Figure 2.5: Iron based phases: a) α-phase or “Chinese script”, b) β-phase, thin plates [15].
2.2.4 Intermetallic Phases

All intermetallic phases are particularly deleterious to the fatigue resistance of cast 319 Al alloys. These phases are typically among the last to solidify, forming at grain boundaries and interdendritic regions. Most intermetallic phases are very brittle and tend to form platelets with sharp edges; thus, they can act as stress raisers for crack nucleation or as low-energy paths for crack propagation.

The two major intermetallic phases in the 319-type aluminum alloys are the Fe-based and Cu-based intermetallics. Iron-based intermetallics tend to form Al₂FeSi (beta-phase), acicular platelets that have a significant effect on the mechanical properties; one study found that doubling the Fe level from 0.15% to 0.30% decreased the ductility by a factor of 2. Usually, Mn is added to the melt to promote the formation of Al₁₅(Fe,Mn)₃Si₂, which is less detrimental. The copper-based intermetallic is primarily Al₂Cu, which forms as blocky plates or as an interdendritic eutectic network. This phase is especially present in the 319 aluminum alloy, which has a large amount (3-4%) of copper that is often not fully dissolved into the aluminum matrix.

Increasing the solidification rate tends to reduce the extent of alloy segregation by reducing the degree of elements portioning on the grain boundary [20]. Therefore, more alloying elements and impurities will solidify inside the dendrites; that consequently decrease the size and volume of the intermetallic phases. Thus, the fatigue and fracture properties of the alloy can be improved.

2.2.5 Non-Metallic Inclusions

Non-metallic inclusions are very deleterious to the fatigue and fracture strength of cast aluminum alloys. Aluminum oxide particles can arise when the surface of the molten metal is disturbed; the natural oxide “skin” is fragmented and/or folded and mixed into the molten metal.
2.3 Liquid Metal Processing and Heat Treatment of the W319 Alloy

2.3.1 Grain Refinement

The grain size in castings typically ranges from several hundred microns to several millimetres in diameter. In general, it is observed that the addition of grain refiners increases the number of grain nucleation sites, thus reducing grain size; therefore it can affect the mechanical properties. In addition, the distribution of porosity has been found to be more uniform when grain refiner is added [11].

Several methods could be applied to accomplish fine grains. These methods could be categorized as follows: mechanical methods, thermal methods, constitutional supercooling methods and chemical additions. Mechanical methods are those that affect the solidifying melt (e.g. ultrasonic vibration, and mechanically or electromagnetically inducted stirring). Thermal methods include reducing local solidification rates by the reduction of section size or by addition of chills and chill fins or placement of cooling lines and application of thermally conductive coatings. Constitutional supercooling is achieved by adding elements of limited solubility to the alloy, thus increasing the Dendrite Growth Restriction Factor, slowing grain growth and allowing additional time for grains to nucleate resulting in an overall finer grain size.

Much research has been focused on the mechanisms of grain refinement. However, those that have been found most favourable over the years include: a change in nucleation entropy [21, 22], constitutional undercooling [23], the particle or boride theory, the duplex particle theory [24, 25], hypernucleation [26, 27], phase diagram based theories [28], and the peritectic “hulk” theory [29]. Still, there is some uncertainty about the effects of grain refiner additions on the casting structure.
2.3.2 Secondary Dendrite Arm Spacing (SDAS)

Secondary Dendrite Arm Spacing (SDAS) is the linear distance between the secondary dendrites (or "arms"). SDAS is governed by the solidification rate and thus can be used as a method for determination of the solidification rate in a local area of the casting. In general, the mechanical properties in aluminum castings tend to correlate better with the SDAS than the grain size; all other things being equal, higher solidification rates yield finer spacing, which in turn give better mechanical properties.

The SDAS of a particular casting is determined by a number of factors such as the cooling rate, the alloy composition, the local solidification time and the temperature gradient.

Changes in distance of the SDAS have a number of effects on the microstructure of the casting [30]:

- The size and distribution of shrinkage porosity.
- The size and distribution of intermetallic particles.
- The rate of homogenization during solidification and heat treatment.
- The mechanical properties of hypoeutectic aluminum-silicon castings.
- The Al-Si eutectic and other minor eutectic(s) morphology characteristics.

2.3.3 Modification

Eutectic Silicon Modification is typically accomplished by adding small amounts of Na or Sr to the melt. Both elements change the morphology, size and distribution, of the eutectic silicon by altering the growth mechanism of the eutectic silicon. In the unmodified 319 aluminum alloy, the eutectic Si has a coarse, plate-like structure. In this structure, the coarse plates act as stress inducers and provide planes of weakness; both
can combine to enhance crack initiation and propagation. Chemical modification of the eutectic silicon creates a three-dimensional network (or “sponge” type structure) that can significantly improve strength and ductility. Also, the increase in the strontium content increases the proportion of blocky $\text{Al}_2\text{Cu}$ and ultra fine $\text{Al}_5\text{Mg}_6\text{Cu}_2\text{Si}_6$ copper phases versus $\text{Al}-\text{Al}_2\text{Cu}$ eutectic copper phases in the solidifying microstructure of the 319 aluminum alloy [31].

Pasz [32] is credited with discovering modifying effects of sodium on the eutectic silicon. Due to issues such as cost, health and safety, and process efficiency, Na and Sr have become the two elements that have found the most use in industry. However, there are secondary negative effects that strontium additions have on the soundness of the casting.

Strontium increases the amount and size of the defect structure of the casting, particularly in the form of porosity. An important fact to emphasize is that pore volume fraction increases with strontium modification, even when hydrogen levels and solidification rate appear to be held constant. Furthermore this increase in pore volume fraction is exaggerated at lower solidification rates.

2.3.4 Heat Treatment

The 3XX series of aluminum alloys are heat-treated in order to obtain the optimum combination of strength and ductility needed for particular application. 319 aluminum alloy castings are not used in their as-cast condition. Generally, heat treatment consists of any combination of the following three steps: a solutionization, a rapid quench, and an aging treatment. Table 2.3 briefly describes a few common heat treatments.
Table 2.3: Heat treatments for the 319 aluminum alloy [7].

<table>
<thead>
<tr>
<th>American Aluminum Association Designation</th>
<th>Solutionization</th>
<th>Quench</th>
<th>Aged at Room/Elevated Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>No</td>
<td>No</td>
<td>No Natural Aging</td>
</tr>
<tr>
<td>T4</td>
<td>Yes</td>
<td>Yes</td>
<td>Room Temperature Only</td>
</tr>
<tr>
<td>T5</td>
<td>No</td>
<td>No</td>
<td>Elevated Temperatures</td>
</tr>
<tr>
<td>T6</td>
<td>Yes</td>
<td>Yes</td>
<td>Elevated (To yield increased strength)</td>
</tr>
<tr>
<td>T7</td>
<td>Yes</td>
<td>Yes</td>
<td>Elevated (To yield dimensional stability)</td>
</tr>
</tbody>
</table>

The most recent reports suggest solution treatment integrated with the solidification processes [33, 34]. This novel heat treatment method has significant economical advantages in comparison with conventional heat treatment processes.

2.4 Porosity

Porosity can be defined as pores, voids, or cavities that arise in the interior of a casting during solidification [7]. Porosity in aluminum castings tends to decrease the mechanical properties of a casting such as tensile strength, fatigue resistance and pressure tightness. In addition to reducing the amount of material that can carry the applied loads, the cavities often act as stress raisers and low energy nucleation sites for cracks.

In general, porosity can result from three sources. The first source is from poor casting design that prevents the casting from properly filling. In these cases, the defect size is usually quite large and easily seen with the naked eye (macroporosity). The next source of porosity is gas that is entrapped or dissolved in the liquid metal during casting (gas porosity). The third source of porosity is due to the natural volume contraction that occurs when a liquid solidifies (shrinkage porosity). Based on pore size it can be distinguished as micro and macro porosity.
Formation of porosity is attributed to two factors: the evolution of hydrogen gas bubbles due to the decrease in the hydrogen solubility during solidification (gas pores) and a lack of interdendritic feeding during mushy zone solidification (shrinkage pores).

2.4.1 Gas Porosity

Gas porosity arises during solidification due to the difference in solubility of hydrogen gas in liquid and solid aluminum. When solidification begins, the decreasing solubility causes the hydrogen to form spherical bubbles in the interdendritic region. This type of porosity is generally circular in appearance, and is usually less than 0.5 mm in diameter. The interior of these voids often looks smooth and has few or no dendritic arms visible. Proper degassing of the molten metal as well as good metal covering and pouring practices can greatly limit entrapped gas porosity. Additionally, gas porosity may be minimized by proper design of the gating and runner systems. This will minimize turbulence during the pouring and filling of the mould, which will reduce the amount of air that is mechanically entrapped during solidification.

2.4.2 Shrinkage Porosity

When a casting solidifies such that the last portion to freeze is not well fed on a local scale (thick sections); thus, the region does not have enough liquid metal to compensate the volume decrease and a void arises. This porosity is very tortuous, often outlining the features of surrounding dendrites; therefore, individual dendrites may be seen in the interior of the void. Any further shrinkage in the area around the pore will lead to void growth and the area of influence can be large since metalostatic tension far from the shrinkage pore can contribute to growth. Pure shrinkage porosity appears only when the level of dissolved hydrogen is low.
2.4.3 Gas Shrinkage Porosity

In most cases, gas evolution and shrinkage occur in the same volume of liquid metal at the same time. As a result, an interaction between these phenomena can be expected. Both the gas and shrinkage pressure aid in the nucleation and growth of the pore as the pressure pushes from the inside and the shrinkage pressure pulls from the outside.

2.5 Formation of Porosity in Aluminum Alloy Castings

The formation of porosity in aluminum alloy castings is attributable to a combination of hydrogen gas evolution and solidification shrinkage which results in reduced pressure in the liquid metal [35]. The criterion for growth of an existing gas pore nuclei is:

\[ P_{\text{gas}}>P_{\text{atm}}+P_{\text{met}}+P_{\text{shrink}}+P_{\text{surface}}=P_{\text{liq}}+P_{\text{surface}} \] (kPa) 2.1

\( P_{\text{gas}} \) promotes expansion of the gas bubble, while the terms on the right side of \( \geq \) sign counteract pore growth. \( P_{\text{gas}} \) is the pressure inside a pore. \( P_{\text{atm}} \) is the atmospheric pressure and \( P_{\text{met}} \) is the pressure resulting from the metallostatic head. Due to the thermal and solidification concentration of the metal, there is a pressure change in the liquid metal, \( P_{\text{shrink}} \), which results in a reduction of the metal pressure in the casting that was established by \( P_{\text{atm}} \) and \( P_{\text{met}} \). \( P_{\text{surface}} \) is the pressure associated with the interfacial free energy between the gas bubble and its surrounding metal. \( P_{\text{atm}} \) is 101 kPa (1 atm), unless external pressure is applied. \( P_{\text{met}} \) is usually neglected because this value is small compared to the atmospheric pressure. \( P_{\text{gas}}, P_{\text{shrink}} \) and \( P_{\text{surface}} \) are the parameters likely to have the largest influence on microporosity formation during the solidification of a casting.
2.5.1 Hydrogen Gas Evolution

Hydrogen is evolved in liquid aluminum through reaction 2.2, and is later absorbed by the aluminum.

\[ 2Al_{(l)} + 3H_2O_{(g)} = Al_2O_3_{(s)} + H \]

The gas pressure rises due to the large difference in hydrogen solubility between liquid and solid aluminum and the fast diffusion of monoatomic hydrogen in liquid aluminum. During solidification, hydrogen is rejected at the solid-liquid interface into the liquid. When the solubility limit of hydrogen in the liquid metal at the local temperature and the atmospheric pressure conditions is exceeded, the gas may precipitate as pores.

2.5.2 Hydrogen Solubility in Aluminum Alloys

Hydrogen is the only gas that has a measurable solubility in aluminum [36]. The solubility of hydrogen in aluminum and its alloys is strongly dependent on the temperature (Figure 2.8). The hydrogen solubility exhibits a sharp drop at the transition point from liquid to solid metal.

The solubility (S), in ml H$_2$/100g alloy at 101 kPa hydrogen pressure, has been measured by Opie and Grant [37]. The temperature range 700-1000°C in pure aluminum, may be expressed as:

\[ \log S_{\text{Liquid}} = - \frac{2550}{T} + 2.62 \]

where T is absolute temperature. The solubility of hydrogen in commercial purity solid aluminum at 101 kPa hydrogen pressures, between 465-620°C, follows the relationship:
Chapter Two, Literature Review

\[ \log S_{\text{solid}} = -\frac{2080}{T} + 0.788 \]

The hydrogen solubility in aluminum alloys is defined as:

\[ S = \frac{f_H [H]}{\sqrt{p_{H_2}}} \]

Where \( f_H \) is the hydrogen activity coefficient, \([H]\) is the hydrogen concentration in the respective phases and \( p_{H_2} \) is the partial pressure of hydrogen.

To date, the direct absorption method is considered to be the only suitable method for measurement in liquid alloys. The results of hydrogen solubility in liquid alloys authors is shown in Figure 2.6.

Figure 2.6: The hydrogen solubility in liquid aluminum as reported by various researchers [38].

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2.5.3 Hydrogen Diffusivity in Aluminum Alloys

The hydrogen diffusivity in aluminum alloys is directly related to the gas bubble formation during solidification; therefore, the formation of gas porosity. The hydrogen diffusivity in pure liquid aluminum for the temperature range 780-1000°C, has been determined to vary with the absolute temperature according to the relationship [39]:

\[ D_l = 3.8 \times 10^{-2} \exp \left( \frac{-2315}{T} \right) \text{ cm}^2/\text{s} \]  \hspace{1cm} 2.6

The diffusivity in solid aluminum between 360-600°C is estimated to be [40]:

\[ D_s = 1.1 \times 10^{-4} \exp \left( \frac{-4922}{T} \right) \text{ cm}^2/\text{s} \]  \hspace{1cm} 2.7

Possible diffusion distances for hydrogen as a function of time at different temperatures, according to Equation 2.6 are shown in Figure 2.7. As is known, the temperature dependence in the solidification range is not very strong. The hydrogen diffusion in liquid aluminum is extremely fast, and a hydrogen atom can travel 500μm in one second. The corresponding value for solid phase diffusion is 200μm. For a casting with a local solidification time of 60s, which corresponds to Dendrite Arm Spacing around 35μm, hydrogen can diffuse at a distance of 4.1 mm in the liquid, provided there are no restrictions on the diffusion path.
2.5.4 Oxide Films

Aluminum in the solid state will readily form a protective oxide layer when exposed to oxygen, preventing further oxidation of the parent metal. Unfortunately the oxidation process with the metal in the liquid state is far from helpful. There are a series of transformations that take place in the liquid aluminum oxidation process. Since these steps are chemical reactions they are sensitive to conditions such as temperature, pressure, and the purity and activity of the reactants [19].

In its pure state, standard pressure and at typical molten aluminum casting temperatures, aluminum will immediately form an amorphous alumina film. The next stage is believed to be the nucleation and growth of a crystalline transition alumina. There are several papers about the nature of this transition that are in contrast. The next transformation is the formation of \( \alpha \)-alumina. This transformation is believed to occur at the oxide melt interface. If left undisturbed, a 1\( \mu \)m thick oxide layer is formed within an hour and after that the rate of oxidation is minimal. This is the situation in a static melt where no movement of the liquid metal occurs. More relevant to casting operations such as ladling, pumping, and mould filling however, would be the situation of the first stage amorphous film forming and immediately fragmenting and being carried off into the bulk of the
flowing metal. This film if allowed will continue the transformation, utilizing the trapped air for oxidation reactions, until the stable \(\alpha\)-alumina phase is formed.

When magnesium is present in an aluminum alloy the reaction sequences are different than those in the pure metal. Due to affinity to oxygen, amorphous \(\text{MgO}\) will be the first oxide formed. If the magnesium content of the alloy is greater than 0.3 wt% only magnesium will be oxidized. This amorphous \(\text{MgO}\) then transforms into crystalline \(\text{MgO}\). The next reaction to occur is conversion of the \(\text{MgO}\) to \(\text{MgAl}_2\text{O}_4\) (spinel). In lower magnesium containing alloys there will likely be concurrent oxidation reactions forming the initial phases of alumina and magnesia according to the local elemental activities.

Other elements have been known to have an influence both on the oxidation reaction rates and on the strength of the oxide films. Selected elements and their influence are summarized in Table 2.4.

Table 2.4: Effect of selected elements on the oxidation rate and strength of aluminum oxide films [19].

<table>
<thead>
<tr>
<th>Element(s)</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, Fe, Cu, Zn, Mn</td>
<td>No effect</td>
</tr>
<tr>
<td>Mg, Na, Se, Ca, Li</td>
<td>Increases rate of oxidation</td>
</tr>
<tr>
<td>Mg, Na, Ca, Li</td>
<td>Increases the strength of film</td>
</tr>
<tr>
<td>Be, Si</td>
<td>Decreases the strength of film</td>
</tr>
</tbody>
</table>

Formed oxides could become nucleation sites for gas pores, shrinkage pores and hot tears. Recent work by Nyahumwa (1998-2001) [41] has suggested that new films are particularly good at nucleating pores while old films remain rather inert in this respect. New films with practically no bounding between the dry sides are easily opened and consequently act as the preferred nucleation sites.
Oxides films have also been shown to considerably reduce the fatigue performance of Al-Si-Mg castings, because of their ability to act as crack initiators and nucleation sites for porosity. Old oxides have been known to act as nucleation sites for fatigue cracks. With a given time and under the correct conditions new oxide films will mature into old films (Table 2.5).

Table 2.5: Characteristics of oxide films [19].

