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ب بي مع



QUANTIFICATION OF THE REDUCED PRESSURE TEST

by

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A Thesis Submitted to the Faculty of Graduate Studies and Research in Partial Fulfilment of the Requirement for the Degree of Doctor of Philosophy

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September, 1994



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ABSTRACT

The concentration of hydrogen is one of the most important parameters in liquid aluminum processing because it is responsible for gas porosity which affects casting quality, ie. pressure tightness, mechanical properties etc. In order to gain optimum quality, the amount of hydrogen dissolved in liquid aluminum must be known prior to casting. This has led to the development of several techniques to quantify hydrogen in liquid aluminum. Among these is the Reduced Pressure Test (RPT). The RPT is simple, very inexpensive and commonly used in aluminum foundries to obtain a qualitative evaluation of the melt hydrogen level.

In this thesis the development of the RPT to a truly quantitative level is discussed. This includes redesigning of the steel mold and the application of a riser. The mold was redesigned to improve the test sensitivity while a CO_2 -bonded sand riser was applied in order to eliminate volumetric shrinkage and ensure a constant volume sample. As the sample has a constant volume, either the sample weight or density can be used to quantify the hydrogen content. The simplest technique is to use the sample weight.

Several parameters that affect the test sensitivity and reproducibility were studied, such as chamber pressure, emount of inclusions, pouring temperature, and mold temperature. It was found that there are two important parameters that strongly affect the test; chamber pressure and amount of inclusions. The lower the chamber pressure the better the test sensitivity but the poorer the test reproducibility. Increasing the amount of inclusions improves the test sensitivity.

The constant volume sample can be used to predict the amount of hydrogen in the melt for various types of alloys including 319, 356, 357 and 413 within a reasonable margin of error. The error as measured by this technique was found to be in the range of ± 0.025 -0.049 ml./100 g.Al. if the sample weight is used, and in the range of ± 0.025 -0.047 ml./100 g.Al. if the sample density is used.

A simple mathematical model based on a mass balance approach was developed to calculate pore size and sample density. The model predicts the density accurately for various types of alloys and different melt treatments.

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RÉSUMÉ

La concentration en hydrogène est un des facteurs les plus importants dans le traitement de l'aluminium liquide car elle est responsable de la porosité de gaz qui affecte la qualité de la pièce coulée, par exemple l'étanchéité sous pression, les propriètés mécaniques, etc... Afin d'obtenir une qualité optimum, la quantité d'hydrogène dissous dans l'aluminium liquide doit être connue avant la coulée. Ceci a conduit au développement de plusieurs techniques pour quantifier l'hydrogène dans l'aluminium liquide, parmi celles-ci l'essai de pression réduite (Reduced Pressure Test, RPT). Le RPT est simple, très peu couleux et est utilisé couramment dans les fonderies d'aluminium pour obtenir une évaluation qualitative du niveau d'hydrogène de la coulée. Dans cette thèse, le développement du RPT à un niveau réellement quantitatif, est discuté. Ceci inclut la conception d'un nouveau désign pour le moule en acier et l'utilization d'une masselotte. Le moule a été remanié pour améliorer la sensibilité de l'essai tandis qu'une masselotte a été utilisée pour éliminer le rétrecissement volumétrique et pour s'assurer d'avoir un échantillon avec un volume constant. Comme l'échantillon a un volume constant, soit le poids de l'échantillon ou soit la densité peut être utilisé pour quantifier la teneur en hydrogène. La technique la plus simple est d'utiliser le poids de l'échantillon.

Plusieurs facteurs, tels que la pression de la chambre, la quantité d'inclusions, la température de coulée et la température du moule, affectant la sensibilité et la reproductibilité de l'essai ont été étudiés. Il a été trouvé qu'il y a deux paramètres importants qui affectent sérieusement l'essai : la pression dans la chambre et la quantité d'inclusions. Plus la pression dans la chambre est élevée, plus la sensibilité de l'essai est meilleure mais moins l'essai est reproductible. L'augmentation de la quantité d'inclusions améliore la sensibilité de l'essai.

L'échantillon avec un volume constant peut être utilisé pour prédire la quantité d'hydrogène dans la coulée pour différents types d'alliages tels que 319, 356, 357 et 413 avec une marge d'erreur raisonable. L'erreur telle que mesurée par cette technique a été 11 - 3

comprise entre ± 0.025 et 0.049 ml./100g.Al. lorsque le poids de l'échantillon est utilisé, et entre ± 0.025 et 0.047ml./100g.Al lorsque la densité de l'échantillon est considérée.

Un modèle mathématique simple basé sur l'approche de la balance des masses a été développé pour calculer la taille des pores et la densité de l'échantillon. Le modèle prédit la densité avec précision pour des types d'alliages variés et des traitements de coulée différents.

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To my parents, and all of my teachers. <u>.</u>

Chapter 1. Introduction

The objective of this thesis is to develop a method to quantify the hydrogen concentration in liquid aluminum. It is therefore important to discuss the effect of hydrogen in liquid aluminum and the methods commonly used to measure it. The theoretical background of the methods used will be discussed and an appropriate literature review of these methods will be presented in this chapter.

1.1 Hydrogen in Liquid Aluminum.

Hydrogen is the only gas that dissolves measurably in liquid aluminum [1], and hence, the only gas that causes porosity in aluminum castings. The porosity occurs because of the large difference in hydrogen solubility between solid and liquid phases at the solidification front. This is illustrated in Fig. 1.1, for pure aluminum where the ratio of solubility in the liquid to that in the solid at the freezing point is 20:1. This dramatic decrease in solubility results in gas evolution on solidification. The hydrogen is rejected into the liquid phase and accumulates at the solid fication front, thus enhancing porosity formation.

The presence of porosity degrades the quality of castings [2-8]. The pressure tightness of a casting is reduced by interconnected porosity [2]. Porosity formed at the skin affects the finished surface of the castings [3-4], and moreover, the mechanical properties are reduced as porosity increases [5-8]. In the foundry industry, it is estimated that about 50-75% of scrap castings are related to this porosity problem. In order to gain optimum casting quality, it is desirable to be able to quantify the amount of hydrogen prior to the casting process.

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Figure 1.1 Solubility of hydrogen in pure aluminum [1].

1.2 Hydrogen Measurement Methods.

There are several techniques that are currently used in the aluminum industry for the determination of the hydrogen content in aluminum alloys. The techniques are divided into two general classes, depending on how hydrogen is analysed. These are sampling techniques and in situ techniques. These two groups will be discussed in the following sections.

There are three frequently used terms that must be clarified in this thesis which are accuracy, reproducibility and sensitivity. The term accuracy as used here means the precision of the technique in comparison to the reference one. Reproducibility means the consistency of measurement, i.e. repeatability of the results obtained from the same sample. Sensitivity applies to the ability to differentiate two values of measurement, i.e. two hydrogen levels. There will be some non SI units, which are widely used in the literature, in this thesis. These include the measuring unit for the amount of hydrogen dissolved in aluminum, ml./100 g.Al. and the unit of the sample density of the Reduced Pressure Test, g./cc. The equivalent SI unit for one ml./100 g.Al. is 1.12 ppm., and for one g./cc. is 10^{-3} kg./m³.

1.2.1 Sampling Techniques.

This group can be divided into two types. The first one is solid sampling techniques in which a sample of liquid is poured into a specially designed mold and the resulting solid sample is analyzed. The second type is liquid sampling techniques in which a liquid sample is drawn and introduced directly into the measuring system.