<table>
<thead>
<tr>
<th>Film age</th>
<th>Formation of phase</th>
<th>Thickness (µm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.01 s</td>
<td>Early</td>
<td>0.056 - 0.127</td>
<td>Observed only as a change in apparent colour of the melt surface</td>
</tr>
<tr>
<td>0.01 - 1s</td>
<td>Early</td>
<td>0.050 - 0.500</td>
<td>Delicate, transparent, thin film, with sharp creases or wrinkles</td>
</tr>
<tr>
<td>10 - 60s</td>
<td>Early</td>
<td>10</td>
<td>Flexible, extensive films</td>
</tr>
<tr>
<td>10min - 1 hour</td>
<td>Transitional</td>
<td>100</td>
<td>Thicker films less flexible</td>
</tr>
<tr>
<td>10 hours - 10 days</td>
<td>Late and stable</td>
<td>1000</td>
<td>Rigid lumps and plates</td>
</tr>
</tbody>
</table>

Remelt the Reduced Pressure Test (RPT) technique has recently been developed in order to experimentally analyze the behaviour of the oxide film and its effect on the crack propagation. A solid sample is remelted and placed into a vacuum chamber with a transparent lid. Glenn Byczynski in his PhD dissertation [19] outlines results after radiography of solidified samples. One can clearly see that by reducing the pressure the trapped air between the entrained oxides is expanded, resulting in planar cracks in the reduced pressure specimen. The ability to visualize the oxide films is related to (at least) three factors: the hydrogen content of the metal, the amount of oxide films present, and the test pressure.

Although still under development the Remelt Reduced Pressure Test shows tremendous promise, as it is the first test to study oxide film characteristics in solidified castings.
2.6 Parameters That Influence the Formation of Porosity

The Hydrogen Solubility (S) limit in liquid aluminum alloys is considerably higher than for other gases and is strongly reduced in solid alloys (Figure 2.8). This means that gas porosity in aluminum alloys is mainly hydrogen porosity.

Other parameters can also influence the hydrogen porosity formation during solidification. These parameters are:

- The chemical composition of the alloy, since alloying elements modify the hydrogen activity.
- The solidification range of the alloy.
- The solidification rate and temperature gradient, which have an effect on the kinetic nucleation and growth of the bubbles.
- The metal cleanliness (the oxide or inclusion content in the melts) which is often considered as a factor influencing the hydrogen gas nucleation.
- The local pressure during solidification, on which the enthalpy of bubble formation depends.

Figure 2.8: Hydrogen Solubility in aluminum.
2.6.1 Influence of Gas Content on Porosity

Hydrogen gas has long been recognized as the major contributor to porosity formation. It is however not, as will be shown in the following sections, the only factor that influences microporosity formation.

Ransley and Neufeld [42] found that the volume fraction porosity in commercial purity aluminum ($\rho_{\text{pureAl}}$ is density of the pure aluminum and $\rho_{\text{Alloy}}$ is density of the aluminum alloy), calculated as:

$$\text{% porosity} = \frac{\rho_{\text{pureAl}} - \rho_{\text{Alloy}}}{\rho_{\text{pureAl}}} \times 100 \quad [\%]$$

followed a roughly linear relationship with the hydrogen content. The shape of the castings were horizontal bars, cast into sand moulds with, according to the authors, adequate feeding. Porosity did not form below hydrogen contents of 0.12 ml H$_2$/100g. They observed that the hydrogen content for 0% porosity was to be three times higher than the solid solubility limit of 0.04 ml H$_2$/100g Al. They attributed this to a required supersaturation before the formation of gas pores would take place. Later works were to term this “the threshold hydrogen content” [43].

In Deoras and Kondic’s [44] experimental work, commercial purity alloy, Al-1.7%Si, Al-6%Si and Al-12%Si, were cast into 25.4mm diameter sand moulds. The porosity was then calculated using Equation 2.8. The authors noted that the threshold hydrogen content in commercial purity aluminum was 0.15 ml H$_2$/100g alloy, which was approximately the same value that Ransley and Neufeld [42] found. In Al-6% Si alloy no porosity was found at 0.13 ml H$_2$/100g. A linear relationship was obtained between hydrogen content and percent of porosity. Different solidification rates were obtained by varying the mould temperature. This showed that the porosity for the same hydrogen level increased with increasing local solidification time. For long solidification times, the threshold hydrogen content was still above the solid solubility level.
J. P. Anson, J. E. Gruzleski and R. A. L. Drew [45] explained that during formation of microporosity in an Aluminum-7% Si Alloy, nucleation and growth occur continuously over a wide time/temperature range. Little porosity exists until 0.17 ml H₂/100g Al, after which the percent porosity increases linearly with the hydrogen content (the threshold hydrogen content).

The different behaviour found above and below the threshold implies that there are two mechanisms of pore growth. Above the threshold, however, the percent porosity increases linearly with respect to hydrogen content, indicating that the growth in pores is directly related to gas evolution.

The pore volume is constant before the threshold. Since there is a large change in pore volume at the threshold, the nucleation of the pores is shown to be partly dependent on the hydrogen content. Work by K. Tynelius [46] has shown that the number of pores is dependent on the solidification times.

2.6.2 The Influence of Cooling Rate on the Formation of Porosity

Gruzleski et al. [47] studied porosity formation as a function of location in cylindrical castings. The mould was immersed up to a third of its height in cooling water. Al-8% Si alloy castings were produced for various hydrogen contents. The porosity was calculated using Equation 2.8 for various parts of the casting. The volume percent porosity inside castings at extreme hydrogen contents of 0.1 and 0.8 ml H₂/100g was found to be evenly distributed throughout the castings. In the range of intermediate hydrogen concentrations, however, the local solidification time had a strong impact on the porosity distribution. The porosity is increased with the hydrogen content at all local solidification times.
Fang and Gragner [48] conducted experiments on rectangular A356 alloy castings which provided conditions for unidirectional solidification via a water cooled baseplate, and they found a non-linear relationship with increases of hydrogen content and local solidification time. Results are reported in Figure 2.9 for a grain refined, unmodified alloy. The porosity was intergranular in nature. The authors redefined the threshold hydrogen content for formation of porosity as the hydrogen content where a finite, but small fraction of porosity will have formed. This was done as ‘zero’ was difficult to define. For example, a fraction porosity of 0.01% had a threshold hydrogen content of 0.15 ml H₂/100g Al at a cooling rate of 7.5°C/s. For a cooling rate of 2.6°C/s the threshold hydrogen content was 0.09 ml H₂/100g.

![Figure 2.9: Percent porosity in the grain refined A356.2 alloy as a function of the hydrogen content and cooling rate [46].](image_url)

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2.6.3 Influence of Melt Cleanliness on Porosity Formation

A research group from Toyota [49] found that in unmodified as well as strontium and sodium modified Al-7% Si castings, the porosity, at equal levels of hydrogen content, was lower in castings where the metal had undergone inclusion removal. The time for vacuum degassing of a melt increased if the inclusion content was high. Again, the results of the research showed that at low hydrogen content levels, the inclusion level is of minor importance.

Laslaz and Laty [50] showed that in 356 and 319 alloys manufactured from scrap metal or ingots respectively, the latter had better melt cleanliness and lower porosity content was obtained at the same hydrogen content level. The samples in this study were solidified under Reduced Pressure Test (RPT) conditions. The pores in the samples with high inclusion content were more numerous and showed a round shape, compared to more elongated pores in the samples of clean metal.

Celik and Bennet [51] found that for super purity aluminum solidified in sand moulds, inclusions had no effect on porosity with hydrogen contents less than 0.17 ml H₂/100g.

In the contrast, Brondyke and Hess [52] showed that the inclusion content in aluminum alloys was of great importance for the density of samples solidified under the Reduced Pressure Test. They found that samples with the same hydrogen content showed much lower density for an unfiltered metal. In a Reduced Pressure Test (RPT), samples with a hydrogen content below 0.3 ml H₂/100g alloy cast from a filtered metal, showed no differences in density.
2.7 The Thermodynamic Approach for Assessing Hydrogen Gas Levels in Aluminum Casting Alloys

The IRC team analyzed several approaches to predict the level of hydrogen in aluminum casting alloys. In this section the thermodynamic method to assessing the level of hydrogen in aluminum casting alloys is highlighted.

The dissolution of atomic hydrogen in liquid/solid aluminum (and its alloys) follows Sievert’s Law:

$$\frac{1}{2} \{H_2\} \rightarrow (H)^* (Al-H)$$

The bracket \( \{H_2\} \) denotes gaseous hydrogen, while the bracket \((H)\) corresponds to hydrogen dissolved in the liquid aluminum. The equilibrium constant for the aforementioned reaction is:

$$K = \frac{a_H}{(p_{H_2})^{0.5}}$$

Where, \( a_H \) is the activity of hydrogen and \( p_{H_2} \) is the partial pressure of hydrogen. For highly dilute solutions such as Al-H, Henry’s Law can be applied. In this case, in the Al-H binary system can be expressed by Equation 2.13:

$$a_H = f_H \times (H, wt\%)$$

Where \( f_H \) is the Henry’s activity coefficient of hydrogen in the liquid aluminum with reference to a 1 wt. % H solution. The actual solubility of hydrogen in a binary Al-H
system is determined by its activity coefficient. According to Equation 2.13, a higher hydrogen activity coefficient corresponds to higher solubility in the liquid aluminum.

Commercial aluminum alloy melts consist of solutions of many alloying elements. In these solutions many different chemical interactions occur, for instance:

- Aluminum interacts with hydrogen.
- Aluminum interacts with the other alloying elements.
- The alloying elements interact with hydrogen.

The nature and relative magnitudes of these interactions thermodynamically control the solubility of hydrogen in multi-component aluminum alloys. The effect of alloying elements on the solubility of hydrogen in a multi-component aluminum alloy system could be explained using the interaction coefficient. Briefly, the activity coefficient of hydrogen in a multi-component system changes with the concentration $X_i$, (where $X_i$ is the molar fraction of a particular element in the aluminum solution):

$$\ln f_H = f \left(X_{Al} * X_{Cu} * X_{Fe} * X_{Mg} * X_{Mn}...X_i\right)$$  \hspace{1cm} 2.14

This is usually expressed using a Taylor’s expansion term in the form of Wagner’s equation:

$$\ln f_H = \ln f_H^0 + X_{H} \frac{\partial \ln \gamma_H}{\partial X_H} + X_{Al} \frac{\partial \ln \gamma_{Al}}{\partial X_{Al}} + ... + X_i \frac{\partial \ln \gamma_i}{\partial X_i} +$$
$$+ \left[ \frac{1}{2} X_{H}^2 \frac{\partial^2 \ln \gamma_H}{\partial X_H^2} + X_{Al}^2 \frac{\partial^2 \ln \gamma_{Al}}{\partial X_{Al}^2} + X_i^2 \frac{\partial^2 \ln \gamma_i}{\partial X_i^2} + ... \right]$$  \hspace{1cm} 2.15

For a highly dilute hydrogen solution in a liquid aluminum alloy, the activity coefficient of hydrogen can be expressed in a simplified version as a function of the molar fraction of the additional elements:

32
\[ \ln f_H = \ln f_H^0 + X_H \frac{\partial \ln \gamma_H}{\partial X_H} + X_{Al} \frac{\partial \ln \gamma_{Al}}{\partial X_{Al}} + \ldots + X_i \frac{\partial \ln \gamma_i}{\partial X_i} \]  

2.16

In other words, the second and higher order terms from Equation 2.15 are negligible, and the differentials of \( \frac{\partial \ln \gamma_H}{\partial X_H} \), \( \frac{\partial \ln \gamma_{Al}}{\partial X_{Al}} \) ...have approximately constant values for a low atomic percent of hydrogen. In this form, \( \ln f_H \) is a linear function of the molar fraction of the various elements.

\[ \ln \frac{f_H}{f_H^0} = X \cdot Al \cdot \varepsilon_H^{Al} + X \cdot Al \cdot \varepsilon_H^{Cu} + \ldots + X_i \cdot \varepsilon_H^{X_i} \]  

2.17

The coefficient \( \varepsilon H^{X_i} \) is an interaction or a Wagner parameter defined by:

\[ \varepsilon H^{X_i} = \frac{\ln f_H}{X_i} \]  

2.18

The interaction parameter expresses the effect of an alloying element "X_i" on the hydrogen activity in the multi-component system Al-H-...X_i. A positive value of the first order of the interaction parameter indicates that by adding an alloying element this decreases the affinity of the liquid aluminum to hydrogen. A negative coefficient indicates the opposite.

It is often more convenient to consider the concentrations of the solutes in terms of weight percents and natural logarithms, so equation 2.17 becomes:

\[ \log \left[ \frac{f_H}{f_H^0} \right] = \%Al \cdot \varepsilon_H^{Al} + \%Cu \cdot \varepsilon_H^{Cu} + \ldots \%X_i \cdot \varepsilon_H^{X_i} \]  

2.19

33
According to Gruzleski [53] and Anyalebechi [54, 55], the literature contains few published values for hydrogen solubility in aluminum alloys. This paucity of knowledge is potentially serious because the effects of the few known alloying elements that have been quantified are strong and diverse (Figure 2.10). There is reason to believe that the effects of unknown elements may be similar.

For the sake of simplicity, the coefficient of activity of hydrogen is expressed as a linear function of the interaction parameter ($\xi$) and the concentration (wt.%) of the observed elements in Equation 2.19. The values of the first order interaction parameter are obtained from the slopes of the linear portions of the plots \( \ln f_H \) versus the concentrations of alloying elements $X_i$ (Figure 2.11).

Using Wagner's model of interaction parameters derived from the data on hydrogen solubility in liquid binary aluminum alloys, Anyalebechi attempted to predict hydrogen solubility in multi-component aluminum alloys. The fit between the models and experimentally determined hydrogen solubility data in all of the investigated alloys (Al-H-Cu-Mg-Si, Al-H-Zn-Mg-Cu and Al-H-Cu-Li) was poor.
Chapter Two, Literature Review

2.8 Methods for Determining the Hydrogen Content in Aluminum Alloy Melts

Over the years many techniques have been evolved for determining the hydrogen content in aluminum alloy melts, and new methods are still being developed. These techniques can be categorized in a variety of ways based on different considerations. In this thesis, these techniques are placed in three categories according to their usage in practice: quantitative laboratory analysis, quantitative in-situ analysis, and semi-quantitative methods [56].

2.8.1 Quantitative Laboratory Methods

These methods yield a quantitative measure of the hydrogen concentration in aluminum and aluminum alloy melts; however, they are limited to laboratory use. Included in this
category are the Ransley sub-fusion method, the Nitrogen Carrier Fusion Method, and the Vacuum Fusion Method.

The Ransley Sub-Fusion Method

The vacuum sub-fusion extraction technique was developed by C. Ransley, R. Eborall, and D. Talbot during 1945-55 [57]. It is often simply called “The Ransley Method”. Because of its accuracy and stability, the method has been used as a reference technique against which other techniques are calibrated or compared.

The Ransley Sub-Fusion Method uses a carefully machined cylindrical sample of given dimensions. The sample is heated under vacuum to a temperature just below the point at which fusion commences. At this temperature, hydrogen is extracted from the sample through diffusion. The extracted hydrogen is collected in a known volume and the hydrogen pressure is measured using a McLeod or Pirani gauge. From these values, the hydrogen content of the sample is calculated. The apparatus used for this method has been improved in many aspects since it was first created. However, because it is not commercially available, the apparatuses used in different laboratories may differ slightly from one other.

One of the complications in determining hydrogen in aluminum by the subfusion method is surface hydrogen, which is generated from surface reactions that result in hydrogen ion additions to what is present in the bulk of the metal. The reactions are mainly due to:

Breakdown of hydrocarbons from contaminating oil or grease.
Reaction of absorbed surface moisture with the metal sample.

The first problem is usually minimized or overcome by dry machining of the sample and by avoiding manual contact. For the second problem, one needs to make a proper surface correction. The solutions can be to minimize the moisture absorbed and/or measure the amount of surface hydrogen generated, which is then subtracted from the total measured
amount of hydrogen. In the Ransley method, this is accomplished by first measuring total hydrogen, then removing the sample from the apparatus, remachining the surface, and replacing the sample in the equipment for the second hydrogen determination.

It was found that hydrogen values measured by the Ransley method are lower than those calculated by some other methods, such as Telegas, AlSCAN, or CHAPEL [58, 59]. For wrought alloys, the results obtained by the Ransley method could differ by as much as 30% from hydrogen values obtained by Telegas and AlSCAN measurement. An experiment conducted by Dupuis et al. [58] showed that the measured hydrogen values from the Ransley method were lower than expected. The difference was attributed to hydrogen loss during sampling, mainly during transfer and/or solidification, or to underestimation of hydrogen content in the subsequent extraction. Hydrogen rejection occurred during solidification, but losses were quite small. Chen et al. [59] considered that the cooling power of the sampling mould was not sufficient to hold hydrogen in a forced solution during solidification, especially at high hydrogen levels. However, the experiments revealed no direct evidence to support this argument.

There may be other factors responsible for the lower values measured by the Ransley method. If hydrogen loss occurred during transfer and/or solidification, the metal transfer time and cooling rate would affect the measured values. Ray's experiment [60], which used Ransley moulds and studied the effects of the mould and sampling technique on hydrogen content, showed that higher hydrogen levels seemed to be associated with a hotter mould. The hydrogen increase was attributed to the slower cooling rate, which, in turn, can lead to increased shrinkage, porosity and gas entrapment. The experiment also showed that measured hydrogen levels were not significantly affected by a reasonable variation in melt temperature.

The lower hydrogen values measured by the Ransley method may be due to the fact that hydrogen is not completely extracted from the sample.
Despite the great stability of the Ransley technique, its consistency is still a matter of concern. The extensive manipulations involved in sampling and sample preparation can be the source of significant variability in results.

The principal advantage of this method is its accuracy. It has been reported that the standard deviation for the Ransley method is generally 0.02ml/100g. The major drawbacks are its long processing time and its cost. Typical extraction requirements are about 3.5 hours. This time can be doubled if a sample requires an individual surface correction factor. Besides costly laboratory equipment and time, this technique must be applied to rigorous standards by trained personnel if consistent results are expected. Therefore, despite its accuracy, the procedure’s time-consuming nature and high costs limit its application as an online control on the foundry floor. However, it is used widely in the wrought alloy industry and in research.

The Nitrogen Carrier Fusion Methods

These methods include the LECO RH and the Ithac device. The development of these two devices was based on the work of Degreve [61]. In this method, a cylindrical sample is placed in a graphite crucible and melted in a stream of nitrogen (carrier gas) [62]. Hydrogen is evolved from the melt, mixed with the nitrogen, and carried downstream. The hydrogen is detected and measured by a catharometer, which determines the thermal conductivity of the gas mixture. This measuring principle is based on the fact that the thermal conductivity of the hydrogen gas is approximately seven times higher than the nitrogen gas.

Two major factors affecting the measuring accuracy are surface hydrogen and the ingress of moisture into the nitrogen gas carrier. The moisture may come from two sources: the carrier gas and the hydroxyl ions in the silica network of the quartz tube in which the sample is melted. During fusion, spurious hydrogen can be generated through the reaction of water and metal vapour; in addition, water and hydrogen may react with carbon to
produce carbon monoxide and methane. Water and its products change the thermal conductivity of the carrier gas.

In this method drying the carrier gas, which is passed through magnesium percolate and a molecular sieve, minimizes atmospheric moisture. With this arrangement, the dew point of the carrier gas can be lowered to approximately −60°C. At a dew point of −78°C, the interference caused by the water reaction will be less than 0.01 ml/100g.

The problem of surface hydrogen is generally dealt with by preheating the specimen. The main problem is that surface hydrogen is evolved at temperatures close to the melting range of some alloys. This suggests that surface treatment is critical to the accuracy of this method.

With adequately dried carrier gas and appropriate surface treatment, the accuracy of the LECO RH-3 device can be about the same as that of the Ransey method (0.02ml/100mg). However, for some alloys, the differences between the two methods become significant in higher hydrogen concentration ranges. The accuracy of the LECO RH-402 method is 1%, relative, with a sensitivity of 0.001 ppm (0.0009 ml/100g). Measured values are higher for the fusion method than for the sub-fusion method. The reasons for this are extensive shrinkage porosity, its non-uniform distribution and the rate of hydrogen release. When they are exposed to the surface, voids can act as traps for hydrogen and water vapour.

The primary difference between the Ithac and LECO RH instruments (taking Ithac-02 and LECO RH-3 as examples) is the fact that the latter has a loading head for the introduction of samples. The loading head permits the sample to be stored in a cavity, which has been purged with dry nitrogen gas and sealed, before it is introduced into the graphite crucible and fused.

This method is much faster than the sub-fusion method. A complete analysis by this method takes approximately 20 minutes, and the fusion/analytical cycle is only about 3 minutes. It has a satisfactory accuracy for some alloys, but generally it is not as accurate as the sub-fusion method. Its equipment is costly and it has strict requirements for sample preparation and operation. Besides, like the Ransley method, it must be operated carefully by trained personnel, maintained rigorously, and used mainly in laboratories.
The Vacuum Fusion Method

The Vacuum Fusion Method was developed initially to determine the gaseous elements, oxygen, nitrogen and hydrogen in ferrous alloys [63]. In this method, a specimen is melted under vacuum and the increase in gas pressure in the vacuum chamber is measured.

The vacuum fusion method could be considered the first feasible method for determining hydrogen content in aluminum alloys.

It consists of a vacuum pump, a chamber in which the sample may be melted, a pressure gauge, and a gas collection system. The gas collection system includes two gas collectors, one for collecting a sample of gases present in the melt chamber prior to the melting of the sample, and the other for collecting the gases after melting.

The specimen must be thoroughly cleaned and dried and carefully weighed before being placed in the crucible. The entire system is then properly assembled and the determination of gas content proceeds in the following three steps:

1. Determining the volume of the melting chamber.
2. Operation for gas content measurement.
3. Calculation of the gas content and identification of the gas species.

A few authors have reported that this method does not require a special specimen [64]. The specimen can be sectioned from any product and from any portion of the product to be analyzed, as long as it fits in the crucible. The method is relatively simple and the results are derived from only a few pressure measurements. The vacuum fusion unit itself is relatively inexpensive to construct and operate. This method measures the total gas content evolved from dissolved and entrapped gases in the specimen. This is one of its advantages. It can be used for hydrogen determination for an aluminum alloy in which hydrogen is the only dissolved gas and there are no entrapped gases. However, this is also a drawback, as the method can not accurately measure a particular gas when other gases are dissolved or entrapped in the specimen, since gas chromatography can only identify the species present but cannot make a quantitative measurement.
The Vacuum Fusion Method uses a solid sample and needs to run at a high temperature to melt it. Thus, the sample surface hydrogen and the evolution of gases from the crucible and tubes of the apparatus may cause errors and need to be treated properly.

### 2.8.2 Quantitative In-Situ Methods

These methods yield an in-situ quantitative measure of the hydrogen concentration in aluminum and aluminum alloy melts. Included in this category are the Telegas and A1SCAN devices, the CHAPEL device and the electrochemical method [56].

The basic principle of the Telegas and A1SCAN methods is closed-loop gas recirculation. A small amount of carrier gas (such as nitrogen, argon or helium) is brought in contact with the molten aluminum alloy and recirculated through a ceramic probe submerged in the molten alloy. Hydrogen diffuses into the recirculating carrier gas until it has reached its equilibrium pressure condition, according to Sievert's law,

\[
[H] = S \sqrt{p_{H_2}}
\] 2.20

Where: \( p_{H_2} \) is the hydrogen partial pressure over the melt; and \([H]\) is the concentration of hydrogen in the melt (ml/100g). At equilibrium, \([H]\) equals the solubility, \(S\), corresponding to the hydrogen partial pressure \(p_{H_2}\).

In the 1970's Hess [65] introduced an empirical equation for determining hydrogen solubility in aluminum alloys. This equation related the hydrogen solubility in an aluminum alloy to the melt temperature and to the alloy’s Si, Cu and Mg content.

\[
S(\text{ml}/100\text{g}) = 0.00606 \times [1.23 - 0.0733(\%\text{Cu}) - 0.033(\%\text{Si}) + 0.0489(\%\text{Mg})] \times (T-585) \] 2.21
where \( T \) is temperature in °C.

In the case of the A1SCAN analyzer, equation is modified to [66]:

\[
[H] = S_0 \cdot \sqrt{p_{H_2}} \cdot CF(T) \cdot CF(A)
\]

Where: \([H]\) equals hydrogen solubility, \( S \), at partial hydrogen pressure \( p_{H_2} \) at equilibrium. \( S_0 \) is the solubility of hydrogen in pure aluminum at a reference temperature taken to be 700°C. \( S_0 \) can be measured and data is available. \( CF(T) \) is a correction factor for metal temperature, which can be derived from the known solubility-temperature curves for pure aluminum; \( CF(A) \) is a correction factor for metal composition [67].

Alcan developed the following equation for calculation the \( CF(A) \), which is based on Hess's work.

\[
\log CF(A) = 0.0170 \%Mg - 0.0269 \%Cu - 0.0119 \%Si
\]

By knowing the alloy composition the temperature, and by measuring \( p_{H_2} \), \([H]\) can be calculated.

Generally, both the Telegas and A1SCAN analyzers consist of a gas recirculation system that includes a changeable, consumable probe, a sensor (thermal conductivity detector), and a data display. The probe houses the open section of the carrier gas recirculating system, where the gas contacts the molten metal.

The A1SCAN analyzer uses a “disposable” probe that consists of small piece of open pore ceramic in which two capillary metal tubes (the outlet and inlet for the carrier gas) are embedded. The pore size of the probe material is large enough to allow good gas circulation, but small enough to prevent metal penetration. For this reason, the ceramic piece serves merely to physically locate a stationary gas bubble inside the molten metal.
The gas/liquid hydrogen exchange takes place at the interface between the open pores of the ceramic piece and the molten metal.

The open pore structure enhances the thermal shock resistance of the ceramic. The metal tubes embedded in the ceramic piece do not contact the melt. A thin ceramic coating protects the section of the tubes that do contact the melt. It has been reported that with this structure, the probe can be simple, inexpensive and robust. There is no tube blockage or thermal shock to worry about. The probe can be inserted directly into the melt without any preheating. Moreover, it can be operated at any convenient angle, even in very shallow metal, as long as the ceramic portion of the probe can be submerged totally in the melt. It is also claimed that this design avoids a possible error associated with Telegas. When using Telegas, some gas bubbles left in the melt from the degassing operation may be collected by the carrier gas bubbles and the hood, leading to unstable or undervalued results. This does not happen with the A1SCAN analyzer. The A1SCAN analyzer is also equipped with a stirring device, which refreshes the probe/metal interface providing for a fast response time and good reproducibility. As a result, the process normally requires about five minutes to achieve hydrogen equilibrium between the carrier gas and the metal, but a 10-minute operation is recommended to insure good reproducibility. It has been reported that the average variability was 0.02 ml H₂/100g under actual production conditions, including temperature variations. Under more favourable conditions, e.g., in a hot but stagnant melt, the reproducibility was 0.01 ml H₂/100g.

Compared to the sub-fusion and fusion techniques, Telegas and A1SCAN are much faster in quantitatively determining the hydrogen content of aluminum alloys. Since it takes 10 to 20 minutes for one determination, the techniques can be used for on-line control.

The Electrochemical Method

Gee et al. worked on an electrochemical method in the 1970's [68]. By that time, solid electrolyte probes had been used for the instantaneous determination of oxygen in steel and copper and in the measurement of sodium content of molten aluminum alloys. The
work by Gee et al. was an attempt to use this technique for hydrogen measurement in aluminum alloys.

In a cell consisting of two electrodes in an electrolyte, the equilibrium electrical potential, $E$, measured across the electrode/electrolyte interfaces, and the chemical potentials of species $i$ at two electrodes, $\mu_{ii}$ and $\mu_{i}$, have a relationship.

\[ \mu_{ii} - \mu_{i} = -z \times F \times E \]  \hspace{1cm} (2.24)

where $F$ is the Faraday constant and $Z$ is the number of electrons involved in the reversible reaction occurring at the interface.

For two gaseous hydrogen electrodes, chemical potentials may be replaced by the corresponding partial pressures $P_{H_2}^{'}$ and $P_{H_2}^{''}$:

\[ R \times T \times \ln \frac{P_{H_2}^{'}}{P_{H_2}^{''}} = -z \times F \times E \]  \hspace{1cm} (2.25)

where $R$ is the gas constant and $T$ is the temperature. This equation indicates that in such a cell, if one of the partial pressures is known or can be measured and $z \times F \times E$, (the electromotive force, emf) can be measured; the other partial pressure can be calculated. This cell may be used as an analytical device.

In using such a cell as a hydrogen probe for aluminum, the aluminum melt containing hydrogen will act as the electrode whose hydrogen partial pressure is to be measured. For this device to be successful, a suitable electrolyte and hydrogen electrode must be found. It is essential that the electrolyte maintain its properties under the system operating conditions. In particular, it must be thermally stable when in contact with the two electrodes. The other electrode must also maintain the hydrogen partial pressure constant. A mixture of a metal with its hydride, which would provide fixed hydrogen potential at a given temperature, would be suitable for making this electrode a hydrogen reference. Gee
et al. [67] constructed such a probe, in which a calcium hydride was chosen as the electrolyte and a mixture of calcium and calcium hydride was selected as the other electrode. The equilibrium hydrogen pressure over the mixture of \( \beta \text{Ca} \) and \( \alpha \text{CaH}_2 \) at composition of 20 to 95 mole\%\text{CaH}_2 and in the temperature range of 873 to 1053 K (600 to 780°C) was given by:

\[
\log P_{H_2} = \frac{-9610}{T} + 10.277
\]

Thus, a given pressure in the range \( P_{H_2} \) (partial hydrogen pressure) over the mixture of calcium and calcium hydride can be calculated.

2.8.3 Semi-Quantitative Methods

These methods yield a semi-quantitative measure of the hydrogen concentration in aluminum and aluminum alloy melts. Included in this category are the Reduced Pressure Test (RPT), together with several minor variations of its basic operational principles, and the Ultrasonic Attenuation Method.

The Reduced Pressure Test (RPT)

The Reduced Pressure Test (RPT) is also called the vacuum solidification test or Straube-Pfeiffer test. In this test a small amount of a molten aluminum alloy sample is allowed to solidify under controlled reduced pressure, and the gas content is estimated or determined by observing the solidification behaviour of the specimen or by density measurement or porosity analysis of the solidified specimen. This method was first employed in the 1920's. In the early stage of its development it was only used for qualitative evaluation of the quality of the molten alloy. Now it is a semi-quantitative method for measuring hydrogen content and is widely used in the aluminum industry.

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As mentioned earlier, hydrogen solubility in liquid aluminum and aluminum alloys is much higher than that in solid aluminum. The significant solubility change may result in the formation of pores during the alloy solidification process. During the formation and growth of the gas pore in the melt, the gas pressure inside the pore should at least be equal to the external pressure. For a stable pore,

\[ p_q = p_0 + \rho_L g_r h + 2 \frac{\sigma_i L}{r} \]  \hspace{1cm} (kPa)  \hspace{1cm} 2.27

where the term on the left side of the equation, \( p_q \), is the total gas pressure inside the pore; the terms on the right side of the equation are the external pressure, which include \( p_0 \) (the ambient pressure), \( \rho_L g_r h \) (\( \rho_L \) is density of the liquid metal, \( g_r \) is gravity and hydrogen is distance from the pore to the melt surface; together they constitute the metallostatic pressure head), and \( 2 \frac{\sigma_i L}{r} \) (the pressure on the pore resulting from the pore-melt interfacial energy \( \sigma_i L \), \( r \) is the pore diameter). In aluminum alloys, only hydrogen can dissolve to a significant extent, so the gas in the pore can be considered a single species. Thus, in alloys, the \( p_q \) at equilibrium dissolved in the surrounding metal can be calculated according to the thermodynamic relation:

\[ \%H_L = K'_L \sqrt{p_{H_i}} \]  \hspace{1cm} 2.28

where \( \%H_L \) is the weight percent of Hydrogen dissolved in the liquid metal, and \( p_{H_i} \) is the Hydrogen partial pressure in the pore. \( K'_L \) is a constant, which depends on alloy composition and temperature, and generally increases with the increase in temperature.

Since Hydrogen is the only gas in the pore, the \( p_{H_i} \) should be equal to \( p_q \). According to equation 2.27, for the formation and growth of pore, \( p_q \) should be greater than \( p_0 \), that is, \( p_{H_i} \) should be greater than \( p_0 \). Therefore, facilitating gas pore formation and growth.
means increasing $p_{H}$ and/or decreasing $p_{0}$. In the conventional solidification, the ambient pressure, $p_{0}$, is constant, at one atmosphere pressure. Pore formation and growth, as described above, are due to the increase of $p_{H}$, caused by the enrichment of hydrogen in the remaining liquid and due to the decrease of $K_{L}$ caused by the temperature decrease [56].

According to Boyle's law, if 0.1 atmospheric pressure is used, the volume occupied by the gas precipitated from the melt is magnified by a factor of 10 compared with 1.0 atmospheric pressure. The RPT was developed on the basis of these phenomena.

Generally, the following characteristics that occur in the RPT are used to evaluate or measure hydrogen content:

1. Surface movement of the specimen;
2. Porosity content in the specimen;
3. Density of the specimen; and
4. The time at which the first pore is formed in the melt.

Various versions of RPTs have been developed based on different characteristics. These methods can be broadly classified as a conventional (basic) test with modifications.

In the conventional test, the specimen is allowed to solidify at a constant, predetermined reduced pressure and hydrogen content is determined by observing or analyzing the solidified specimen. The following three methods are generally used in hydrogen determination.

The surface of the specimen may move during solidification because its volume increases due to porosity formation and pore expansion under low pressure. This can be indicated by visual observation through a viewing window or transparent hood on the vacuum chamber during solidification, or by observation of the surface shape of the solidified specimen. The surface moving up and/or gas bubbles coming to the surface indicate the
presence of hydrogen. The more gas dissolved in the original melt and the lower the pressure, the more severe the surface movement and the more gas bubbles come to the surface, resulting in a puffed specimen with a convex surface. This visually interpreted test is simple and fast. It can only give a rough estimation of hydrogen content in the melt on a comparative basis. However, by setting a standard for fixed pressure, this can serve as a very good acceptance test for routine quality control and it has been widely used.

Obviously, the porosity level in a specimen is related to its gas content. Hydrogen is the only gas that can be substantially dissolved in aluminum alloys. In controlled conditions, the hydrogen loss can be eliminated, and the amount of the dissolved hydrogen in the solid can be kept at a fixed level (generally small). Thus, the porosity level will be the only variable needed for assessing the total hydrogen content. The porosity level can be measured in several ways.

Visual Observation: the simplest approach is to cut the sample in half on the transverse plane and examine the cut surface. A photographic standard has been set up for determining the porosity level. Using the porosity level, hydrogen content can be estimated.