1.2.1.1 Solid Sampling Techniques.

There are three methods used to analyze solid samples:

1. Vacuum subfusion extraction,

2. Inert carrier gas extraction from liquid,

3. Vacuum extraction from liquid.

Each method will be discussed separately below.

_____)

1.2.1.1.1 Vacuum Subfusion Extraction (VSE) Technique.

This technique has earned a reputation for reliability, and has been used as a standard method against which other techniques are calibrated and evaluated. The technique was developed by Ransley, Eborall and Talbot [9-10] to quantify the absolute content of hydrogen in a solid sample. The procedure is to collect and measure hydrogen which is desorbed into an evacuated system from a heated solid sample. Hydrogen which

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diffuses from the sample is measured directly via a mass spectrometer to give the absolute hydrogen content. Fig. 1.2 illustrates the analytical system schematically. It is constructed mainly in pyrex glass and consists of four important parts; a pumping system, pressure measuring instruments, an extraction system, and a gas analysis system. It can be seen that the system is quite complicated with many joining parts, which can easily lead to error because of system contamination by vacuum grease or leakage.



Figure 1.2 Hot Vacuum Extraction Apparatus for hydrogen content measurement.

The procedure for hydrogen measurement begins with the heating of a cylindrical sample in an evacuated clear silica tube to a temperature below the eutectic or solidus, but high enough to allow the hydrogen to diffuse out of the sample in an acceptable time. The diffused hydrogen is collected in an evacuated volume. The extraction continues until an endpoint is observed via an extraction curve obtained from the pressure measuring instruments, ie. Pirani or Baratron gauges. After the extraction is complete, the amount of gas is quantified by a mass spectrometer or by measuring certain gas physical properties. It is interesting to note here that VSE equipment is not commercially

available. The equipment set up, although based on the same principle, thus varies from one laboratory to another. The accuracy of this technique was found to depend strongly on both the equipment and the user [11]. Despite this fact, the reproducibility of the technique is about ± 0.01 ml./100 g. Al. However, the method has a major drawback in that it requires a very long extraction time, about 1-2.5 hrs. Moreover, the technique is definitely of the laboratory type, and its operation requires highly skilled personnel. As such it is expensive and is not suitable for use in the plant or on the foundry shop floor.

1.2.1.1.2 Inert Carrier Gas Extraction From the Liquid.

This technique was developed by Degreve [12-13] in order to overcome the long extraction time problem of the VSE technique. The principle of this method is similar to the VSE except that the solid sample is melted in a flowing nitrogen gas stream at atmospheric pressure. The hydrogen is extracted by diffusion from the liquid sample into the nitrogen stream. The evolved hydrogen is then measured by a katharometer (thermal conductivity cell). Results are obtained in about 15 mins., and reportedly are in good agreement with those of the hot vacuum extraction method [12-13].

There are, however, several sources of error in this technique. The first one is hydrogen contamination on the sample surface by moisture in the air. This surface hydrogen cannot be eliminated by the usual heating of the sample for 60 secs. at 673-773 K as reported by Anyalebechi [14] and Lamb [15]. In order to completely eliminate the surface hydrogen, the sample must be heated at high temperature and held for a longer period of time, a procedure which could lead to evolution of some of the bulk hydrogen. This will result in lower hydrogen analyses. Another source of error is the evolution of moisture from the unbaked silica furnace tube. While the sample is melting, the heat radiation from the sample is high enough to raise the temperature of the silica tube and cause spurious hydrogen evolution. This source of error is particularly significant when the analysed sample contains a low hydrogen level (< 0.10 ml./100 g. Al.). The accuracy of this technique is about ± 0.04 ml./100 g. Al.[16]. Like the VSE method, this

is a laboratory technique which is not suitable for use on the foundry floor.

1.2.1.1.3 Vacuum Extraction From a Liquid Sample.

This technique involves melting of a solid sample in a crucible (made of boron nitride, graphite, alumina or steel) under a high vacuum. The hydrogen evolved is extracted and analyzed in a similar fashion to the VSE technique. This method thus shares the same problems as the VSE technique. System contamination because of vacuum grease, and leakage problems can easily occur at the high vacuums (10^{-3} Pa) applied. Moreover, a high temperature is required to melt the sample, and spurious hydrogen can easily be involved because of heat radiation and moisture at the wall of the analytical system. The error of this method is quite large (about ± 0.07 ml./100 g. Al. in pure aluminum) and results are not reproducible [17]. This method is outdated and is no longer used routinely.

1.2.1.2 Liquid Sampling Techniques.

There are three methods that used to analyse hydrogen from a liquid sample. They are:

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1. Reduced Pressure Test,

2. Vacuum extraction of gas during solidification, and

3. First Bubble Technique,

1.2.1.2.1 Reduced Pressure Test.

The simple principle of this technique is based on the formation of gas porosity in slowly solidifying liquid aluminum under reduced pressure. The size of the porosity formed is magnified by the effect of the reduced pressure, resulting in a visibly porous .

sample as shown in Fig. 1.3. The samples so solidified are evaluated either by visual observation for bubble formation during solidification, or by determining the density of the solidified sample. Visual evaluation of the sectioned sample is often done by comparing the result to a standard chart such as provided by Stahl Specialty Co. [18] and shown in Fig. 1.4.





The major drawback of this technique is believed to be due to the presence of inclusions [19]. Inclusions in the melt reduce the nucleation energy required by gas bubbles, thus enhancing the formation of porosity. At the same hydrogen level, samples rich in inclusions may have a lower density than ones with fewer inclusions. This inclusion problem requires careful attention if this method is to be developed to a fully quantitative level.

The RPT system components are easy to find and very simple to assemble. The system consists of a vacuum pump, a reduced pressure chamber, crucible, pressure gauge, timer, and a valve to adjust the pressure, as shown in Fig. 1.5. The sampling procedure is very simple. A small amount, about 200 g., of aluminum melt is poured into a thin wall steel crucible seated in the chamber. The pressure in the chamber is



Figure 1.4 The standard chart developed by Stahl Specialty Co. [18] shows ratings and percent surface area porosity.

reduced to a specified point and remains constant until the melt is fully solidified. When the melt is solidified, one can observe the surface of the sample. A puffed-up (convex) surface indicates a high gas level whereas a flat surface relates to lower gas levels. After solidification, the sample is removed from the mold and evaluated either by density measurement or by sectioning to observe the porosity. The entire process requires

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roughly about 10 min. for completion. This technique thus has an advantage over other hydrogen measuring methods because of its simplicity and low cost.

This test is quite popular and widely used by hundreds of foundries worldwide. However, the test is not quantitative. It will be seen in the following chapter that it may be possible to develop this method to a fully quantitative level. Such development would bring about a simple and inexpensive method for measuring the hydrogen level in liquid aluminum.



Figure 1.5 Schematic diagram of the Reduced Pressure Test Unit.

1.2.1.2.2 Vacuum Extraction of Gas During Solidification.

This technique [20] is similar to the VSE except that the liquid sample is introduced directly into the system. Once the sample is introduced into the vacuum chamber, the pressure is rapidly reduced to a low value (~ 132 Pa) in a short period of

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time. The sample is then slowly solidified in the chamber. The hydrogen evolved from the sample accumulates in the vacuum chamber and is measured by either a Pirani gauge or a mass spectrometer. As with the the reduced pressure test, inclusions can be a factor. Moreover, a certain amount of gas is trapped in the solid sample as porosity, or in solid solution. This affects the sensitivity and reproducibility of the method. Reported data [21] indicate that the accuracy of this method is about ± 0.05 -0.10 ml./100 g. Al.