Metallographic Analysis: In this analysis, the sample halves are polished to better delineate porosity. This method can reveal the fine pores, which could be masked by the saw marks from the cutting process. An Image Analysis (IA) technique can be utilized on the polished surface to measure the porosity.

Radiography and Ultrasonic Techniques: these methods can provide some quantitative information about the porosity in the specimen. However, using x-ray and γ-radiography requires special equipment and the process is not economical in terms of the time consumed in preparing the radiographs and measurements. The ultrasonic technique is a promising method for measuring porosity; however, its use in the RPT was not reported.
Volume Measurement: If the volume of the solidified specimen can be precisely measured the difference between the measured volume and porosity-free volume will be the weight and density of the specimen. This method was not used in the conventional RPT; however, a similar method was used in the Density Measurement Technique.

The visual observation of a cut specimen is widely used in production for quality control because it is simple and fast, but it can only give a rough estimation. Among all the available methods, the image analysis is the only one that can provide an accurate porosity level from the measured surface. However, it needs sophisticated equipment and is time consuming, and its measured surface may not be representative of the bulk of the specimen. Therefore, the Image Analysis Technique is only suitable for use in research. To date, an accurate method is not available for measuring porosity for the reduced pressure process; the determination of the hydrogen content in this process relies mostly on density measurement.

Density measurement is another way to determine the porosity level that is calculated by:

A Gravitometer:
This apparatus consists of a cylinder that contains two immiscible liquids, the lighter liquid floating above the heavier liquid. Mercury and ethyl alcohol are typically used [69]. A specimen submerged in the alcohol will float on the surface of the mercury. The density of the specimen is calculated from the relative displacements occurring in each liquid. It permits determination of the density of aluminum specimens within 30 seconds with the reproducibility of ±0.02 g/cm³.

The Archimedes Method [70]:
Density is calculated from the weight difference of the specimen weighted in two different media—for example, in air and in a liquid (such as distilled water or ethyl alcohol). The procedure follows the Standard Test Method for Density of Glass by Buoyancy (ASTM Standard C-893).
The determination of hydrogen content through density measurement can be done in various ways such as comparison of the measured density with predetermined standards or calculation of the gas volume in the specimen from the measured density.

The comparison of the measured density using the predetermined standards method can be fast, but standards need to be prepared for various conditions (type of alloy, sample size and shape), making the technique difficult for practical use. The comparison can also be performed on a series of specimens taken at different stages in a casting and production processes. Though this does not give quantitative hydrogen values, it can serve as an indication for process performance, such as degassing.

The standard density can be calculated from the alloy’s composition or measured from a porosity-free specimen. The porosity-free sample can be obtained from a well-fed casting. The derivation of the formula is as follows [71]:

\[
D = \frac{\text{Weight}}{\text{Volume}} \quad \rightarrow \quad \frac{1}{D} = \frac{\text{Volume}}{\text{Weight}} = \frac{\text{Volume(metal)} + \text{Volume(gas)}}{\text{Weight(metal)} + \text{Weight(gas)}} \quad 2.29
\]

where \( D \) is the density of the measured specimen.

Since the weight of the gas can be neglected,

\[
\frac{1}{D} = \frac{\text{Volume(metal)}}{\text{Weight(metal)}} + \frac{\text{Volume(gas)}}{\text{Weight(gas)}} \quad \rightarrow \quad \frac{\text{Volume(gas)}}{\text{Weight(metal)}} = \frac{1}{D} - \frac{1}{D_0} \quad 2.30
\]

where \( D_0 \) is density of the porosity-free specimen.

\[
\frac{\text{ml(gas)}}{100\text{g(metal)}} = 100\left(\frac{1}{D} - \frac{1}{D_0}\right) \quad 2.31
\]

Therefore, the volume of gas under standard conditions of pressure and temperature (STP) can be calculated:
Chapter Two, Literature Review

\[
\text{Volume(\text{STP})} = \frac{P}{760} \times \frac{273}{273+T} + \left( \frac{1}{D} - \frac{1}{D_0} \right) \tag{2.32}
\]

\[
\frac{\text{cc(\text{gas})(\text{STP})}}{\text{100g(\text{metal})}} = \frac{P}{7.60} \times \frac{273}{273+T} + \left( \frac{1}{D} - \frac{1}{D_0} \right) \tag{2.33}
\]

The density measurement by gravitometer is not accurate and the measurement by weighing specimens is time consuming; therefore, the gas content calculated by density or porosity measurement in the RPT can reveal the true (total) gas content in the metal only if:

1. The solid solubility of hydrogen is negligible and all the gas originally dissolved in the liquid is expelled during the test.
2. The gas precipitated from the specimen is registered.
3. The voids in the specimen contain gas at the pressure equal to the sum of the reduced pressure and the metallostatic pressure (not shrinkage porosity).
4. The porosity free density of the metal is accurately known.

These conditions can be roughly met in common RPTs even if the equilibrium solubility of hydrogen in solid aluminum is small, being approximately 0.012 ml/100g at 10 kPa pressure. The commonly used specimen design in the conventional RPT (the truncated cone with its larger end up) minimizes shrinkage of voids in the specimen. The effect of density variation caused by the alloy chemistry is reduced by a factor \(P_1/P_0\) (\(P_1\) – reduced pressure; \(P_0\) – normal ambient pressure, 1 atm.) in the RPT (about 10 times at commonly used reduced pressure) according to Equation 2.33. This makes the effect of the density variation negligible.

The sensitivity of the RPT depends, to a large extent, on the applied pressure. In practice, various pressures, ranging from 1 to 100 mm Hg, were used successfully under different conditions [72]. When the test is used on a qualitative basis for low gas content alloys, a
low solidification pressure must be used to meet premium casting requirements (that is, maximum freedom from hydrogen and inclusions) should be conditioned at a maximum pressure of 6.7 kPa. At this low pressure, the information provided by observation of the specimen’s solidification behaviour is considered superior to that obtainable from the specimen solidified under atmospheric pressure.

Subsequent determinations of specimen density may provide a convenient and supplemental numerical rating of melt quality. However, with lower pressure, the volume of gas lost from the specimen is increased. By employing a density measurement to provide quantitative data, it was found that approximately $\frac{1}{8}$ atmosphere provides sufficient sensitivity for most foundry test purposes, for example, in the melt acceptance test, where an extremely high quality metal is not required. This permits a workable degree of sensitivity for purposes of density measurement without excessive gas loss from the specimen [72].

Rosenthal et al. [71] studied the effect of pressure on the measured values of gas content. The gas content of the same melt was analyzed by density measurement, under atmospheric pressure and reduced pressure and at different temperatures and holding times. It was found that the gas contents calculated from the atmospherically solidified specimens were consistently higher than the gas contents calculated from the reduced pressure sample. It was also found that the divergence of the data was greater at higher gas contents than at lower gas contents. It was believed the difference was due to the loss of gas from the specimens solidified at reduced pressure.

The sampling temperature in the range of 676-760°C are commonly used for the RPT. High pouring temperatures are undesirable for alloys that contain considerable sodium, calcium, zinc or magnesium, because these elements may boil out under reduced pressures and give false indications of hydrogen in the vacuum density test. Losses of cadmium and zinc cause low density values, whereas losses of sodium and magnesium have the opposite effect. Low density will also result if bubbles of the vapour of these elements are trapped in the specimen.
Hydrogen solubility in the bulk of solid aluminum is dependent on the ambient pressure and inclusions as well. At the atmospheric pressure hydrogen solubility is approximately 0.036 ml/100g for solids, and the amount of supersaturated hydrogen can be in the order of 0.014-0.044 ml/100g [56]. This would be the maximum amount of hydrogen the inclusions can act on. In the RPT, the sample solidifies at a slower cooling rate to allow pores to develop. This would reduce the amount of hydrogen for inclusions to act on. The effect of the reduced pressure is not clear. It decreases hydrogen solubility in the solid, which may provide more hydrogen for inclusions, but it also facilitates pore nucleation and growth, which would make less hydrogen available for the inclusions. Quantitative attempts have been made to evaluate the effects of inclusions on the porosity, but no reliable data have been reported.

To retain gas within the specimen, consideration should be given to the geometry of the sampling cup. The ratio of free surface area to the volume of the specimen should have an important bearing on the gas loss that occurs.

The conventional RPT has been widely used in the aluminum industry. It is simple, inexpensive and versatile. Because it has various ways to show the existence and quantity of hydrogen, it has served a variety of purposes in production and research, such as quantity control and hydrogen detection and measurement. It has a workable accuracy for many applications. However, its accuracy is generally lower than that of some other methods, such as the sub-fusion and the fusion methods and Telegas. Since in a quantitative analysis, the density or porosity measurement requires prolonged time, this method has been used qualitatively for the most part.

The porosity level produced in RPT depends not only on hydrogen content, but also on the amount of inclusions. This is considered an important factor affecting the accuracy of the RPT. However, it makes this a unique quality control tool to measure the combining effects of hydrogen and inclusions.
2.9 Inclusion Sources and Detection in Molten Aluminum

Inclusions in aluminum are of great importance as they relate to the diminishing quality of the cast components. Thus during processing operations, attention should be given to diminish the formation of inclusions, and more importantly, to remove those which are present in the melt. However, the weak link is how one quantitatively determines the level of inclusions.

Metal quality depends of three interrelated factors: the control of trace elements, reduction of dissolved gas content and removal of non-metallic inclusions. Inclusions in aluminum alloys reduce mechanical properties, are detrimental to surface finish, increase porosity, as well as have a tendency to increase corrosion. Non-metallic inclusions act as stress raisers, and can cause premature failure of a component.

Inclusion Classification

Inclusions in molten aluminum can be classified according to their size, chemical content and phases (solid or liquid) [73]. Table 2.6 summarizes the experimental data for various inclusion types.
Table 2.6: Classification of Inclusions Observed in Molten Aluminum [73].

<table>
<thead>
<tr>
<th>Type</th>
<th>Form</th>
<th>Density, g/cm$^3$</th>
<th>Dimensions, µm</th>
<th>Melting Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXIDES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgAl$_2$O$_4$ (Spinel)</td>
<td>Particles, skins, flakes</td>
<td>3.60</td>
<td>0.1-100, 10-5000</td>
<td>2825</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (Corundum)</td>
<td>Particles, skins</td>
<td>3.97</td>
<td>0.2-30, 10-5000</td>
<td>2047</td>
</tr>
<tr>
<td>MgO</td>
<td>Particles, skins</td>
<td>3.58</td>
<td>0.1-5, 10-5000</td>
<td>2115</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Particles</td>
<td>2.66</td>
<td>0.5-30</td>
<td>1650</td>
</tr>
<tr>
<td>CaO</td>
<td>Particles</td>
<td>3.37</td>
<td>&lt;5</td>
<td>2630</td>
</tr>
<tr>
<td>CARBIDES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_4$C$_3$</td>
<td>Particles, clusters</td>
<td>2.36</td>
<td>0.5-25</td>
<td>2100</td>
</tr>
<tr>
<td>SiC</td>
<td>Particles</td>
<td>3.22</td>
<td>0.5-5</td>
<td>2540</td>
</tr>
<tr>
<td>BORIDES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>Particles, Clusters</td>
<td>4.5</td>
<td>1-30</td>
<td>2790</td>
</tr>
<tr>
<td>AlB$_2$</td>
<td>Particles</td>
<td>3.19</td>
<td>0.1-3</td>
<td>2160</td>
</tr>
<tr>
<td>NITRIDES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlN</td>
<td>Particles, skins</td>
<td>3.26</td>
<td>10-50</td>
<td>2227</td>
</tr>
<tr>
<td>OTHER</td>
<td>Chlorides and salts (CaCl$_2$, NaCl, MgCl$_2$)</td>
<td>Liquid droplets</td>
<td>1.9-2.2</td>
<td>712-800</td>
</tr>
<tr>
<td></td>
<td>Fluorides (cryolite)</td>
<td></td>
<td>2.9-3.0</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Sludge Al(FeMnCr)Si</td>
<td></td>
<td>&gt;4.0</td>
<td></td>
</tr>
<tr>
<td>ULTRAFINE GAS BUBBLES</td>
<td></td>
<td></td>
<td>0.5-1</td>
<td></td>
</tr>
<tr>
<td>Argon bubbles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen bubbles</td>
<td></td>
<td></td>
<td>10-30</td>
<td></td>
</tr>
<tr>
<td>INTERMETALLICS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiAl$_3$, TiAl, NiAl, Ni$_3$Al</td>
<td>Particles, clusters</td>
<td>-</td>
<td>10-100</td>
<td>-</td>
</tr>
</tbody>
</table>

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2.9.1 Sources of Inclusions

Oxide films and particles are formed during melting and alloying processes. The Al$_2$O$_3$ films are either suspended on the melt surface and/or entrapped within it due to metal turbulent flow during casting. Oxide inclusions have a tendency to float out despite their greater density than molten aluminum. Oxide inclusions also have a tendency to agglomerate, because they are poorly wetted by molten aluminum, and in effect Al$_2$O$_3$ inclusions become buoyant as a result of absorbed gases and rise to the melt surface [74].

Spinel inclusions originate from melting scrap as well as magnesium additions into the holding furnace. MgO has a tendency to form preferentially to Al$_2$O$_3$ due to a lower free energy of formation. The addition of magnesium to molten aluminum causes non-metallic inclusions other than spinels to form. Nitride inclusions AlN originate from magnesium nitride Mg$_3$N$_2$. MgF$_2$ and MgS particulates have been observed to form when ‘dirty’ magnesium is added to the melt. Silica particulates mostly originate from erosion of ceramic materials used as accessories in the melting operation. These refractory particles do agglomerate, and compounds such as Al$_2$O$_3$SiO$_2$CaO are often observed. Recycled aluminum melts usually contain a large amount of aluminum carbides due to the exposure to hydrocarbons [75].

2.9.2 Inclusion Detection Methods

It is well known that it is difficult, if not impossible, to control a process if key parameters cannot be measured. In molten metal processing, the assessment of the level of inclusions present in the melt has been and is the key parameter which needs to be monitored. Table 2.7 summarizes the various methods available for inclusion detection.
Table 2.7: Methods for Inclusion Detection [73].

<table>
<thead>
<tr>
<th>Detection Methods</th>
<th>Sample weight, g</th>
<th>Particle size detected, μm</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRESSURE FILTER TESTS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PoDFA</td>
<td>≤2000</td>
<td>All sizes</td>
<td>Off-line</td>
</tr>
<tr>
<td>LAIS</td>
<td>≤1000</td>
<td>Off-line</td>
<td></td>
</tr>
<tr>
<td>Prefil Footprinter</td>
<td>-</td>
<td>Off-line</td>
<td></td>
</tr>
<tr>
<td>ELECTRIC RESISTIVITY TEST</td>
<td>S≤100 per minute</td>
<td>&gt;15</td>
<td>On-line</td>
</tr>
<tr>
<td>LiMCA, LiMCA II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACOUSTIC DETECTION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Signal-noise technique</td>
<td></td>
<td>&gt;10</td>
<td>On-line</td>
</tr>
<tr>
<td>Pulse-echo technique</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELECTROCHEMICAL DISSOLUTION</td>
<td>≤100</td>
<td>All sizes</td>
<td>Off-line</td>
</tr>
<tr>
<td>CHEMICAL ANALYSIS</td>
<td>0.5-30</td>
<td>All sizes</td>
<td>Off-line</td>
</tr>
<tr>
<td>Emission spectroscopy; Hot extraction;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combustion analysis; Neutron activation;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromatography</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDDY CURRENT METHOD</td>
<td></td>
<td></td>
<td>On-line</td>
</tr>
<tr>
<td>CAPACITANCE PROBE</td>
<td></td>
<td></td>
<td>On-line</td>
</tr>
<tr>
<td>X-RAY DETECTION</td>
<td></td>
<td></td>
<td>Off-line</td>
</tr>
<tr>
<td>ELECTROMAGNETIC DETECTION TECHNIQUE</td>
<td>≤200 per minute</td>
<td>&gt;10</td>
<td>On-line</td>
</tr>
</tbody>
</table>

2.9.3 Pressure Filter Tests

In this technique, a certain volume of metal is passed through a fairly impermeable filter which collects the inclusions, present in the melt, as the cake on the filter. The collected inclusions are then analyzed metallographically. An advantage is that the volume of inclusions collected per volume of metal sampled is known. The main disadvantage is that the test is tedious, labour intensive and is an off-line test. The Porous Disk Filtration
Apparatus (PoDFA) and the Liquid Aluminum Inclusion Sampler (LAIS) are based on the same principle. The LAIS and PoDFA methods allow for measuring of the amount of inclusions, as well as determination of the types of inclusions. These tests are widely accepted to assess inclusion levels in foundries.

2.9.4 Resistivity Tests

Today, LiMCA is considered to be a reliable tool for on-line detection of small particles in liquid metals. It can be used either alone or together with PoDFA or LAIS for larger inclusions [76]. The cost of the LiMCA system is quite high, and it is clear that this method will not be widely used by the foundry industry but it is widely used throughout primary producers of aluminum.

In the LiMCA apparatus a tubular aperture is used to flow molten metal through it (Figure 2.12). The flow path from electrode 1 to electrode 2 includes the aperture and the surrounding metal volume. The key point of the method is the voltage drop, when particle passes through the aperture, it is directly related to the particle radius [77].

![Figure 2.12: Schematic of LiMCA system.](image)

During the LiMCA test, the momentary voltage drops are counted and classified according to their magnitudes. Hence, both number and size distribution of inclusions larger than 15-20 μm are determined.
Chapter Three

Enviro-AlTAP Experimental Methodology

Experiments and analysis performed in this thesis are part of a Novel Thermal Quality Control Platform for ingots and melts developed by the IRC team.

Figure 3.1 summarizes sampling, testing and measurement techniques used for the thermal, structural and mechanical analysis of ingots, master alloys, melts and engine blocks.

The main goal of the performed Enviro-AlTAP experiments was to establish an experimental procedure and develop a technique that can be used to assess the amount of porosity in an as-cast product. The Enviro-AlTAP utilized the AlTAP with integrated RPT hardware.

Experiments by the IRC team [78] have shown that certain parameter(s) from the cooling curve(s) can be used to assess the amount of dissolved hydrogen in the liquid aluminum melt. This thesis tries to answer the following question:

How do different pressures (from 6 kPa to 101 kPa) and amount of dissolved hydrogen (from 0.06 ml H\textsubscript{2}/100g Al alloy to 0.25 ml H\textsubscript{2}/100g Al alloy) influence the cooling curve characteristics?

Two levels of hydrogen were studied. The low level (LH) which is below 0.15 ml H\textsubscript{2}/100g Al and the high level (HH) which is above 0.15 ml H\textsubscript{2}/100g Al.

The applied pressure was investigated at three levels. Experiments performed at an atmospheric pressure of 101 kPa were considered to be low vacuum level conditions.
Experiments performed at 50 kPa were at the middle vacuum level (MV), while pressure at 6 kPa was considered as the higher vacuum (HV) level.

Secondary W319 aluminum ingots from the WAP production line were used in all experiments. Every ingot was cut into eight equal pieces and every piece was marked. In
order to preserve the same chemical composition of the melts, the first piece of each ingot was used in the first experiment; the second piece of each ingot was used in the second experiment, and so on. OES samples were made and chemical analysis was carried out at the NEMAK Windsor Aluminum Plant WAP.

Table 3.1: Design of Enviro-AITAP Experiments*.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Hydrogen Level</th>
<th>Exp. #</th>
<th>Hydrogen Level</th>
<th>Exp. #</th>
<th>Hydrogen Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>LH</td>
<td>1</td>
<td>LH</td>
<td>7</td>
<td>LH</td>
</tr>
<tr>
<td>14</td>
<td>LH</td>
<td>13</td>
<td>LH</td>
<td>24</td>
<td>LH</td>
</tr>
<tr>
<td>35</td>
<td>LH</td>
<td>29</td>
<td>LH</td>
<td>26</td>
<td>LH</td>
</tr>
<tr>
<td>37</td>
<td>LH</td>
<td>40</td>
<td>LH</td>
<td>49</td>
<td>LH</td>
</tr>
<tr>
<td>11</td>
<td>LH</td>
<td>22</td>
<td>LH</td>
<td>12</td>
<td>LH</td>
</tr>
<tr>
<td>16</td>
<td>LH</td>
<td>34</td>
<td>LH</td>
<td>17</td>
<td>LH</td>
</tr>
<tr>
<td>33</td>
<td>LH</td>
<td>38</td>
<td>LH</td>
<td>30</td>
<td>LH</td>
</tr>
<tr>
<td>41</td>
<td>LH</td>
<td>47</td>
<td>LH</td>
<td>39</td>
<td>LH</td>
</tr>
<tr>
<td>4</td>
<td>HH</td>
<td>5</td>
<td>HH</td>
<td>3</td>
<td>HH</td>
</tr>
<tr>
<td>21</td>
<td>HH</td>
<td>15</td>
<td>HH</td>
<td>18</td>
<td>HH</td>
</tr>
<tr>
<td>32</td>
<td>HH</td>
<td>28</td>
<td>HH</td>
<td>27</td>
<td>HH</td>
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<tr>
<td>44</td>
<td>HH</td>
<td>51</td>
<td>HH</td>
<td>52</td>
<td>HH</td>
</tr>
<tr>
<td>20</td>
<td>HH</td>
<td>8</td>
<td>HH</td>
<td>9</td>
<td>HH</td>
</tr>
<tr>
<td>25</td>
<td>HH</td>
<td>19</td>
<td>HH</td>
<td>23</td>
<td>HH</td>
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<tr>
<td>43</td>
<td>HH</td>
<td>31</td>
<td>HH</td>
<td>36</td>
<td>HH</td>
</tr>
<tr>
<td>45</td>
<td>HH</td>
<td>50</td>
<td>HH</td>
<td>42</td>
<td>HH</td>
</tr>
</tbody>
</table>

Note: LH – low hydrogen; HH – high hydrogen
* The cooling curves of four Enviro-AITAP experiments failed and can not be used for further analysis.

All experiments were performed in the IRC’s casting laboratory at the University of Windsor. Figure 3.2 shows the equipment used during the laboratory experiments.
Chapter Three, Enviro-AITAP Experimental Methodology

Figure 3.2: The equipment used in the Enviro-AITAP experiments performed at the University of Windsor; 1. Electric-resistance furnace; 2. Degassing unit; 3. AISCAN unit; 4. and 5. Environmental AITAP with integrated RPT hardware.

The chemical composition of the alloys used in the laboratory experiments at the University of Windsor is presented in Table 3.2.

Table 3.2: Chemical composition of the W319 alloy used in the Enviro-AITAP experiments and its Si$_{eq}$ value (wt%).

<table>
<thead>
<tr>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>Ti</th>
<th>Ni</th>
<th>Sn</th>
<th>Pb</th>
<th>Si$_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.77</td>
<td>3.48</td>
<td>0.42</td>
<td>0.17</td>
<td>0.25</td>
<td>0.18</td>
<td>0.12</td>
<td>0.04</td>
<td>0.04</td>
<td>0.008</td>
<td>10.07</td>
</tr>
</tbody>
</table>
3.1 Adaptation of the RPT Apparatus for Enviro-AITAP Experiments

The basic elements of the RPT apparatus include the vacuum chamber, crucible (test cup), chamber base, vacuum gauge, vacuum regulator, release valve and vacuum pump. Pressure in the chamber was monitored and kept constant from sample to sample.

Figure 3.3: Reduced Pressure Test Apparatus.

In order to satisfy the experimental program a few modifications were made to the commercial RPT apparatus:

- The chamber stand, together with the bell and cup stand was detached from the RPT apparatus.
- The cup holder was replaced with one especially prepared for modified RPT experiments (Figure 3.4).
- A new chamber stand was built out of steel (Figure 3.5).
- The bell was redesigned in order to hold two thermocouples (Figure 3.6).
- The silicon rubber pads were added to the bottom of the RPT and the chamber stand in order to eliminate vibrations.
Thick construction of the chamber stand with a low center of gravity provided a vibration-free set up. The stand has three pins which keep the bell in the right position during thermal analysis processes. An additional gauge was linked to the vacuum chamber. This gauge provides accurate pressure (vacuum) measurements for each experiment.

To ensure that the heat flow from the solidifying sample was only radial, the bottom of the cup holder was made with low expansion fused silica foam (Rescor 310-M). This silica foam has a low thermal conductivity (~1.3 BTU in/Hr °F/ft²). The cup holder kept the cup filled with liquid metal in the proper position. The silica foam was porous to provide a vacuum and withstand the high temperature.

Figure 3.4: Different constructions of the Enviro-AITAP cup holders.
1) Original RPT cup holder; 2) Ceramic cup holder with dike on the edge; 3) Ceramic cup holder with a copper chill.

Close to the wall of the bell there was a dike to catch any melt spills. The dike was high enough to hold any spilled liquid metal and far enough away from the sample that it did not hinder heat transfer.

The bell was made of cast iron (Figure 3.5). At the top there were two openings that offered the possibility of connecting two thermocouples. In these experiments only the thermocouple in the central position was used (the second opening was sealed).
opening had a different diameter on the top and inside of the bell (Figure 3.6). The countersink allowed the thermocouple to be immersed to the same depth. Also, the countersink provided good sealing.

![Figure 3.5: Enviro-AITAP chamber.](image)

At the base of the bell there is a lip that is grooved to accept an O-ring. The O-ring is made of high temperature resistant silicon rubber. The ring was coated with high temperature resistant gel that makes a tight seal. The seal keeps the vacuum down to 6 kPa without leaking.

![Figure 3.6: The sealing of the thermocouple and bell's interface.](image)
3.2 Thermocouple Preparation for Thermal Analysis Experiments

High sensitivity, low thermal mass, K type thermocouples developed by the IRC group were used in the experiments. They consist of the following components: Alumel wire, Chromel wire, a ceramic sleeve, a Teflon ring, a stainless steel tube and a plastic plug (Figures 3.6 and 3.8a to 3.8e).

Step one in the thermocouple preparation was to thread 0.125 mm diameter wire through the two passages in the ceramic sleeve (Figure 3.8b).

Step two was the preparation of the bimetal junction. At one end of the ceramic sleeve, the thermocouple leads were twisted tightly together and resistance welded. The weld should be as small as possible, not bigger than two diameters of the wire. After welding,
the wires were untwisted and pulled into the ceramic sleeve. The bimetal connection was tested with an ohmmeter to ensure a circuit (Figure 3.8c).

The thermocouple welded tip was protected with high temperature resistant cement. The Alumel lead was connected to the negative terminal of the plug, and the Chromel lead was attached to the positive terminal (Figure 3.8e).

The thermocouples were connected to the National Instruments Data Acquisition System.

![Image of thermocouple preparation stages](image)

**Figure 3.8:** Different stages of thermocouple preparation: a) Ceramic sleeve; b) Alumel and cromel wires threaded through the ceramic sleeve; c) Thermocouple with welded tip and protected with high temperature resistant cement; d) The steel sheath and Teflon ring are attached to the thermocouple; e) The thermocouple is ready for calibration.

Thermocouples were calibrated, in order to eliminate any bias in temperature measurements. Calibration was performed in a Carbolite® furnace (Model...
EUROTHERM 902P), by comparing the thermocouple signals recorded with the signal of a certified Resistance Temperature Detector (RTD) probe (Model OMEGA DP95). The RTD probe was calibrated in an International Standards Organization (ISO) certified laboratory.

3.3 Test Cup Preparation for Thermal Analysis Experiments

The cup was made of stainless steel foil. The thickness of the foil was 0.025mm. For these experiments, the cup was placed in the Enviro-AITAP cup holder (Figure 3.4).

Figure 3.9: Different stages of preparation of the stainless steel cup.
3.4 Experimental Procedure

Table 3.3 summarizes operations conducted during these laboratory experiments and their corresponding temperatures and times.

Table 3.3: Time table for Enviro-AITAP laboratory tests.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Time &amp; Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting</td>
<td>4 hours</td>
</tr>
<tr>
<td>Degassing</td>
<td>760°C 20 min</td>
</tr>
<tr>
<td>Hydrogen Measurement</td>
<td>750°C 45 min</td>
</tr>
<tr>
<td>Transferring Metal to Test Cup</td>
<td>760°C 15 sec</td>
</tr>
<tr>
<td>Thermal Analysis</td>
<td>740°C 45 min</td>
</tr>
<tr>
<td>Preparation of Enviro-AITAP Platform</td>
<td>390°C 15 min</td>
</tr>
<tr>
<td></td>
<td>25°C</td>
</tr>
</tbody>
</table>

Total Time = 125 minutes
3.5.1 Melting

Secondary W319 aluminum alloy ingots (Figure 3.10) were used in these experiments. Twelve kilograms of ingots were cut and loaded into the crucible of an electric-resistance furnace (Figure 3.11). The crucible and ingots were preheated for a few hours at 400°C. The temperature was then raised to 760°C. The melt temperature was chosen to be constant at 760°C, which represents the WAP melt holding and pouring temperatures. The time needed to melt ingots was approximately 4 hours. The temperature of the melt was controlled with a thermocouple inserted into the liquid metal, while the chamber temperature of the furnace was controlled with the thermocouple attached to the inner wall of the furnace. The top of the furnace was covered with high temperature resistant bricks.

After the temperature of the liquid metal reached 760°C, dross was removed with a preheated steel spoon that was coated with Mica coating.

Figure 3.10: W319 aluminum alloy ingots. Figure 3.11: Electric-resistance furnace.
3.5.2 Degassing

Following the removal of the dross, a graphite propeller was introduced into the melt, and the top of the furnace was again protected. The Foseco Degassing Unit (Figure 3.12) was used to reduce the level of hydrogen in the melt to the lowest feasible level. The graphite propeller rotated 100 cycles per minute, and the argon flow was 10-12 SCFH (0.28-0.34 SCMH). The gas rate was adjusted to provide small bubbles, which percolated through the melt. The degassing process took 20 minutes, at which time the hydrogen level reached its lowest level. The 40 minutes degassing process did not show a significant reduction in the hydrogen level in the liquid melt in comparison with the 20 minute degassing process.

Figure 3.12: Foseco Degassing Unit. Figure 3.13: AISCAN Unit.
3.5.3. Hydrogen Measurements

Hydrogen measurements were made using the AISCAN Unit (Figure 3.13). The AISCAN probe and thermocouple were immersed into the liquid metal. The top of the furnace was protected and covered in order to reduce the loss of heat and eliminate additional dissolution of hydrogen into the aluminum melt. The temperature during hydrogen measurements was kept constant at 760°C±5°C. Each hydrogen measurement was repeated three times.

Hydrogen level measurements took 45 minutes. The AISCAN probe was in the stirring mode during measurements. The temperature and the amount of hydrogen in the melt were shown on the AISCAN unit screen.

3.5.4. Transferring Metal and Thermal Analysis

After the hydrogen content was recorded, the metal was poured into a steel cup with a preheated ladle. The bell, with the previously prepared and connected thermocouple, was placed over the cup containing the liquid metal. Then, a vacuum level was set and the sample was allowed to solidify. The level of vacuum was maintained at 0, 15 and 26.5 inches of Hg (101, 50 and 6 kPa). The triggering temperature for the beginning of the thermal analysis was 730°C. The temperature-time curve was constantly recorded (5 Hz) and monitored on the computer screen.
Chapter Four

Results of Enviro-AlTAP Analysis

Several metallurgical characteristics of the ingots, melt and actual WAP cast components were extensively quantified using the Aluminum Thermal Analysis Platform (AlTAP) and Method and Apparatus for Universal Metallurgical Simulation and Analysis (UMSA, Patent #: PCT/CA02/01903). Previous IRC research documented in reports and published papers, proved that some cooling curve characteristics can be used for quantitative analysis of the hydrogen dissolved in the aluminum melt. This was the first scientific analysis of hydrogen using the thermal analysis technique. It proved that integrated thermal analysis technique(s) can be developed to address the complex quality control requirements for most metal casting operations.

Successful measurements of the hydrogen dissolved in the melt and in the cast component and the level of inclusions could potentially be used for the on-line quantitative assessment of the melt quality, especially the casting porosity. Measurements of the hydrogen dissolved in the melt are also of paramount importance for diagnosing the root cause of casting porosity.

This thesis continues the effort to develop novel and universal quality control techniques based on the AlTAP technology platform(s) for both WAP and general aluminum processing plants.
4.1 Enviro-AITAP Analysis of Characteristic Solidification Temperatures of the W319 Alloy

Statistically designed experiments were performed in the IRC's Light Metals Casting Laboratory at the University of Windsor. The cooling curve analyses were done using the Enviro-AITAP platform.

![Graph showing the relationship between characteristic temperatures of solidification of the W319 aluminum melt and the amount of dissolved hydrogen.](image)

Figure 4.1: Relationship between characteristic temperatures of solidification of the W319 aluminum melt and the amount of dissolved hydrogen.
Parameters from the cooling curves were analyzed in order to find the most significant one that could be used as a criterion for the prediction of dissolved hydrogen in the W319 aluminum melt. Figure 4.1 summarizes the effect of different amounts of dissolved hydrogen into the aluminum melt on the characteristic solidification temperatures for the W319 aluminum alloy.

Analysis of the data, presented in Figure 4.1 reveals that liquidus temperatures ($T_{\text{den}}^{\text{NUC}}$) decreased slightly with increasing hydrogen content. The same tendency was observed for the aluminum-silicon eutectic nucleation temperature ($T_{\text{Si}}^{\text{NUC}}$). The difference in $T_{\text{Si}}^{\text{NUC}}$ between tests with high and low hydrogen levels was 5.52°C. This difference is greater than that for liquidus temperatures but still not large enough for the technique to be used on industrial floor for the determination of the hydrogen level in a W319 aluminum melt. More precisely, the increases of hydrogen from 0.06 to 0.22 ml H$_2$/100g Al melt decrease the $T_{\text{den}}^{\text{NUC}}$ and $T_{\text{Si}}^{\text{NUC}}$ by only 2.89°C and 5.52°C respectively.

However, the effect of different amounts of hydrogen on the $T_{\text{AlSiCu}}^{\text{NUC}}$ temperature is much more significant. As can be seen in Figure 4.2, under normal atmospheric pressure, the addition of 0.18 ml H$_2$/100gr Al melt aluminum decreases the $T_{\text{AlSiCu}}^{\text{NUC}}$ by approximately 5°C. This effect is even more significant when the thermal analysis sample was solidified under low pressure. In that case the absolute decrease of the $T_{\text{AlSiCu}}^{\text{NUC}}$ for the same addition of hydrogen was 12.3°C. Figure 4.2 shows that experimental data collected from the thermal analysis of the sample solidified under low pressure (6 kPa) were statistically more significant ($R^2=0.91$) than those that were collected during solidification under normal (101 kPa) pressure ($R^2=0.77$).
Chapter Four, Results of Enviro-AITAP Analysis

Figure 4.2: Relationship between $T_{\text{AlSiCu}}$ and the amount of dissolved hydrogen in the W319 aluminum melt.