1.2.1.2.3 First Bubble Technique.

This technique was proposed by Dardel [22] some forty years ago. The technique involves slowly solidifying a liquid sample and gradually applying vacuum until the first bubble is observed at the melt surface. The pressure and temperature at which the bubble appears are recorded. The hydrogen content can then be calculated from the following equation:

$$\log\left[\frac{H}{H^{0}}\right] - 0.5 \log\left[\frac{P}{P^{0}}\right] = -\frac{A}{T} + B$$
(1.1)

where

 \underline{H} = solubility of hydrogen in the alloy at a given hydrogen pressure, P and melt temperature, T;

 \underline{H}^{0} = standard solubility of hydrogen equal to 1 ml. of hydrogen at 273 K and 101325 Pa per 100 g. of metal;

P = pressure, Pa;

 P^0 = standard pressure equal to 101325 Pa;

T = temperature, K;

A and B = Sievert's constants determined from the equilibrium solubility of hydrogen in the alloy.

Reproducibility and accuracy of this test are not comparable with the results of

the VSE technique as shown in Fig. 1.6. The main reason for this is that the test is extremely sensitive to inclusions. At the same hydrogen level, samples rich in inclusions may easily form a bubble compared to cleaner samples. Moreover, the test is insensitive in a melt which contains a low hydrogen level (<0.15 ml./100 g. Al.), as detection of the first bubble is difficult. Overall the accuracy of this technique is about ± 0.05 -0.10 ml./100 g. Al.



Figure 1.6 Comparison of First-Bubble Test and Vacuum Subfusion Extraction Results [23].

1.2.2 In Situ Techniques.

There are four in situ techniques that have been reported:

- 1. Closed-loop Recirculation method.
- 2. Continuous Hydrogen Analysis by Pressure Evaluation in Liquids,
- 3. Electrochemical Determination, and
- 4. Immersible Probe Technique.

1.2.2.1 Closed-loop Recirculation Technique.

This system is shown schematically in Fig. 1.7. Inert gas bubbles are circulated through the melt until the gaseous hydrogen which diffuses into them is in equilibrium with the solute hydrogen in the melt. At equilibrium, the Sievert's relationship between the concentration of dissolved atoms and the pressure of molecular gas holds:

$$H = S \sqrt{P_{gas}} \tag{1.2}$$

where

<u>H</u> = dissolved hydrogen level, ml./100 g. Al.,

S = solubility of hydrogen at given temperature and pressure, ml./Pa^{0.5}.100 g. Al.,

 P_{gas} = partial pressure of hydrogen gas in contact with metal, Pa. The solubility of hydrogen in aluminum and its alloys is a function of temperature according to the equation:

$$\log S = -\frac{A}{T} + B \tag{1.3}$$

In order to predict the hydrogen content in the melt correctly, the Sievert's constants (A and B) must be known precisely for each aluminum alloy. Several scientists [23-25] have worked on this subject and established a correction factor to apply to the result when the system is used for alloys as shown in the equation:

$$\underline{H}_{A} = C.F. \times S_{AI} \sqrt{\frac{P_{gas}}{101325}}$$
(1.4)

where

C.F. = correction factor.

 S_{Ai} = solubility of hydrogen in pure aluminum at a given temperature and 101325 Pa.



Figure 1.7 Simplified diagram of Closed-loop recirculation technique.

If S_{Al} and the correction factor are known then the hydrogen content of the alloys can be calculated from P_{gus} . P_{gus} is measured indirectly by measuring the thermal conductivity of the gas mixture with a katharometer. The hydrogen content is obtained either from a microprocessor or a calibration chart which relates the thermal conductivities to hydrogen contents as affected by temperature and hydrogen solubility in the various alloys. The reproducibility and accuracy of the technique is reasonably good in comparison to the VSE method and is about ± 0.025 ml./100 g.Al.[11,14,26]. This technique is widely used because of its on-line measurement ability, and shorter response time of only 10-15 min.

There are however two limitations to this method. The first one is the use of correction factors, and the second one is the ceramic probe. The correction factors of some important Al-Si alloys are shown in Table 1.1. This factor is, in fact, a ratio between the solubility of hydrogen in the alloy to that in pure aluminum at the same temperature and pressure. Experimental data for the solubility of hydrogen in foundry alloys is scarce since the measurement of hydrogen solubility is time consuming and expensive, although extensive work on hydrogen solubility has been carried out on pure

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aluminum and some important binary alloys such as Al-Si, Al-Cu, and Al-Mg [1,27]. In alloys, the correction factor is determined from only three alloying elements (Si, Cu, and Mg) with the effect of other elements being neglected, due to insufficient data. Furthermore, the interaction of these alloying elements as affecting the solubility of hydrogen is not clearly known. Nevertheless when these correction factors were applied to the technique an accuracy of ± 0.03 ml./100 g. Al.[23] in comparison to VSE method was obtained.

This technique is strongly dependent on diffusion of hydrogen into the measuring system. The probe used must provide a good path for hydrogen diffusion and be highly resistant to mechanical and thermal shock. Such probes have been difficult to develop, with the best one developed by Alcan [16]. This probe consists of a block of porous alumina joined to two stainless steel capillary tubes with a high temperature adhesive, as shown in Fig. 1.8. It is reported to be highly resistant to both mechanical and thermal shock; however, the probe deteriorates with time as shown by an increase in response time [16] which may suggest that the probe is susceptible to plugging. As such the probe life is guaranteed for only 10 readings, and this increases the analysing cost. Another disadvantage of this technique is the capital cost of the system which makes the equipment unattractive to medium and small foundries. Moreover, operation of sophisticated equipment also requires special attention and trained personnel, hence increasing maintenance and operating cost.

Tat	ole	1.1	Correcti	ion 1	factors	of	some	Al-Si	alloy	/ S .
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Alloys	319	356	357	413
Correction Factors	0.69	0.82	0.84	0.68



Figure 1.8 Alcan hydrogen probe.

1.2.2.2 Continuous Hydrogen Analysis by Pressure Evaluation in Liquids (CHAPEL) Method.

This technique was originally developed by Ransley [28] and then abandoned as impractical. However, advances in instrumentation and electronics have now made the procedure feasible. Scientists in Germany [29-30] have perfected the system shown in Fig. 1.9. A porous probe connected, via an impermeable ceramic tube, to a pressure measuring instrument (e.g. a piezoelectric transducer) is dipped into the melt and quickly evacuated. The porous probe acts as an artificial bubble into which hydrogen from the melt can diffuse until the pressure in the probe and the hydrogen partial pressure in the melt are in equilibrium. At this time it is only necessary to record the hydrogen pressure and the temperature of the melt. From these values the gas content may be easily calculated from the equation:

$$\log H = 0.5 \log P_{H_2} - \frac{A}{T} + B \tag{1.5}$$

Since the solubility of hydrogen varies with alloy chemistry [10,27], a proper correction factor must be applied for aluminum alloys. This technique thus faces the same limitation as the closed-loop recirculation technique.



Figure 1.9 Schematic of CHAPEL method [30].