Other analyzed parameters from the cooling curves (CC) that show a statistically significant relationship between certain CC parameters and different amounts of hydrogen are Fraction Solid ($f_s$) and Apparent Fraction Solid ($af_s$) [79, 80].
The advantage of Fraction Solid in respect to the $T_{\text{AlSi}_{j\text{NUC}}}$ temperature is that this parameter could be used not only to assess the level of dissolved hydrogen in the aluminum melt but also potentially to assess the feeding efficiency for that aluminum alloy.

Figure 4.3: Assessment of the hydrogen level(s) using Fraction Solid and Apparent Fraction Solid obtained from the cooling curves.
Fraction Solid at the $T^{\text{AlSiCu}_{\text{E.NUC}}}$ was very similar for all samples; which mean that Fraction Solid at $T^{\text{AlSiCu}_{\text{E.NUC}}}$ does not depend on different solidification conditions. Earlier phases of solidification had more sensitivity to Fraction Solid; therefore Apparent Fraction Solid was mostly dependable on Fraction Solid at $T^{\text{AlSi}_{\text{E.NUC}}}$. Assessment of the hydrogen level(s) using Fraction Solid and Apparent Fraction Solid obtained from the cooling curve are shown in Figure 4.3.

Figure 4.4 presents the comparison between the hydrogen level(s) using the A1TAP, and RPT/A1TAP Platforms (Enviro-A1TAP). Previous results obtained by IRC group [78] are correlating very well with the results obtained by using the Enviro-A1TAP technique without a vacuum. The Multiple Regression Coefficient ($R^2$) for measured $T^{\text{AlSiCu}_{\text{E.NUC}}}$ was higher due to a smaller cooling rate, a thinner cup and a better controlled surrounding atmosphere. Experiments performed by applying a vacuum had a wider temperature range, therefore higher sensitivity. $R^2$ for different systems is shown in Table 4.1.

Table 4.1: Multiple Regression Coefficients ($R^2$) for measured $T^{\text{AlSiCu}_{\text{E.NUC}}}$ by different systems for assessment of the hydrogen level in the W319 aluminum melt.

<table>
<thead>
<tr>
<th>System</th>
<th>Level of Hydrogen, (ml H₂/100g Al)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1TAP</td>
<td>$-0.0222 \times T^{\text{AlSiCu}_{\text{E.NUC}}} + 11.327$</td>
<td>0.76</td>
</tr>
<tr>
<td>Enviro-A1TAP, (101 kPa)</td>
<td>$-0.0274 \times T^{\text{AlSiCu}_{\text{E.NUC}}} + 13.961$</td>
<td>0.77</td>
</tr>
<tr>
<td>Enviro-A1TAP, (6 kPa)</td>
<td>$-0.0114 \times T^{\text{AlSiCu}_{\text{E.NUC}}} + 5.8994$</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Figure 4.4: Assessment of the hydrogen level(s) using the AITAP and Enviro-AITAP Platforms.
4.2 Scanning Electron Microscope (SEM) Observations of the Enviro-AITAP Test Samples

SEM observations of the as-cast samples solidified under the Enviro-AITAP (under 6 kPa) with a high level of hydrogen (0.175-0.225 ml H₂/100g Al) were performed to identify the morphology of the cavities.

Samples were cut longitudinally and two notches were made (Figure 4.5a). A longitudinal wedge was made and SEM samples were prepared by cryogenic fracturing. The dark grey surface in Figure 4.5b was analyzed by using the SEM technique.

![Figure 4.5: Sample preparation for cryogenic fracturing (a and b) and a fractured SEM sample (c).](image)

SEM analysis conducted on the JEOL SEM revealed that cavities were relatively uniformly distributed throughout all samples. Three characteristic features of the cavities were recognized:

- Cavities open to surroundings.
- Thick oxide film covered the surface of the cavities.
- Round cavities with clean dendrites.
Cavities in the upper part of the samples, close to the surface were connected with the surroundings above the sample (Figure 4.6). These cavities were completely covered with a very thick layer of oxide.

![Figure 4.6: SEM and BSE micrographs of cavities open to the surroundings.](image)

In the same samples (the upper part of the samples) several cavities were covered with oxides where a mostly wrinkled morphology could be observed. The surface was like elephant skin (Figure 4.7).

![Figure 4.7: SEM micrographs of cavities covered with thick oxide layers.](image)
Most of the cavities close to the top of the Enviro-AITAP sample were interconnected. These cavities were completely covered with oxides (Figure 4.8).

![Figure 4.8: Interconnections between cavities.](image1)

Some of the observed cavities in the middle and at the bottom part of the samples were almost perfectly round with very clean dendrites without oxides (Figure 4.9). These types of cavities were smaller than previous ones.

![Figure 4.9: SEM micrographs of cavities with clean dendrites.](image2)
4.3 Area Percent Porosity Measurements of the Enviro-AITAP Samples

Enviro-AITAP samples were metallographically prepared and the area percent porosity were measured. Samples were cut longitudinally and the dark grey surface in Figure 4.10a was prepared for metallographic observations. Forty-eight fields, that covered an area of 40mm x 20mm (Figure 4.10b), were measured in every sample. Images were acquired using the Leica Light Optical microscope. Area percent porosity was marked manually in every figure (Figure 4.10c). The Image Analysis System automatically calculated the area percent porosity for every field. A total of 48 fields with area percent porosity measurements for every sample were recorded in one file. The average value of 48 fields was accepted as the area percent porosity for a given sample. The average area percent porosity is shown in Table 4.2.

![Figure 4.10: Area percent porosity analysis; a) Part of the Enviro-AITAP test sample prepared for metallographic analysis; b) Analytical surface c) Analytical field for image analysis.](image-url)
Table 4.2: Average Area Percent Porosity for the Enviro-AITAP samples.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Low Hydrogen (0.060-0.150 ml H₂/100g Al)</th>
<th>High Hydrogen (0.151-0.225 ml H₂/100g Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area % Porosity</td>
<td>Area % Porosity</td>
</tr>
<tr>
<td>101 kPa</td>
<td>0.94</td>
<td>0.97</td>
</tr>
<tr>
<td>50 kPa</td>
<td>2.89</td>
<td>4.03</td>
</tr>
<tr>
<td>6 kPa</td>
<td>3.79</td>
<td>10.87</td>
</tr>
</tbody>
</table>

As previously mentioned, T_{AlSiCu, E,NUC} shows the highest sensitivity to the hydrogen level in the 3XX aluminum melt. The area percent porosity and T_{AlSiCu, E,NUC} have the same dependence (Figure 4.11).

Table 4.2 shows the average porosity content as measured by image analysis for the different hydrogen levels and applied pressures. It can be seen from Figure 4.13, that a considerable increase in the porosity content occurs when the amount of dissolved hydrogen in the aluminum melt increases beyond 0.15ml H₂/100g Al melt. This observation is consistent with the literature data, where, it is known that for any given alloy and specific solidification conditions there is a “threshold hydrogen content” below which no observable gas based primary porosity is formed.
Chapter Four: Results of Enviro-AITAP Analysis

Figure 4.11: Correlation between $T_{\text{ASCu}}$, $E_{\text{NUC}}$ and area percent porosity as a function of the hydrogen level and applied pressure [81].
The different behaviour found above and below the threshold implies that there are two mechanisms of pore growth. Above the threshold, however, the percent porosity increases linearly with respect to hydrogen content, indicating that the growth in pores is directly related to rapid gas evolution.

When solidification occurs under reduced pressure, the decreasing $P_0$ (ambient pressure) facilitates the formation and growth of the pore, leading to pores formation at a higher temperature or even in full liquid or at lower hydrogen content than that under one atmosphere pressure. The hydrogen solubility, $S_0$, in the liquid metal decreases with the decrease of hydrogen gas partial pressure and temperature. When the melt is under reduced pressure, the hydrogen gas partial pressure is reduced accordingly. A certain hydrogen content that is initially below the hydrogen solubility at ambient, the 101 kPa pressure, may become higher than the hydrogen solubility under the reduced pressure. This may result in pore formation at a higher temperature. Consequently, more hydrogen can be released from the liquid metal under reduced pressure. In addition, the volume of the pore is expanded. If all the pores are maintained in the metal during the solidification, a greater level of porosity will result. In this manner, the effect of dissolved hydrogen on porosity and density are magnified by reduced pressure; therefore, the accuracy of values using the Enviro-AITAP, for quantification of both amounts of dissolved hydrogen and porosity, are higher.
Chapter Five

UMSA and PoDFA Feasibility Studies of the Melt Contaminated with Aluminum Films

The novel concept of utilizing the thermal analysis technique(s) for the assessment of melt cleanliness including insoluble inclusions (e.g., aluminum oxide films) is extremely important for scientific and applied research. To date the literature does not provide any information in this regard. Therefore, following the successful analysis of hydrogen by using AITAP and Enviro-AITAP (Chapter 4) it was decided to extend this project to study the potential for quantifying the effect of alumina films on the UMSA cooling and heating curve parameters. If these studies prove that this task is feasible it will provide the opportunity for the quantitative assessment of melt cleanliness (both, hydrogen and insoluble inclusions), resulting in the ability to evaluate melt quality in terms of potential casting porosity. Also, the AITAP technology platform was extensively used for the new alloy and its processing technology development [80] and for several other projects related to ingot and master alloy manufacturing and performance, WAP processes and cast components characterization.

A major obstacle in the W319 melt experiments involved naturally formed alumina films and their creation under well controlled conditions. After unsuccessful initial attempts including the utilization of skimmed and crushed dross from the laboratory melt, the Porous Disc Filtration Apparatus (PoDFA) technique was chosen.
5.1. Generation of Alumina Films Using the PoDFA Apparatus

Alumina films were generated using the PoDFA Apparatus in the IRC’s laboratory using ingots from two of the biggest suppliers of WAP. Analysis was also conducted at the WAP following melting, before degassing and on the melt processing line before pouring (Figure 5.1a). The bottom part of the PoDFA sample, solidified in the holding cup that is close to the filter, was extracted and analyzed (Figure 5.1b, Section 5.1.). The UMSA test samples were extracted from the PoDFA samples (Figure 5.1c, Section 5.2.).

![Diagram](image)

**Figure 5.1:** a) PoDFA test; b) Analysis of the sample close to the filter, Section 5.1; c) UMSA sample extraction and analysis, Section 5.2.

In the IRC’s metalcasting laboratory the previously prepared W319 aluminum alloy was melted in an electric-resistance furnace and poured into a special cup prepared for PoDFA experiments (Figure 5.2). The bottom of the cup had a ceramic filter that was connected to a vacuum chamber. When the vacuum is induced, liquid metal from the cup drips through the filter into the vacuum chamber into the collecting tank. The collecting tank
was sitting on a weighing scale. When 1.25kg of liquid metal was collected, the vacuum pump was automatically stopped, and the vacuum chamber was opened to induce faster cooling. The overview of the PoDFA Unit is presented in Figure 5.3.

![Pouring spoon and holding cup](image1)

![PoDFA Unit](image2)

**Figure 5.2:** Pouring spoon and holding cup.  **Figure 5.3:** PoDFA Unit.

In the open vacuum chamber, the collecting tank (with 1.25kg of melt) was replaced and the remaining droplets were collected. The remaining melt that fell from the PoDFA's filter in the form of droplets (size 2-3mm in diameter) was exposed to the air. This technique allowed for the formation of in-situ alumina films. UMSA test samples were made out of alumina "coated" droplets solidified in the replaced collecting tank.

After solidification, the structure of the metal sample above the filter was observed and compared with the sample prepared out of the droplets below the filter, which is enriched with alumina films.
5.2 UMSA Cooling Curve Analysis of the Melt Using the PoDFA Technique

It was found that one of the unique features of the Method and Apparatus for Universal Metallurgical Simulation and Analysis (UMSA) (Figure 5.4) is to run heating and cooling cycles in a pre-determined thermal regime with a very high level of repeatability. This is of paramount importance since a very limited number of PoDFA test samples were available for this in-depth investigation. In addition, these capabilities will allow for the determination of which cycle is more sensitive to detect contaminated melt conditions and recognize the effects of the metallurgical hysteresis, observed when both melting and solidification processes were recorded.

Figure 5.4: The 1kW Output UMSA Platform (Patent PCT/CA02/01903).
The UMSA test samples extracted from the PoDFA test samples after insertion of the low thermal mass thermocouples had been re-melted for the creation of a perfect metallurgical contact allowing for unbiased temperature measurements. Re-melting and solidification in this zero cycle allow the droplets to be fused through the area(s) that had not been coated by the alumina films; therefore, some films could be folded. Formation of the pore cavities around the film needs to be analyzed as a very important step to understand the pore nucleation phenomenon.

An UMSA test sample is presented in Figure 5.5. The longitudinal centric hole was used for the insertion of the low thermal mass thermocouple. UMSA tests were conducted under the protective atmosphere of argon. Each test sample was melted and solidified three times.

![Figure 5.5: a) Pictograph of the UMSA test sample, b) schematic of the UMSA test sample with dimensions.](image)

The first heating/cooling (melting/solidification) cycle was used to ensure full thermal contact between the thermocouple and the tested material that is essential for unbiased TA results. The second and third cycles representing the test casting material, were used to ensure the repeatability of the results. Figure 5.6 presents the second and third cycles of the sample extracted from the PoDFA sample from the holding cup (the sample from the Alchem ingot).
The first derivatives were calculated for the second and third UMSA runs in order to precisely determine all characteristic temperatures of the heating and cooling curves. The first derivatives are depicted in Figures 5.6 to 5.8.

In order to investigate metal cleanliness using the thermal analysis technique, samples from two PoDFA runs were chosen. One set of samples was obtained from the Alchem ingot that was melted, degassed and processed using the PoDFA unit. The other set of samples was obtained at WAP, from the reveratory furnace, before cleaning and degassing of the melt.
The most important thermal characteristics on the cooling curve were analyzed (Appendix 1). The UMSA first derivatives of the heating/cooling curves of the Alchem sample from the holding cup (clean sample) and from the collecting tank (sample contaminated with alumina films) are presented in Figure 5.7.

![First derivative of the UMSA heating/cooling curves analysis of the Alchem melt sample using the PoDFA unit.](image)

**Figure 5.7:** First derivative of the UMSA heating/cooling curves analysis of the Alchem melt sample using the PoDFA unit.

In order to determine if a similar relationship between cooling/heating curves parameters and melt cleanliness exists as established for the Alchem ingot (PoDFA test samples from holding cup vs. collecting tank), the melt sample from the WAP reverberatory furnace was run through the PoDFA unit as mentioned above. UMSA first derivatives of the heating/cooling curves of the WAP sample before and after the PoDFA test are presented in Figure 5.8.
Analysis of characteristic solidification temperatures has shown that the alumina films contaminated melt (ACM) always has a higher $T_{\alpha^{\text{DEN}}_{\text{NUC}}}$, $T_{\alpha^{\text{AlSi}}_{\text{E,NUC}}}$, $T_{\alpha^{\text{AlSiCu}}_{\text{E,NUC}}}$, as well as the other characteristic temperatures, than compared to the clean melt (Figures 5.9-5.11).

Also, a comparison between two different melts shows that the melt with more insoluble particles has higher characteristic solidification temperatures. Samples obtained from the WAP reverberatory furnace have lower characteristic solidification temperatures than samples acquired from the Alchem ingots.

![First derivative of the UMSA heating/cooling curves analysis of the WAP melt sample before degassing using the PoDFA unit.](image)

Figure 5.8: First derivative of the UMSA heating/cooling curves analysis of the WAP melt sample before degassing using the PoDFA unit.
Figure 5.9: UMSA analysis of the $T_{\text{DENNUC}}^{\text{G}}$ Temperature from the PoDFA Test Samples (Cooling curves).

Figure 5.10: UMSA analysis of the $T_{\text{NUC}}^{\text{AI1}}$ Temperature from the PoDFA Test Samples (Cooling curves).
Results obtained in this research are in correlation with expected behaviour of the clean and alumina films contaminated samples. A melt with more insoluble elements is expected to have higher characteristic temperatures than a clean melt due to the higher number of centres of crystallization and the lowered nucleation energy. Comparison of clean samples and samples contaminated with alumina films from the same ingot, as well as samples from the clean and dirty melts revealed the same correlation.
Chapter Six

Analytical Procedures for the Quality Control of Aluminum Ingots and Melts

The use of cast aluminum components in automotive applications is increasing worldwide. Cast aluminum products have been used primarily in engine components, including blocks, cylinder heads, pistons, intake manifolds, brackets and housings. Components in use today include suspension control arms, steering gear components, front strut support bearings and wheels [82].

The 3XX series (aluminum-silicon) of aluminum alloys are being widely used in many of the automotive components listed above. These alloys have good casting characteristics, reasonable mechanical properties and are heat-treatable, but have very complex chemistries.

Due to the many factors that can change their properties and characteristics, experimental trials involving these alloys are not an easy task. In order to overcome the above-mentioned problems and improve the understanding of solidification of casting alloys and enhance their quality, several mathematical models have been developed [83, 84].

The mathematical model, used in this thesis, is based on the knowledge of the bulk chemistry of the 3XX series of aluminum alloys. The effect of major and minor alloying elements on the thermal and structural properties of these alloys has been expressed through an equivalent amount of silicon. Therefore, this model is called the Silicon Equivalency model [85, 86].
6.1 Implementation of Analytical Methods in the Metal Casting Industry

Prior to the development of the Silicon Equivalency Method several models were established for other alloys. The most recognized is the carbon equivalent in iron alloys. The effect of other elements can be estimated by equating them to an additional amount of carbon. Over several decades this method has been used for various characterizations of iron alloys and the prediction of their properties such as liquidus temperature, eutectic temperature, dendrite size, austenite/ferrite ratio, graphite/cementite ratio, fluidity, latent heat, weldability, lamellar/vermicular/spheroidal graphite formation, hardness, tensile strength, chilling characteristics and others [87].