The major problem with this method is that diffusion of dissolved hydrogen into the measuring system is relatively slow, and the time required to reach equilibrium is about 20-60 min. To alleviate the difficulty the probe is doped with a small amount of hydrogen. With this doping procedure, equilibrium can be attained in a few minutes. The accuracy of this technique is about ± 0.025 ml./100 g.Al.[30]. The capital cost of this system is quite expensive with the result that it is not attractive to medium and small foundries.

1.2.2.3 Electrochemical Determination.

Hydrogen in the melt is measured by an electrochemical sensor. This sensor was developed by Gee and Frey [31] in 1978. They used CaH_2 as an electrolyte and a mixture of Ca and CaH₂ as the reference electrode, as shown in Fig. 1.10. Operation involves measuring by a millivoltmeter the electromotive force (emf) induced in the probe as well as the temperature. The hydrogen content of the melt is obtained from the equation:

$$\log\left[\frac{H}{H^0}\right] - 0.5 \log\left[\frac{P}{P^0}\right] = -\frac{nFE}{4.606RT} - \frac{A}{T} + B$$
(1.6)

where

n = number of electrons involved in the reversible reaction,

F = Faraday constant, 96,487 coulomb/mol.

E = equilibrium electrode potential measured across the electrode/electrolyte interfaces,

T = temperature, K,

R = gas constant, 8.314 J/K mol.

This equation is based on the solubility of hydrogen in pure aluminum. A knowledge of the constants A and B for various alloys is required in order to correctly calculate the gas content in alloys.

The problem with this technique is that the probe life is extremely short, and the electrolyte (CaH_2) is very unstable and reacts with molten aluminum. The device thus has not found commercial success.

1.2.2.4 Immersible Probe Technique.

This technique was developed by Russian scientists [32] for direct measurement of hydrogen in aluminum and its alloy melts. It involves the extraction of hydrogen from



Figure 1.10 Schematic of Electrolyte Probe [32].

a fixed quantity of molten aluminum admitted into an immersible probe. While the melt in the probe is isolated from the environmental melt by a gas seal, a stream of argon is circulated into the melt and strips away the dissolved gas for analysis. The hydrogen evolved is measured by an integrating gas analyzer. Among the in situ techniques, this is the only one that is capable of yielding absolute hydrogen values. It is doubtful that the liquid sample in the probe can be isolated completely from the surrounding melt with a seal gas, and the system is bulky and requires the use of a laboratory based analyzer. Application of this type of system on the shop floor would be difficult.

1.3 Hydrogen Measurement Method Comparison.

Having reviewed the available hydrogen measurement methods it is useful to analyze them in order to find the most suitable technique for use on the foundry floor. A suitable technique in this case refers to one that is accurate, inexpensive, rapid and easy to use. These criteria will be considered with different weighting depending on their importance. Among the criteria, accuracy and speed are the most important since they strongly affect the quality of the castings. An accurate and prompt result provides user confidence and time to readjust the melt quality. These two criteria will be weighted 10 points. Analyzing cost is second in importance since it relates to the price of the castings. This cost includes maintenance and operating cost, and is weighted at 8 points. Capital cost is also included, but over the long term, this cost will be minimal. A weight given to this criterion is 6 points. Simplicity of the technique is important, as a simple technique eliminates the need for highly skilled personnel. A weight of 6 points is used for operational simplicity.

Rating in each category will be by 4 grades; A,B,C, and D as summarized in Table 1.2.

Grades	Meanings	Rating Points			
А	very good	10			
В	good	8			
с	fair	6			
D	poor	4			

Table 1.2. Grading, its meaning, and rating points.

Wherever appropriate, the minus grade (A-, B-, etc.) will be applied. For a minus grade, the rating point will be less than the original point by one.

For the sake of simplicity, only important techniques will be considered. These include currently available commercial techniques or those that soon will be on the market. The exceptions are the VSE technique and the RPT. The VSE technique is not commercially available but is used as a reference method. The RPT is not yet a quantitative method, but has the potential to be a suitable technique since it is fast, inexpensive, and simple. In total, seven techniques are considered:

1. VSE technique,

2. Inert Carrier Gas Extraction from Liquid (ICGE),

- 3. Vacuum Extraction of Gas during Solidification (VEGS),
- 4. First Bubble Technique (FBT),
- 5. Closed-loop Recirculation Technique (CRT),
- 6. Continuous Hydrogen Analysis by Pressure Evaluation in Liquids (CHAPEL), and
- 7. Reduced Pressure Test (RPT).

Techniques	Accuracy		Resp time	Response di time di		Analyzing cost		oital t	Simplicity		Total points	Rank		
	x 10		x 10		x 10		x 8		x 6		хб			
VSE	Α	100	D	40	D	32	С	36	D	24	232	6		
ICGE	В	80	Α	100	D	32	D	24	D	24	260	5		
VEGS	D	40	A	100	В	64	С	36	В	48	288	4		
FBT	D-	30	Α	100	A-	72	В	48	В	48	298	3		
CRT	A-	90	A	100	B -	56	D	24	В-	42	312	2		
CHAPEL.	A-	90	A	100	В	64	D	24	B-	42	320	1		
RPT	?	?	Α	100	A	80	A	60	Α	60	300+	?		

Table 1.3. Evaluation of quantitative techniques and RPT.

Grading and ranking of these techniques are summarized in Table 1.3. The top two are the in situ techniques which are CHAPEL and CRT respectively. They are ranked on the top because of their accuracy and good response time. CRT is second because the analyzing cost is higher than that of the CHAPEL technique. This is mainly due to the shorter life of the CRT probe. The third and fourth techniques are found in the liquid sampling group, FBT and VEGS. These have the advantage of good speed, low cost, and simplicity, but relatively low accuracy. The fifth and sixth places are occupied by the ICGE and VSE techniques. The main disadvantages of them are lack of simplicity and high analyzing cost because they are laboratory methods which require highly trained personel. It is important to note here that, even without rating in the accuracy criterion, the RPT ranked third. This is mainly because of its superior speed, simplicity, and low cost. If one could develop this technique to a quantitative level, with acceptable accuracy, the technique could be ranked first among commercially available methods. Development of this technique to a quantitative level clearly would be a major breakthrough in simple and inexpensive control of melt quality.
Chapter 2.

Theoretical Background and Previous Work.

It was demonstrated clearly in the previous chapter that the RPT has the potential to be an excellent quantitative hydrogen measurement technique. Thus in this chapter the RPT will be discussed in detail.

Since the basis of the technique deals with the formation of gas bubbles, the theoretical background of porosity formation during solidification will be reviewed. This will be followed by a discussion of previous work on the RPT, and finally, the aims of the present work will be outlined.

2.1 Formation of Gas Porosity.

The formation of gas porosity requires two important steps, nucleation and growth. These two steps will be discussed separately.

2.1.1.Pore Nucleation.

It is generally accepted that homogeneous nucleation of gas bubbles in an aluminum melt is quite unlikely. This is because the energy required for homogeneous nucleation is very high. For homogeneous nucleation, the fracture pressure, or the pressure required to form a small cavity in the liquid can be expressed as [34]:

$$P_F = -\left(\frac{16\pi\sigma^3}{3kT \ln\left(\frac{NkTt}{h}\right)}\right)^{\frac{1}{2}}$$
(2.1)

where

T = temperature, K,

 σ = surface energy, N/m,

 $\mathbf{k} = \text{Boltzmann's constant, J/K},$

- N = number of gas molecules in liquid,
- t = time allowed for nucleation, s.,
- h = Planck's constant, J.s.

The pressure required for pore nucleation at different hydrogen concentrations and a nucleation time of 300 sec. is shown in Table 2.1. As can be seen, the pressure required for homogeneous nucleation is of the order of 3.55×10^9 Pa (35000 atm.). This pressure is much higher than can be achieved during cooling of the melt. Gas porosity thus forms heterogeneously with the aid of some foreign nucleus such as inclusions.

Table 2.1. Fracture pressure required for homogeneous nucleation of hydrogen pores in aluminum at 973 K.[34]

H ₂ level,	Fracture Pressure			
ml./100 g.Al.	Pa	atm.		
0.1	3.55x10°	35035.78		
0.2	3.53x10°	34838.39		
0.3	3.52x10 ⁹	34739.70		

In the presence of foreign substrates in the melt, the activation energy for nucleation decreases. The mechanism of heterogeneous nucleation is normally treated by considering a nucleus formed on a flat substrate [35]. The fracture pressure is reduced by a factor $f(\theta)$, which is given as:

$$P_F = f(\theta) \cdot \left(\frac{16\pi\sigma^3}{3kT\ln\left(\frac{NkTt}{h}\right)}\right)^{\frac{1}{2}}$$
(2.2)

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$
(2.3)

where,

 θ = contact angle between liquid and solid, as shown in Fig. 2.1.

It is also shown in Fig. 2.1. that as the contact angle decreases, i.e. the liquid does not wet the solid, $f(\theta)$ decreases, and hence the energy required for nucleation decreases. Materials or particles that are not wetted by the melt will be nucleants for porosity. Examples are the crucible, a mould wall or particles suspended in the melt such as inclusions.



Figure 2.1 Contact angle, θ , and $f(\theta)$ plots as a function of θ , $\sigma_{g,s}$, $\sigma_{l,g}$, and $\sigma_{l,s}$ are solid-gas, liquid-gas, and solid-liquid interfacial energies, respectively.

2.1.1.1 The Effect of Inclusions on Porosity Formation.

Inclusions enter the melt from a variety of sources. They may be of any size and they are trapped mechanically during solidification. Table 2.2 identifies some of the types of inclusions that can be found in aluminum alloys and a possible source of each type. Besides these, foreign particles may be added intentionally as in the case of metal matrix composites or grain refiners. In the case of ordinary melting, inclusions of as many as 35/500 mm² are found [36]. Among these inclusions, alumina was found to be the major contributor to porosity formation. ÷1

Туре	Source	Characteristics
Alumina	Furnace Refractory	Crystalline, Hard
Alumina	Surface Oxidation	Amorphous, Soft, Films
Spinels	Oxidation of Al-Mg	Crystalline, Hard
Chlorides	Fluxes	Deliquescent, Corrosive
Fluorides	Fluxes	Deliquescent, Corrosive
Sludge	Low Temperature	Hard dense crystals
SiC	Furnace Refractory	Crystalline, Hard

Table	2.2	Sources	of	Inclusions	and	Characteristics	[36].
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In aluminum, the oxygen partial pressure required to avoid alumina formation is of the order of 1.01^{43} MPa. at 973 K [37]. Thus it is impossible to avoid the presence of alumina in molten aluminum. Alumina skimmed from the melt [38] has a rough surface. It contains cracks, holes, and other defects from 1 to 40 μ m in size which are not wetted by the aluminum melt. These particle or oxide films are abundant and facilitate pore formation.

Quantification of inclusions in the melt is a difficult task. Thus detailed study on the effect of different types and amount of inclusions on porosity and mechanical properties is rare [36,39-41]. Among the existing work on this subject are studies carried out on an extreme case basis where inclusion-full melts and presumably inclusion-free melts were compared. The exact amount of inclusions in these experiments is not known, but it has been shown that inclusion-full melts tend to generate more porosity on solidification than inclusion-free melts.

Iwahori et al [36] found that in unmodified as well as Sr and Na modified Al-7%Si castings, the porosity, at equal hydrogen contents, was lower in castings where the metal had undergone inclusion removal. The results of the research showed that at low hydrogen contents, the inclusion level is of minor importance. Celik and Bennet [39] have also found that for superpurity aluminum solidified in sand molds, inclusions had

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no effect on porosity at hydrogen contents less than 0.17 ml./100 g. Al.

Laslaz and Laty [40] showed that in 356 and 319 alloys manufactured from scrap or ingots respectively, the latter had better melt cleanliness and a lower porosity content was obtained at the same hydrogen content.

Similar results have been reported by Shivkumar, Wang and Lavigne [41]. They have used the RPT to study the effects of metal cleanliness on porosity. The melts were dirtied intentionally by bubbling a nitrogen and air mixture through the molten metal. The concentration of oxide inclusions could be controlled roughly by varying the bubbling time. They found that, for the same hydrogen concentration, the amount of porosity, the number of pores and the maximum pore size increase significantly with the oxide concentration. They also reported that degassing the melt has a stronger effect on reducing the porosity than filtration alone. Their results are summarized in Table 2.3.

Approximated concentration of added oxides, ppm.	% porosity	Pore density, #/m ²
0	0.17	4.28x10 ⁶
3750	0.61	1.96x10 ⁷
9000	2.81	9.06x107

Table 2.3. Pore characteristics in A356 alloy as reported by Shivkumar et al [41].

It can be clearly seen from Table 2.3 that, under the same casting condition, ie. the same hydrogen level, cooling rate, and mold shape, high porosity is the result of an increasing amount of inclusions in the melt.

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2.1.2 Pore Stability and Growth.

Once a pore nucleates, it requires energy to be stabilized and to continue to grow. Consider a gas bubble in a liquid metal. This bubble must have an internal gas pressure to counterbalance the external forces which can act to collapse the bubble, as shown in Fig. 2.2. These external forces are: the pressure exerted by the atmosphere, the metallostatic head pressure, and the pressure due to surface tension. As solidification proceeds, this bubble is also subjected to shrinkage pressure. This is a negative pressure which enhances the formation of the bubble; hence the equation for bubble stability becomes,

$$P_{g} = (P_{a} + P_{m} - P_{s}) + P_{st} = P_{ex} - P_{st}$$
(2.4)

where,

 $P_g = gas pressure,$

 $P_s = shrinkage pressure,$

 $P_{\bullet} =$ ambient pressure,

 P_m = metallostatic head pressure,

 P_{st} = pressure due to surface tension, and

 P_{cx} = pressure acting on porosity = $(P_a + P_m - P_s)$.

The unit of these pressures is in Pa.

 P_m is usually neglected since it is small compared to ambient pressure. P_g , P_s , and P_m will be discussed in detail, since they are the parameters likely to have a notable influence on porosity formation during solidification of a casting.

2.1.2.1 The Internal Gas Pressure.

The internal gas pressure can be calculated using various approaches. The first approach is to determine the hydrogen rejection at the solid-liquid interface, and the second is to perform a mass balance. For the first approach, one begins with Sievert's



Figure 2.2 Various types of pressure acting on gas bubble.