Several carbon equivalent empirical formulas have been devised. They are calculated in different ways according to their applications. The most accepted formula is:

\[
C_{eq} = C\% + \frac{Si\% + P\%}{3} \quad \text{(wt\%)}
\]  

6.1

Carbon Equivalent Liquidus (CEL) is the most commonly used formula to calculate the liquidus temperature of an alloy as it is the only one that can be directly confirmed by thermal analysis [88]. Therefore, thermal analysis provides a fast and economical foundry floor method of determining \( C_{eq} \) for iron alloys. A record of the temperature change during the cooling of the grey cast iron molten sample with hypoeutectic composition shows the precipitation of austenite which is related to the liquidus temperature and this is directly linked to the composition of iron.

The ability of iron to fill a mould and to give a sharp definition of the pattern is assessed by measuring fluidity. The Carbon Equivalent Fluidity (CEF) cannot be directly
measured, but could be calculated from the melt composition. The influence of carbon, silicon and phosphorus on fluidity is represented by the expression:

\[ CEF = C\% + \frac{Si\%}{3} + \frac{P\%}{2} \quad (\text{wt}\%) \]

Figure 6.1 indicates that an alloy has a eutectic composition where the \( C_{eq} \) is 4.3 wt% according to Equation 6.1. A value of \( C_{eq} \) less or greater than 4.3 wt% indicates hypoeutectic or hypereutectic alloys, respectively [89].

For a given cooling rate the \( C_{eq} \) value determines how close a given composition of iron is to the eutectic and therefore how much free graphite is likely to be present, and consequently, the probable strength of iron. The carbon equivalent value is also a useful guide to the chilling tendency of a given section.
Increasing the silicon content of Fe-Si-C alloys shifts the eutectic composition to the left (Figure 6.1). This eutectic shift can be expressed by the following equation [90]:

\[
\% \text{ Eutectic Carbon (Fe-C-Si alloy)} = 4.3 - 0.33 \times \% \text{ Si (in alloy)}
\]

6.3

The most significant alloying element of iron alloys affecting weldability, is carbon. With a good approximation, the weldability of the steel can be estimated from its composition. The total alloy content has the same effect on weldability as an equivalent amount of carbon. The formula used by the International Institute of Welding for judging the risk of underbead cracking (cold cracking) is as follows [91]:

\[
C_{eq} = C + \frac{Mn}{6} + \frac{Cr + Mo + V}{5} + \frac{Ni + Cu}{15} \quad (\text{wt%})
\]

6.4

In general, steels with low \(C_{eq}\) values have high weldability. Steels can be assessed in terms of the \(C_{eq}\) which scales the concentration of each element by its ability to retard the austenite/ferrite transformation (Equation 6.4). Steels with a \(C_{eq}\) greater than 0.4 wt% cannot be welded successfully unless precautions are taken.
6.2 Calculation of Characteristic Temperatures in the 3XX Series of Aluminum Alloys

A number of published equations for calculation of $T^{\alpha_{DEN}}_{NUC}$ temperature from the known chemical composition of iron base melts is available in the literature. Unfortunately, there are only two published equations for calculation of $T^{\alpha_{DEN}}_{NUC}$ temperature, related to multi component aluminum alloys [83, 84, 85, 86, 92, 93].

The most known equation for calculating the $T^{\alpha_{DEN}}_{NUC}$ temperature of aluminum alloys, based on their known chemical compositions, was developed by Drossel [83] using multiple regression analysis of the experimental data:

$$T_{LIQ} = 661 - 4.97Si - 0.15(Si)^2 - 6.13Cu - 17.4Mg + 2.72Zn + 5.08CuMg \text{ (°C)} \quad 6.5$$

A second equation for predicting $T^{\alpha_{DEN}}_{NUC}$ of aluminum alloys was recently (1996) developed by Vijayaraghavan et al. [84]. This equation was derived from the aluminum-silicon copper (Al-Si-Cu) ternary phase diagram through the use of multiple regression analysis:

$$T_{LIQ} = 664 - 6.9 \text{ Si} - 2.5 \text{ Cu} \text{ (°C)} \quad 6.6$$

Both equations published in the literature are valid only for a given chemical range and cannot be applied for a wide chemical range of 3XX aluminum alloys. Therefore, in this thesis an algorithm called Silicon Equivalency (SiEQ) has been used for calculation of characteristic solidification temperatures of 3XX alloys. The SiEQ algorithm has been derived based on the binary aluminum-silicon phase diagram. This is a binary eutectic type phase diagram with limited solubility of both aluminum and silicon. The solubility of silicon in the aluminum melt reaches a maximum of 1.6 wt% (1.54 at%) at the 577°C eutectic temperature. The maximum solubility of aluminum in silicon at the eutectic
temperature is still questionable, and according to some literature data is about 0.015 wt% [93]. Usually, the amount of silicon in these types of aluminum alloys seldom exceeds eutectic concentration, therefore the part of the Al-Si phase diagram with a higher eutectic concentration of silicon will not be analyzed in detail.

6.3 Procedures for Calculation of the Silicon Equivalent \((\text{Si}_{\text{EQ}})\) Algorithms

The phase diagram presented in Figure 6.2, shows several important characteristics such as the melting point of pure Al and Si, the eutectic temperature and the eutectic concentration. Many other parameters of the Al-Si alloy can be recognized on the Al-Si phase diagram. The concentration of silicon, which corresponds to the eutectic reaction, is still not accurately defined or accepted among researchers, even through this diagram is very well investigated. In the available literature the following values for eutectic concentration of silicon were found: 11.9wt.% (11.49 at%) [94], 12.3wt.% (11.87 at%) [95] and 12.6wt.% (12.16 at%) [96]. In this thesis the value of 11.49 at% of Si will be used as the eutectic concentration of silicon as well as 577±1°C as a temperature at which the eutectic reaction occurs.

![Figure 6.2: Al-Si binary phase diagram [96].](image-url)
As seen in Figure 6.2, the $T^{\alphaDEN}_{NUC}$ and solidus temperatures of the Al-Si binary phase diagram decrease uniformly, up to the eutectic concentration, with an increase in the amount of silicon reaching the minimum at the eutectic concentration (11.87 at%). The same behaviour of $T^{\alphaDEN}_{NUC}$ and the solidus lines can be observed in most binary eutectic aluminum alloys (Figure 6.3).

![Figure 6.3: Al-Xi binary phase diagrams [97].](image)

Mathematically, liquidus ($T^{\alphaDEN}_{NUC}$) and solidus ($T_{SOL}$) curves of these binary systems can be approximated by a linear equation or can be more accurately expressed in the second order polynomial equation as follows:

$$T^{Al-Xi}_{LIQ} = A - B \cdot X_i - C \cdot X_i^2 \quad 6.7a$$

$$T^{Al-Xi}_{SOL} = A - D \cdot X_i - E \cdot X_i^2 \quad 6.7b$$
where:

$X_i$ is the content of alloying element at at%.

$A$ is the melting point of pure aluminum at 660.452°C.

$B$, $C$, $D$, and $E$ are polynomial coefficients.

This means that the liquidus and solidus lines for an Al-Si binary system can be analytically expressed as:

$$T^{\text{AlSi}}_{\text{LIQ}} = 660.452 - 6.3707 \text{ Si} - 0.05786 \text{ Si}^2 \text{ (°C)}$$

The analysis of two binary phase diagrams, Al-Si and Al-Cu presented in Figure 6.3, show that a high degree of similarity exists between these two diagrams.

- Both of them are eutectic types.
- In both diagrams the $T_{\text{DEN}}^{\text{NUC}}$ line related to the aluminum rich side, starts at the same temperature, 660.452°C, the melting point of pure aluminum.
- Additions of alloying elements change the shape of the $T_{\text{DEN}}^{\text{NUC}}$ lines in a similar way, up to the related eutectic concentrations.

The main difference is recognized in the slope of the $T_{\text{DEN}}^{\text{NUC}}$ line.

![Figure 6.4: Al-Si and Al-Cu binary phase diagrams.](image-url)
Figure 6.4 shows that the same equivalent suppression of the $T^{\text{DEN}}_{\text{NUC}}$ temperature of the aluminum alloy for two binary phase diagrams is obtained by different concentrations of alloying elements. In this example, the suppression of $T^{\text{DEN}}_{\text{NUC}}$ temperature to 620°C is reached by alloying aluminum either with 6.28 at% of Si or 7.50 at% of Cu. There is an isothermal concentration difference between the two, Si and Cu alloying elements can be mathematically expressed as follow:

$$\text{Si}^{\text{Cu, EQ, T=CONST}} = \text{Si(mol.\%)} - \text{Cu(mol.\%)}$$

Silicon is a major alloying element for this type of aluminum alloy and was chosen as the reference element. It also has the most significant influence on the casting properties of the 3XX series of alloys (e.g. fluidity and shrinkage).

Because the isothermal concentrations of Si are usually smaller than the corresponding concentrations of most other $X_i$ elements, values for $\text{Si}^{X_i, EQ, T=CONST}$ in Equation 6.9, are given a positive value.

As seen in the two binary Al-Si and Al-Cu phase diagrams, by applying Equation 6.9, the value of $\text{Si}^{\text{Cu, EQ, T=CONST}}$ for each isotherm can be calculated. Each concentration of alloying element (Cu) has a particular value of $\text{Si}^{\text{Cu, EQ, T=CONST}}$. For any temperature $T$, where $T$ is observed in the range between $660.452 > T > T_{\text{EUTECTIC}}$ the relationship between the Silicon Equivalency $\text{Si}^{\text{Cu, EQ}}$ is changed by adding a different amount of Cu into the aluminum melt.

Taking into consideration the whole temperature range between the melting temperature of pure aluminum and the eutectic temperature of an observed binary alloy and following the relationship established between $\text{Si}^{X_i, EQ}$ and the concentration of the alloying element, $X_i$ can be expressed as follows:

$$\text{Si}^{X_i, EQ} = a_0 X_i + b_0 X_i^2 + c_0 X_i^3$$

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where,
\( a_0^{X_i} \), \( b_0^{X_i} \) and \( c_0^{X_i} \) are polynomial coefficients.

\( X_i \) is the concentration of alloying element at at%

Figure 6.5 shows that polynomial coefficient \( a_0^{X_i} \) must always be equal to zero and this simplifies the expression for Silicon Equivalency.

![Figure 6.5: Silicon Equivalency, Si\textsubscript{Cu\textit{EQ}} as a function of the different concentrations of Cu.](image)

Calculations were made in molar as well as in weight percents. Table 6.1 summarizes the necessary coefficients derived from the binary phase diagrams that must be used to calculate the value of the Silicon Equivalent for multi-component systems.

The \( \text{Si}_{\text{EQ}} \) for major and minor alloying elements as well as some impurity elements can be determined as the sum of individual contributors (\( \Sigma \text{Si}_{\text{EQ}}^{X_i} \)) plus the effect of silicon itself:

\[
\text{Si}_{\text{EQ}} = \text{Si} + \Sigma \text{Si}_{\text{EQ}}^{X_i}
\]  

6.11
Therefore, the $T_{\text{Nuc}}^{\text{DEN}}$ temperature for multi component aluminum alloys can be calculated using the following equation:

$$T_{\text{Al-Si}^{\text{EQ}}}^{\text{LIQ}} = 660.452 - 6.3707 \text{Si}_\text{EQ} - 0.05786 \text{Si}_\text{EQ}^2$$

Which is basically Equation (6.8) written in terms of $\text{Si}_\text{EQ}$ instead of $\text{Si}$.

Table 6.1: Polynomial coefficients for different binary Al-$X_i$ alloys.

<table>
<thead>
<tr>
<th>Al-$X_i$ Alloy</th>
<th>$b_0$</th>
<th>$c_0$</th>
<th>$b_0$</th>
<th>$c_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Cu</td>
<td>0.529</td>
<td>-0.0004</td>
<td>1.0482</td>
<td>-0.03061</td>
</tr>
<tr>
<td>Al-Mg</td>
<td>0.0258</td>
<td>-0.0088</td>
<td>0.30629</td>
<td>-0.00058</td>
</tr>
<tr>
<td>Al-Mn</td>
<td>0.8221</td>
<td>-0.0349</td>
<td>0.65192</td>
<td>-0.01334</td>
</tr>
<tr>
<td>Al-Fe</td>
<td>0.6495</td>
<td>0.0003</td>
<td>0.30305</td>
<td>0.00833</td>
</tr>
<tr>
<td>Al-Zn</td>
<td>0.1227</td>
<td>-0.0002</td>
<td>0.34381</td>
<td>0.00623</td>
</tr>
<tr>
<td>Al-Sn</td>
<td>0.7849</td>
<td>-0.0313</td>
<td>0.60888</td>
<td>1.7163</td>
</tr>
<tr>
<td>Al-Bi</td>
<td>0.9076</td>
<td>-0.0092</td>
<td>0.22608</td>
<td>-0.25264</td>
</tr>
<tr>
<td>Al-Pb</td>
<td>0.859</td>
<td>0.02976</td>
<td>-0.01486</td>
<td>1.5807</td>
</tr>
<tr>
<td>Al-Sb</td>
<td>0.8255</td>
<td>-0.0327</td>
<td>-0.00276</td>
<td>1.21955</td>
</tr>
<tr>
<td>Al-Ni</td>
<td>0.5644</td>
<td>0.0285</td>
<td>-3.3E-05</td>
<td>0.07608</td>
</tr>
<tr>
<td>Al-Sr</td>
<td>0.7854</td>
<td>-0.0157</td>
<td>0.32709</td>
<td>-0.13477</td>
</tr>
<tr>
<td>Al-Ti</td>
<td>-0.8159</td>
<td>0.00993</td>
<td>-0.90873</td>
<td>-0.00032</td>
</tr>
<tr>
<td>Al-B</td>
<td>0.00075</td>
<td>7.5E-05</td>
<td>0.56113</td>
<td>-0.03724</td>
</tr>
</tbody>
</table>

Note: The above mentioned coefficients are valid up to a particular Al-$X_i$ eutectic concentration.

In order to evaluate the accuracy of the presented algorithms twelve synthetic 3XX compositions were prepared by melting a charge of Al-5wt.% Si, Al-7wt.% Si, Al-9wt.% Si and Al-11 wt.% Si base alloys and adding 1, 2 and 4 wt.% Cu. The chemical
compositions of the alloys, where determined using Optical Emission Spectroscopy (OES), and are presented in Table 6.2.

![Graph showing calculated versus measured TaDenn temperature using Equation 6.12 [85].](image)

During processing, the melt was covered with a protective nitrogen gas atmosphere to prevent hydrogen and oxygen contamination. No grain refining agents were added to the melt. The ingots used were pre-modified with Sr.
Samples with masses of approximately 300g ± 10g were poured into stainless steel cups. Two specially designed supersensitive K type thermocouples were inserted into the melt and temperatures between 750 – 400 °C were recorded. The data for TA was collected using a high-speed National Instruments Data Acquisition System linked to a personal computer. Each Thermal Analysis trial was repeated three times. Consequently, a total of 36 samples were gathered.

Table 6.2: Chemical compositions (wt.%) of the experimental synthetic aluminum alloys and their characteristic $T_{\text{DEN}}^{\text{NUC}}$ and $T_{\text{A1TAP}}^{\text{NUC}}$ temperatures measured using the Aluminum Thermal Analysis Platform (A1TAP) (Note that only major alloying elements are presented).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>$T_{\text{DEN}}^{\text{NUC}}$</th>
<th>$T_{\text{A1TAP}}^{\text{NUC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/1</td>
<td>4.85</td>
<td>1.03</td>
<td>0.09</td>
<td>0.14</td>
<td>0.01</td>
<td>0.01</td>
<td>626.6</td>
<td>572.4</td>
</tr>
<tr>
<td>5/2</td>
<td>5.01</td>
<td>2.06</td>
<td>0.10</td>
<td>0.15</td>
<td>0.01</td>
<td>0.01</td>
<td>622.8</td>
<td>569.2</td>
</tr>
<tr>
<td>5/4</td>
<td>4.89</td>
<td>3.85</td>
<td>0.09</td>
<td>0.16</td>
<td>0.01</td>
<td>0.01</td>
<td>618.3</td>
<td>562.4</td>
</tr>
<tr>
<td>7/1</td>
<td>7.13</td>
<td>0.96</td>
<td>0.12</td>
<td>0.28</td>
<td>0.01</td>
<td>0.01</td>
<td>613.3</td>
<td>573.1</td>
</tr>
<tr>
<td>7/2</td>
<td>7.05</td>
<td>1.98</td>
<td>0.13</td>
<td>0.28</td>
<td>0.01</td>
<td>0.01</td>
<td>610.0</td>
<td>569.1</td>
</tr>
<tr>
<td>7/4</td>
<td>6.75</td>
<td>4.38</td>
<td>0.12</td>
<td>0.29</td>
<td>0.01</td>
<td>0.01</td>
<td>604.6</td>
<td>569.3</td>
</tr>
<tr>
<td>9/1</td>
<td>9.16</td>
<td>1.05</td>
<td>0.12</td>
<td>0.31</td>
<td>0.01</td>
<td>0.01</td>
<td>597.3</td>
<td>572.4</td>
</tr>
<tr>
<td>9/2</td>
<td>9.02</td>
<td>2.44</td>
<td>0.12</td>
<td>0.31</td>
<td>0.01</td>
<td>0.01</td>
<td>589.9</td>
<td>570.2</td>
</tr>
<tr>
<td>9/4</td>
<td>9.45</td>
<td>4.38</td>
<td>0.14</td>
<td>0.27</td>
<td>0.01</td>
<td>0.01</td>
<td>584.4</td>
<td>566.4</td>
</tr>
<tr>
<td>11/1</td>
<td>10.8</td>
<td>0.94</td>
<td>0.11</td>
<td>0.19</td>
<td>0.01</td>
<td>0.01</td>
<td>579.4</td>
<td>574.5</td>
</tr>
<tr>
<td>11/2</td>
<td>10.9</td>
<td>1.95</td>
<td>0.10</td>
<td>0.16</td>
<td>0.01</td>
<td>0.01</td>
<td>576.7</td>
<td>573.2</td>
</tr>
<tr>
<td>11/4</td>
<td>10.5</td>
<td>4.36</td>
<td>0.13</td>
<td>0.17</td>
<td>0.01</td>
<td>0.01</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

In order to statistically evaluate the accuracy of the Equations 6.5-6.15, an additional twelve alloys (Table 6.3) were chosen from the literature [99-104]. The main purpose for

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taking into consideration all 24 alloys (12 alloys from the literature and 12 alloys from the
current experiments) was to statistically prove the reliability of the developed Silicon
Equivalency concept and to check the accuracy of the Equations 6.12, 6.14 and 6.15 over
a wide chemical range. All calculated $T_{\text{DEN}}^{\text{NUC}}$ temperatures were compared with the
measured temperatures, and the corresponding statistical parameters of this data are
presented in Table 6.4. The $S_{\text{EQ}}$ calculations of the melt chemistries in Tables 6.2 and 6.3
were summarized in Figure 6.7.