Law (equation 2.3) which assumes thermodynamic equilibrium between the molecular gas in the bubble and the diatomic hydrogen dissolved in the melt.

$$P_g = \left(\frac{C_{HL}}{S}\right)^2 \tag{2.5}$$

where,

 P_{g} = equilibrium partial pressure of the dissolved gas, Pa,

 C_{HL} = amount of hydrogen dissolved in the melt, ml./100 g.Al.,

S = solubility constant of the melt, ml./Pa^{0.5}.100 g.Al.

The gas pressure in the bubble can be assumed to be equal to P_g . In order to determine P_g , C_{HL} must be known. When complete diffusion of hydrogen in the solid is assumed, it is possible to use the lever rule for calculating the hydrogen content in the melt as:

$$C_{HL} = \frac{C_{HO}}{(1 - f_s (1 - k_h))}$$
(2.6)

where,

 C_{HO} = initial concentration of hydrogen in the melt, ml./100 g.Al.

 $f_{I} = fraction of solid,$

 k_h = equilibrium partition ratio of hydrogen in aluminum.

The value k_h , like the solubility of hydrogen for various foundry alloys, is not known accurately, and this can be an important source of error in the calculation.

The criterion for porosity formation using this approach is that the internal gas pressure must be equal to or greater than the external pressure acting on the bubble. From equation 2.3, it is seen that the gas pressure is proportional to the square of the amount of gas dissolved in the melt, C_{HL} . Thus gas pressure rises rapidly as hydrogen in the melt increases. As solidification proceeds, rejected hydrogen which accumulates in the residual melt results in increasing gas pressure. The initial amount of hydrogen dissolved in the melt thus plays a key role in pore formation. The higher the gas level dissolved in the melt, the faster the gas pressure rises, and the more rapidly porosity can form and grow. This approach was applied by several researchers [42-45]. However, the experimental agreement observed by the investigators has been described as "better than can reasonably be expected" to "poor". The problem with this approach arises from the melt, and thus Sievert's law can be applied. This may not be true since the temperature in the melt changes quite quickly, and the assumption of equilibrium may not be valid.

The second approach in calculation of gas pressure is use of a mass balance. The principle of this technique is to assume that the gas bubble forms when the amount of gas in the liquid exceeds the maximum solubility limit in the liquid and the solid. The amount of gas which may be present as porosity, C_{HP} , can be calculated from a mass balance as,

$$C_{HP} = C_{HO} - (f_s C_{HS} + f_l C_{HL})$$
(2.7)

where,

 C_{HP} = amount of hydrogen in porosity, ml./100 g.Al.,

 C_{HO} = initial amount of hydrogen in the melt, ml./100 g.Al.,

 C_{HS} = maximum hydrogen content in solid, ml./100 g.Al.,

 $f_1 =$ fraction of liquid, and

 C_{HL} = maximum hydrogen content in liquid, ml./100 g.Al.

From equation 2.7, the initial amount of hydrogen in the melt is important to porosity formation. The higher the initial amount of hydrogen, the easier gas porosity can form and the higher the total amount of hydrogen in the pore. Other parameters that can contribute to porosity formation are C_{HS} and C_{HL} . At the end of solidification, ie. $f_i=0$, the total amount of hydrogen in porosity is equal to C_{HO} - C_{HS} . Parameters that affect C_{HS} can affect the amount of hydrogen in the pore as well. While C_{HS} affects the amount of hydrogen in the pores in terms of formation time. As stated previously porosity can form only when the amount of hydrogen exceeds the amount of hydrogen that can dissolve in liquid and solid. C_{HS} is small compared to C_{HL} , and hence can be neglected. In order to overcome the solubility of hydrogen in the liquid, the melt requires some solidification time in order for the hydrogen to become concentrated in the melt. The higher the C_{HL} for pore nucleation, the longer the accumulation time, hence the shorter time that the porosity can grow. Thus C_{HL} in this case is the key to predict the porosity size in the solidified metal.

It can be concluded at this point that the internal gas pressure is dependent on two important parameters, C_{HO} and C_{HS} , since the total amount of hydrogen in the pore after solidification is equal to C_{HO} - C_{HS} .

2.1.2.2 Pressure due to Surface Tension.

Pressure due to surface tension is important particularly at small bubble radius. A parameter which reduces the surface tension should lead to increased porosity. Such a parameter could be the effect of melt treatments such as modification in which a small amount of Sr is added to the melt in order to improve the mechanical properties. This hypothesis has been used to explain the porosity problem in modified alloys [46], and has recently been verified by Emadi and Gruzleski [47].

From thermodynamics, the free energy required for nucleation of a gas pore in a liquid can be estimated using the relationship:

$$\Delta G = 4\pi \sigma r^2 + \frac{4}{3}\pi r^3 (P_{ex} - P_g)$$
(2.8)

where

 ΔG = activation energy for nucleation, N.m,

 σ = the gas-liquid surface tension, N/m,

 $\mathbf{r} = \mathbf{radius}$ of the bubble, m.

The critical radius for growth, r^{*} , of a pore nucleus is obtained when equation 2.8 reaches its maximum value. Equation 2.8 can then be rewritten as:

$$r^* = \frac{2\sigma}{P_g - P_{ex}} \tag{2.9}$$

Equation 2.9 clearly shows that reducing the surface tension results in reduction of the critical radius of the gas bubble, thus increasing the chance of porosity formation.

It is important to note here that the critical radius of the gas bubble can also be reduced by increasing P_g or reducing P_{ex} . The parameter that affects P_g the most, as discussed before, is the initial amount of hydrogen in the melt. For P_{ex} , ie. P_a-P_s , since P_a is always constant, P_{ex} thus directly relates to P_s . This shrinkage pressure will now be discussed.

2.1.2.3 Shrinkage Pressure.

The shrinkage pressure is related directly to the ease of feeding during solidification. There are two important feeding mechanisms that occur during solidification. The first is liquid feeding which occurs at any stage until the end of solidification. The second is mass feeding which occurs only in the mushy zone. Microporosity is caused by the limitations of each of these feeding mechanisms.

Mass feeding occurs during the early stages of solidification until crystals are no longer free to move. In the initial stages of freezing, the primary crystals are able to move to some extent in the mixture of solid and liquid, and shrinkage caused by the phase change is compensated by such movement. Mass feeding is believed to compensate for roughly two-thirds of the total liquid-to-solid shrinkage of the alloy [48]. Mass feeding stops when the primary crystals become so large that they interlock with each other. This is called the point of coherency.

Liquid feeding at the early stage of solidification does not have a strong effect on porosity formation since the flow resistance is small. However, when a coherent dendritic network forms in the mushy zone, liquid feeding through this network, which is known as interdendritic feeding, is considered to be the most important contributor to the creation of microporosity. When the volume contraction occurs during solidification, liquid must flow through the dendritic network to compensate for this contraction. This results in a pressure difference between the free liquid (the riser, in a casting), and points within the casting. When this pressure difference becomes sufficiently large, a cavity forms. In short, when resistance to fluid flow within the casting become sufficiently large, the fluid cannot flow to compensate for the volumetric shrinkage, and a void will nucleate. This void is a suitable nucleus for pore formation since it is not wetted by the melt.