Table 6.3: Chemical compositions (wt.%) of the 3XX aluminum alloys and their
characteristic $T_{\text{DEN}}^{\text{NUC}}$, $T_{\text{AI}3}^{\text{NUC}}$ and $T_{\text{AI}3\text{Si}C}^{\text{NUC}}$ temperatures measured
using the Aluminum Thermal Analysis Platform (AITAP) [98]. These were
compared with the literature data [99-104].

<table>
<thead>
<tr>
<th>Lit</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>$T_{\text{DEN}}^{\text{NUC}}$</th>
<th>$T_{\text{AI}3}^{\text{NUC}}$</th>
<th>$T_{\text{AI}3\text{Si}C}^{\text{NUC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>6.87</td>
<td>0.005</td>
<td>0.14</td>
<td>0.477</td>
<td>0</td>
<td>0</td>
<td>616.0</td>
<td>579.0</td>
<td>NA</td>
</tr>
<tr>
<td>98</td>
<td>6.823</td>
<td>1.562</td>
<td>0.10</td>
<td>0.458</td>
<td>0</td>
<td>0.01</td>
<td>613.6</td>
<td>572.3</td>
<td>NA</td>
</tr>
<tr>
<td>98</td>
<td>7.034</td>
<td>2.325</td>
<td>0.08</td>
<td>0.503</td>
<td>0</td>
<td>0.01</td>
<td>610.8</td>
<td>571.6</td>
<td>NA</td>
</tr>
<tr>
<td>98</td>
<td>7.362</td>
<td>3.693</td>
<td>0.10</td>
<td>0.491</td>
<td>0</td>
<td>0.02</td>
<td>606.7</td>
<td>568.0</td>
<td>NA</td>
</tr>
<tr>
<td>99</td>
<td>5.10</td>
<td>2.91</td>
<td>0.30</td>
<td>0.27</td>
<td>0.05</td>
<td>0.03</td>
<td>622.8</td>
<td>567.2</td>
<td>NA</td>
</tr>
<tr>
<td>99</td>
<td>5.75</td>
<td>3</td>
<td>0.31</td>
<td>0.30</td>
<td>0.05</td>
<td>0.04</td>
<td>615.7</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>100</td>
<td>12</td>
<td>3.39</td>
<td>0.20</td>
<td>1.55</td>
<td>0.01</td>
<td>0.03</td>
<td>565.7</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>101</td>
<td>6.05</td>
<td>2.99</td>
<td>0</td>
<td>0.27</td>
<td>0</td>
<td>0.03</td>
<td>614</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>102</td>
<td>7</td>
<td>0.003</td>
<td>0.05</td>
<td>0.35</td>
<td>0.01</td>
<td>0.02</td>
<td>612.8</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>103</td>
<td>9.2</td>
<td>0.01</td>
<td>0.26</td>
<td>1.28</td>
<td>0.06</td>
<td>0.06</td>
<td>592</td>
<td>576.0</td>
<td>NA</td>
</tr>
<tr>
<td>103</td>
<td>9.3</td>
<td>2.6</td>
<td>0.52</td>
<td>0.59</td>
<td>0.11</td>
<td>0.51</td>
<td>585</td>
<td>566.0</td>
<td>492.0</td>
</tr>
<tr>
<td>104</td>
<td>5.9</td>
<td>3.3</td>
<td>0.21</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>616</td>
<td>563.8</td>
<td>520.0</td>
</tr>
<tr>
<td>104</td>
<td>5.01</td>
<td>1.4</td>
<td>0.22</td>
<td>0.52</td>
<td>0.02</td>
<td>0.02</td>
<td>622</td>
<td>570.0</td>
<td>540.0</td>
</tr>
</tbody>
</table>
Figure 6.7: Summary of measured and calculated characteristic solidification temperatures for alloys with chemical compositions as presented in Tables 6.2 and 6.3.

Table 6.4 summarizes the following statistical parameters: multiple regression correlation coefficients – $R^2$, standard deviation - $\sigma$, average values, minimum and maximum differences between calculated and measured temperatures.
Table 6.4 shows that all three equations used to calculate $T_{DEN}^{NUC}$ temperature of the 3XX series of aluminum alloys. Statistical analysis reveals that the application of Equations 6.5 and 6.6 for calculation of $T_{DEN}^{NUC}$ temperature results in a higher standard deviation, and more scatter in the predictions compared to the proposed model Equation 6.12.

Table 6.4: Regression Coefficients, Standard Deviations and Average Values of the $T_{DEN}^{NUC}$ Temperature (°C) Calculated using the Silicon Equivalency Method and the Method developed by Drossel and Vijayaraghavan.

<table>
<thead>
<tr>
<th>Statistical Data</th>
<th>Si$_{EQ}$ Method</th>
<th>Drossel Equation</th>
<th>Vijayaraghavan Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation #</td>
<td>(6.8)</td>
<td>(6.1)</td>
<td>(6.2)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>2.70</td>
<td>4.75</td>
<td>3.22</td>
</tr>
<tr>
<td>Average Value</td>
<td>-1.24</td>
<td>6.17</td>
<td>-1.21</td>
</tr>
<tr>
<td>Minimum</td>
<td>3</td>
<td>15.62</td>
<td>4.85</td>
</tr>
<tr>
<td>Maximum</td>
<td>-6.6</td>
<td>-3.12</td>
<td>-7.09</td>
</tr>
</tbody>
</table>

Equation 6.5 developed by Drossel is less accurate than the other two Equations, 6.6 and 6.12. One of the reasons for this is the fact that this equation is valid only for the following ranges of chemical alloy compositions (expressed in weight percent):

Si $\leq$ 9.30; Cu $\leq$ 2.50; Mg $\leq$ 0.60; Fe $\leq$ 1.15; Mn $\leq$ 0.40; Zn $\leq$ 0.63; Ni $\leq$ 0.43; Ti $\leq$ 0.05

Therefore, the applicability of Drossel's Method is limited to alloys that have chemical compositions in given ranges.
Vijayaraghavan's Equation 6.6, which shows statistically better results than Drossel's Equation 6.5 is limited because it applies only to those alloys for which $T_{DEN}^{NUC}$ can be estimated using only Al, Si and Cu concentrations as independent variables. It fails to account for the important influence of other components (e.g. Mg, Mn, Fe, Zn and Ti). Therefore, substantial error is created in its estimate of $T_{DEN}^{NUC}$ temperature in those cases where the components mentioned above have a considerable influence. This is evident from the fact that the equation's constant (664°C) is considerably higher than the known melting point of pure aluminum (660.452°C).

The accuracy of the calculated $T_{DEN}^{NUC}$ temperature in the proposed model Equation 6.12 depends solely on the accuracy of the polynomial coefficients presented in Table 6.1. However, these coefficients are derived from the $T_{DEN}^{NUC}$ lines in the respective binary systems, and their reliability is related to the accuracy with which the $T_{DEN}^{NUC}$ curves are experimentally determined and numerically fitted. Therefore, the SiEQ algorithm performed better than Drossel's and Vijayaraghavan's equations due to the number and concentration range of alloying and impurity elements. Also, the SiEQ algorithm has a better Regression Coefficient and a lower Standard Deviation than the methods developed by the other two authors.

Some inaccuracy is also observed by applying this method. In order to exclude this source of error a re-examination of $T_{DEN}^{NUC}$ lines on the silicon rich side of the respective binary system or even better for the ternary Al-Si-X$_j$ system would be necessary.
6.4 Application of SiEQ in the Calculation of Al-Si and Al-Si-Cu Eutectic Nucleation Temperatures

Another advantage of the new SiEQ method is its application to calculate the temperatures of both eutectics in the 3XX series of aluminum alloys. Potentially, a similar approach could be used to develop an equation for calculation of the solidus temperature of aluminum multi component alloys.

The available literature provides one equation [105] that can be used to calculate the aluminum-silicon eutectic growth temperature of the 3XX series of aluminum alloys. This equation is based on the effect of chemical composition of the melt on the depression of aluminum-silicon eutectic temperature. The effect of each particular element has been derived using literature data and the author's own experimental data. The equation reads as follow:

\[
T_{\text{AlSi,NUC}}^{\text{AlSi}} = 660.452 - (6.11\text{Si} + 0.057\text{Si}^2) (12.6/\text{Si}) - (3.4\text{Cu} + 1.34\text{Fe} + 6.3\text{Mg} + 1218.9\text{Sr} - 32965\text{Sr}^2 - 4.293\text{Sb} + 186.3\text{Sb}^2 - 495.5\text{Sb}^2) \ (°\text{C})
\]

- all the elements content are given in wt%.

The aluminum-silicon binary system has a eutectic temperature of 577°C. From the literature and from the IRC's experimental data any additions of alloying elements to the aluminum-silicon melt decreases this temperature. In the case of the 319 alloy the aluminum-silicon eutectic temperature for the standard chemical composition is in the range of 561 to 563°C.
This $\text{Si}_{\text{EQ}}$ algorithm can be used to calculate the aluminum-silicon eutectic, temperature $T^{\text{AlSi}}_{\text{ENUC}}$ based on the chemical composition of the aluminum melt. The $T^{\text{AlSi}}_{\text{ENUC}}$ is calculated as follow:

$$T^{\text{AlSi}}_{\text{ENUC}} = 660.452 - ((6.3707 \text{Si}_{\text{EQ}} + 0.05786 \text{Si}_{\text{EQ}}^2) \times (11.87/\text{Si}, \text{at\%})$$

Figure 6.8 depicts a plot of the calculated aluminum-silicon eutectic temperature using Equation 6.14 for each of the aluminum alloys presented in Table 6.2, versus the experimentally determined values.

![Graph showing calculated versus measured aluminum-silicon eutectic nucleation temperature](image)

Figure 6.8: Calculated versus measured aluminum-silicon eutectic nucleation temperature [106].

$R^2 = 0.86$

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Due to the nature of the interaction between atoms of different alloying elements into the liquid (short-range order of atoms) and solid (long-range order of atoms) solutions more significant error in the calculation of the characteristic temperatures of solidification should be observed for these temperatures (that followed their $T_{\text{DENNUC}}$ temperatures). In high alloyed aluminum systems these effects may be much more prominent. Therefore, there was no attempt in the literature to develop an equation that can be used to predict the solidification temperature of the aluminum alloys below their Al-Si eutectic temperatures such as the Al-Si-Cu eutectic nucleation temperature or solidus temperature.

![Figure 6.9: Calculated versus measured aluminum-silicon-copper eutectic nucleation temperature using equation 6.15 [106].](image)

$R^2 = 0.77$

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The Si\textsubscript{EQ} method can be applied to estimate values of $T^{AlSiCu}_{E,NUC}$ for slow cooling rates using Equation 6.15:

$$T^{AlSiCu}_{E,NUC} = T_{LIQ} - (6.3707 \times \text{Si}_{\text{EQ}} - 0.05786 \times \text{Si}_{\text{EQ}}^2) \times (11.87/\text{Si}) \text{, at\%} \quad 6.15$$

Figure 6.9 as well as the corresponding value of the multiple regression coefficient $R^2$ shows that the Si\textsubscript{EQ} equation can calculate $T^{AlSiCu}_{E,NUC}$ temperature for a selected series of aluminum alloys.
Chapter Seven

Summary and Conclusions

In recent years great emphasis has been placed on quality control of cast aluminum alloys. Hydrogen content in liquid aluminum alloys is one of the factors which must be controlled since the level of porosity in solidified cast aluminum products strongly depends on the amount of hydrogen soluble in the liquid aluminum.

Previous IRC research [78] proved that cooling curve characteristics can be used for quantitative analysis of the hydrogen dissolved in the aluminum melt. This was the first time that the IRC team experimentally confirmed that thermal analysis can be used to quantify the amount of dissolved hydrogen in the aluminum melt. In this thesis, the statistically designed experiments have been run with different amounts of dissolved hydrogen (0.063-0.225 ml H₂/100g Al melt) in order to find parameter(s) that can be used to assess the level of porosity in an as-cast aluminum structure. The cooling curve analysis run under atmospheric pressure (101 kPa) and under low pressure (6 kPa) was done by using the Enviro-AITAP platform. Parameters from the cooling curve were analyzed in order to obtain the most significant parameters that can be used as a criterion for predicting the level of dissolved hydrogen in the aluminum melt as well as the amount of porosity in the as-cast product.

Experiments were carried out to observe the effect of high and low pressures and the hydrogen content on the level of porosity of the 319 aluminum alloys and in order to find the parameter(s) from the cooling curve(s) that could be used to assess the amount of porosity in as-cast components. It was found that the Thermal Analysis technique could
be used to estimate the level of porosity in the solidified aluminum cast components. The best statistical correlation between the Enviro-AITAP cooling curve parameter and the amount of porosity was obtained using the $T_{AISiCu}^{E,NUC}$ temperature. The level of hydrogen was varied between 0.063 ml H$_2$/100g Al and 0.225 ml H$_2$/100g Al.

The difference in the $T^{DEN}_{NUC}$ and $T^{AISi}_{E,NUC}$ temperature between tests with high and low hydrogen is not large enough for the technique to be used on the industrial floor for the determination of the hydrogen level in a W319 aluminum melt and the casting porosity. However, the effect of different amounts of hydrogen on the $T_{AISiCu}^{E,NUC}$ temperature is much more significant. The absolute decrease of the $T_{AISiCu}^{E,NUC}$ temperature for the addition of 0.18 ml H$_2$/100gr Al melt is 12.3°C. Experimental data collected from the thermal analysis of the samples solidified under low pressure were statistically more significant than those that were collected during solidification under normal pressure.

The hydrogen solubility in the liquid metal decreases with the decrease of pressure and temperature; therefore more hydrogen can be released from the liquid metal under reduced pressure, thus resulting in a greater level of porosity. In this manner, the effect of dissolved hydrogen on porosity and density are magnified by the reduced pressure; consequently, the accuracy of values using the Enviro-AITAP platform, for quantification of both amounts of dissolved hydrogen and porosity are higher.

Further experiments should be carried out in a foundry environment to test the experimentally obtained results from this work under actual casting conditions. Future work should also attempt to establish a correlation between cooling curve(s) parameter(s), hydrogen and the content of non-metallic inclusions in the liquid aluminum melt and porosity in the as-cast components.

A major factor that may affect the ability of the analysis conducted under reduced pressure to measure hydrogen content is the amount of inclusions in the melt. It has been well established that inclusions can act as nucleating sites to facilitate hydrogen bubble
formation. It has been suggested that the RPT actually reveals the combining effects of hydrogen and inclusions. Several studies have reported this phenomenon. The experiments they describe showed that the same melt sample behaved differently before and after filtration under the RPT. In the filtered melt, much less porosity was evident. The increase in porosity may be due to the large quantity of gas bubble nuclei created by inclusions, which leads to the formation of a large number of pores. It may also be related to the high pore density in the melt, which reduces the average distance that hydrogen needs to diffuse a pore. Also, these pores may start to form at a higher temperature during metal solidification than those formed in melts with fewer inclusions; thus, these pores have a longer time to grow.

To what extent do inclusions affect the porosity level? Can this effect be minimized, separated or corrected? Inclusions only create nucleating sites. They do not change the hydrogen content of the melt, neither the hydrogen solubility of the solid metal. The only way inclusions increase the porosity level is by reducing levels of alloy supersaturated with hydrogen in the solid solution in the specimen. The literature reviews have shown that in conventional casting, the hydrogen content that may be tolerated before the onset of porosity is of the order of 0.05-0.08 ml/100g at a cooling rate of 0.1-20°C/s. Hydrogen solubility in solid aluminum is dependent on hydrogen partial pressure. During pore growth in castings, hydrogen pressure within a pore is approximately equal to the ambient pressure. This means that hydrogen solubility of solid aluminum depends on ambient pressure.
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Appendix 1

The W319 Aluminum Alloy Experimental Cooling Curve, Its First Derivative and Base Line

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Selected Measured and Calculated AITAP Metallurgical Characteristics

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<th>Fraction Solid Symbol, (%)</th>
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Appendices

Appendix 2

Characteristic Temperatures for the Enviro-AlTAP Experiments

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Appendix 3

Cooling Curves and First Derivatives of the Enviro-AITAP Experiments

![Graph](image-url)
Appendices

Exp 06

Exp 07

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