The shrinkage pressure has been analysed by several researchers [43,49-54]. However, the most acceptable work is that of Piwonka and Flemings [43]. They studied shrinkage in a cylindrical sand casting with various types of solidification. In the case of

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plane front solidification, the shrinkage pressure can be expressed as:

$$P_s = \frac{32.\mu.\beta'.k^2.L^2}{r^4}$$
(2.10)

where

k = heat flow constant = b. $(T_m-T_0)/(\sqrt{\pi}.\rho_*.H)$, β' = corrected shrinkage coefficient, $\beta/(1-\beta)$, μ =viscosity, Pa.s, β = shrinkage coefficient, $\beta = (\rho_*-\rho_0)/\rho_*$ ρ_* = solid density, kg./m³, ρ_1 = liquid density, kg./m³, T_m = melting point of the metal, K, T_0 = ambient temperature, K, H = latent heat of fusion, kJ/kg, b = thermal diffusion of the mold, W/m.K, L = length of the flow channel, m. r = radius of the flow channel, m. R = outside radius of the cylindrical casting, m., as shown schematically in Fig.

2.3.

For mushy solidification, D'Arcy's Law was applied. In this case, τ (branching factor) and n (number of channels per area) were introduced to take the branching of the intercrystalline and interdendritic channels into account, as:

$$P_{s} = \frac{32.\mu.\beta'.k^{2}.L^{2}}{r^{4}} \left(\frac{\tau^{2}}{\pi.R^{2}.n} \right)$$
(2.11)

The difficulty of the calculation lies in the fact that the number of channels per unit area is not known accurately. For mushy solidification, the number of channels per unit area can be related to the spacing of the primary and secondary dendrite arms. Poirier [49] studied these parameters and found that when the flow was parallel to the primary dendrite arms, P, depended on the primary dendrite arm spacing, but not on the



Figure 2.3 Schematic representation of mushy zone and parameters in equation 2.10.

secondary dendrite arm spacing. If flow was normal to the primary dendrite arms, P_s depended on both. Based on this idea, several researchers attempted to calculate P_s in several aluminum alloys [49-54]. However, these studies lead to the conclusion that P_s has only a slight effect on the formation of porosity. Most reported that P_s reduced P_a by roughly about 10% [49-53]. The only significant effect of P_s , that was be found [54], was at a very late stage of solidification, ie. $f_s > 0.97$, but at this stage, porosity will not have sufficient time to grow to an appreciable size.

2.1.3 Hydrogen and Porosity Relationship.

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Hydrogen has long been recognized as the major contributor to porosity formation. Ransley and Neufeld [1] found that the volume fraction porosity in commercial purity aluminum followed a roughly linear relationship with the hydrogen content. They found that in slowly cooled sand castings porosity will not form below hydrogen contents of 0.12 ml./100 g.Al. This threshold hydrogen content was three times higher than the solid solubility limit (0.04 ml./100 g.Al.).

In Deoras and Kondic's experimental work [55], commercial purity alloys, Al-7%Si, Al-6%Si and Al-12%Si, were also cast in a sand mold. They noted that the threshold hydrogen content in commercial purity aluminum was 0.11 ml./100 g.Al., which was approximately the same value as that found by Ransley and Neufeld. In Al-6%Si no porosity was found at 0.13 ml./100 g.Al. A linear relationship was obtained between hydrogen and volume percent porosity. Different solidification rates were obtained by varying the mold temperature, and they 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.

Thomas and Gruzleski [56] studied porosity in Al-8%Si solidified at two cooling rates with hydrogen contents in the range of 0.10-0.82 ml./100 g.Al. They showed that there was a linear relationship between the hydrogen content and level of porosity. The threshold hydrogen level was about 0.053 ml./100 g.Al. for a slow cooling rate. However, for samples solidified at the higher cooling rate, the threshold value was found to increase.

Iwahori et al.[36] have studied the occurrence of porosity in Na- and Sr-modified Al-Si alloys. Their results showed that the threshold value of modified alloy is slightly less than that of unmodified alloy. The linear relationship was again observed, but the amount of porosity increased faster with hydrogen in a modified than in an unmodified alloy.

Chen and Engler [57] have studied the relationship between hydrogen level and porosity for various types of Al-Si alloys, ranging from 0-12%Si. They found that the linear relationship of hydrogen level and porosity was also obtained in all alloys with different cooling rates. Fig. 2.4 shows their results for an AlSi7Mg alloy. It can be seen that porosity increases in all cases proportionally with increasing hydrogen content. The steepest slope corresponds to the slowest solidification, and the curve with the flattest slope to the fastest solidification. However, threshold hydrogen as affected by the cooling rate was not clearly observed in this study. Tynelius [53] has done an intensive study on the relationship between hydrogen content, solidification time and amount of porosity in A356 alloy. She also observed the threshold hydrogen level and found the value to increase as the solidification time decreased. The relationship between threshold hydrogen content and local solidification time is illustrated in Fig. 2.5. for untreated and modified A356 alloy. For modified alloy, the threshold hydrogen content is slightly less than that of untreated alloy. The threshold hydrogen level at the slowest solidification time (350 sec.) was found to be 0.04 and 0.03 ml./100 g.Al. for untreated and modified alloy respectively. These value are still higher than the solubility limit of hydrogen in solid which is about 0.02 ml./100 g.Al.



Figure 2.4 Porosity and hydrogen relationship at various cooling rates in AlSi7Mg (356) alloy [57].

It can be concluded at this point that a linear relationship between hydrogen and amount of porosity exists. A threshold hydrogen level for porosity formation is generally observed, and this is a function of local solidification time. The tendency for porosity formation is reduced with an increase in cooling rate, ie. time is an important variable in the process.

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Figure 2.5 Threshold hydrogen as a function of solidification time of untreated (----) and Modified (---) A356 alloy [53].

Untreated

Modified -

2.1.4 Modeling of Porosity Using A Mass Balance Approach.

A simple mass balance method can be applied to predict the amount of porosity from the experimental results as previously shown. At the end of solidification, ie. $f_1=0$, $f_s=1$, the amount of hydrogen in the pore can be expressed as $C_{HO}-C_{HS}$ where C_{HS} , is the maximum amount of hydrogen dissolved in the solid, ie. the threshold hydrogen content. Knowing C_{HO} and C_{HS} , C_{HP} can be obtained. Since the units of C_{HP} are cubic centimeters at standard temperature and pressure (273 K at 101325 Pa), they must be corrected from the pore formation temperature and pressure by applying a simple Gas Law calculation as:

$$V_{P} = C_{HP} \cdot \frac{P_{std}}{T_{std}} \cdot \frac{T_{P}}{P_{P}}$$
(2.12)

where

 V_P = volume of pore, ml./100 g.Al., P_{std} = standard gas pressure = 101325 Pa.,

- T_{sid} = standard gas temperature = 273 K,
- P_P = pressure of gas inside pore, Pa, and
- T_P = temperature of gas inside pore, K.

A reasonable value of T_P can be estimated as the eutectic temperature since most of the porosity is trapped at this stage. P_P could be estimated as the ambient pressure, P_s ; however, it was found that P_P must be adjusted in order to predict the amount of porosity correctly. For example, taking the results of Chen and Engler [57], P_P must be 1.3 MPa for the slow cooling rate, and must be increased to 3.5 MPa in order to match the result at the high cooling rate, as shown in Fig. 2.6. When this is done, the predictions agree fairly well with experimental results, indicating that a mass balance approach may be valid.



Figure 2.6 Experimental results [57] compared to the predicted values using a simple mass balance method. (---) represents experimental results for the melt at slow cooling rate, (---) represents that at fast cooling rate, (\blacksquare) represents predicted value at slow cooling rate and (\bigcirc) represents predicted value at fast cooling rate.

It can be seen that P_P is the major key to the success of this approach. The gas pressure inside the pore could be as high as 3.5 MPa if the pore radius is very small, ie. the surface energy term becomes dominant. This was verified experimentally by many researchers [53,57] who found that melts of high cooling rate tend to have smaller gas pore sizes. If one can calculate the gas pore size, then it should be possible to calculate the solidified sample density correctly.

The important step of this approach is to convert C_{HP} from a standard unit into an actual volume of gas at the point where the pore nucleates and grows. As can be seen from equation 2.12 the unknown parameters involved are V_P , T_P and P_P . However, it was shown that in order to predict the porosity correctly P_P must be changed and found to be a function of solidification time. Thus solidification time must be included in this calculation. Based on this observation, it appears that a simple model to predict the amount of porosity can be developed, providing that the relationship between V_P , T_P , P_P and solidification time is established.

A mass balance approach has been applied by many researchers [65-67]. Most of them have shown good agreement with experimental results; however, many have used some unrealistic parameters. Kubo and Pehlke [65] set C_{HL} , and C_{HS} in Al-4.5%Cu to 0.6 and 0.06 ml./100 g.Al., respectively. These values are 27 % higher than reported data [27]. Alam et al [56] reported C_{HL} and C_{HS} to be 0.0019 and 0.00019 ml./100 g.Al. in their A357 alloy. These values are too low in comparison to reported data for this alloy which are 0.37 and 0.02 ml./100 g.Al.[1]. These latter values will be utilized in this work.

2.2 Previous Work on The Reduced Pressure Test.

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The simple approach to making this technique fully quantitative would be to measure the amount of hydrogen dissolved in the melt, and to correlate this number to an easy to determine quantity such as the density or weight of the RPT sample. It will be seen in the following that this is a possibility if certain problems can be solved.

Two approaches have been taken to the hydrogen quantification from the sample density of the RPT. One is to calculate the hydrogen from the volume of pores as obtained from the sample density, and the other is to relate the sample density to the hydrogen level determined by an independent means.

2.2.1 Hydrogen Calculation from RPT Sample Density.

The idea of quantifying the gas content from the density of a solidified sample was originally described by Ohira and Kondic [58]. They measured the density of a wellfed atmospherically solidified test piece and related this density to the gas content of the melt. Their simple idea was to calculate the volume of the pores in the sample from its density. It was then assumed that these pores are all filled with hydrogen gas. Thus the volume of hydrogen equals the pore volume of the sample, and the hydrogen content can then be calculated by applying the Gas Laws and assuming that gas pressure is equal to pressure during solidification as shown below:

$$H_c = K \left[\frac{1}{D_a} - \frac{1}{D_{th}} \right]$$
(2.13)

where,

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 H_c = calculated hydrogen level, ml./100 g. Al.,

 $D_a = density of the sample, g./cc.,$

 D_{th} = theoretical density, g/cc.,

K is a gas law constant which corrects the hydrogen volume from the solidification temperature and pressure to standard temperature and pressure (STP). Thus:

$$K = \frac{T_1}{T_2} \times 100$$
 (2.14)

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where,

 $T_1 = 273 \text{ K},$

 T_2 = solidus temperature of the alloy, K.

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However, this test does not lend itself particularly well to the foundry floor because the density of the sample solidified under atmospheric pressure is not very sensitive to hydrogen level with the result that very high precision is required for the density measurement. In order to overcome this problem Rosenthal and Lipson [59] attempted to quantify gas content by the reduced pressure test sample. They showed that the reduced pressure solidification of a sample resulted in magnification of the effect of dissolved gas on the density of the test sample, and in this way reduced the accuracy requirement of the density measurement. The only change in the calculation of the hydrogen content is in the gas law constant, K, which must be modified to:

$$K = \frac{P_2}{P_1} \times \frac{T_1}{T_2} \times 100$$
 (2.15)

where,

 $P_1 = 101325 Pa$,

 P_2 = pressure in the test chamber during solidification, Pa.

Sulinski and Lipson [60] have pointed out that this simple calculation is unlikely to lead to a correct value for the hydrogen concentration since it assumes that:

i) no hydrogen is retained in solid solution in the alloy.

ii) all hydrogen originally present in the liquid forms pores in the solid and none is pumped out of the system during the test.

iii) the gas forms at the solidus temperature of the alloy and at a pressure equal to the chamber pressure.

iv) the theoretical density of the alloy is known accurately.

Among these assumptions, they suggested that only the second assumption would lead to significant errors. Since the test is conducted in a partial vacuum condition and the diffusion coefficient of hydrogen is very high, it is likely that hydrogen may be lost into the pumping system. The hydrogen which remains in the melt thus forms a smaller pore volume, and the hydrogen content calculated from the reduced pressure test should be less than the actual melt hydrogen.

In the same paper, Sulinski and Lipson [60] introduced a correction factor to correct the calculated hydrogen from the reduced pressure test, as it was observed that a simple Gas Law calculation yields hydrogen values much less than the actual hydrogen

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in the melt. This factor is obtained by solidifying similar samples from the same melt with the same hydrogen concentration at atmospheric pressure and under reduced pressure. The hydrogen concentrations are then calculated from the density, and the correction factor is determined as:

$$C.F. = \frac{\left[\begin{array}{c}H_{c}\right]_{A}}{\left[\begin{array}{c}H_{c}\end{array}\right]_{R}} \tag{2.16}$$

where,

C.F. = correction factor,

 $[H_c]_A$ = calculated hydrogen level from atmospheric pressure sample, ml./100 g.Al.,

 $[H_c]_R$ = calculated hydrogen level from reduced pressure sample, ml./100 g.Al.

It is important to note here that this correction factor is based on the assumption that the calculated hydrogen content from the sample solidified under atmospheric pressure yields an accurate value for the hydrogen in the melt.

An accurate $[H_c]_A$ will only be measured if the crucible is designed properly in such a way that volume shrinkage is well fed by liquid metal, so that porosity is formed solely by gas in the melt. This realization has led to the concept of a risered constant volume test. Sulinski and Lipson [60] developed a well-fed constant volume crucible, and with application of the C.F. to $[H_c]_R$, they found that their results were reproducible to within 0.002 ml./100 g.Al. However, the accuracy of their calculated hydrogen concentration was not checked by any independent means, and there is no way to determine if their values were, in fact, correct. It then became apparent that it was necessary to study the relationship of sample density to hydrogen level as measured by some independent means.

2.2.2 Density and Hydrogen Relationship.

Hess and his co-workers [61-62] were probably the first investigators who studied

the relationship between melt hydrogen measured by an independent means and the density of the RPT sample. Unfortunately, they found a lack of the correlation between the densities of the sample and the hydrogen content in the melt, which they attributed to inclusions.

Brondyke and Hess [61] compared several methods of measuring hydrogen in the melt including the reduced pressure test and the solid-extraction method. By comparing the amount of hydrogen determined by solid-extraction and the density of reduced pressure test samples in 2014 alloy, they found that there was no correlation between hydrogen content and the sample density. However, when filtration was applied, they found that the correlation was improved, as shown in Fig. 2.7. It was also demonstrated that there was less porosity in a cleaner melt. It is interesting to note here that this work was carried out at hydrogen levels between 0.3-0.7 ml./100 g. Al. These are very high values which are not representative of normal casting conditions.



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In 1989, Mulazimoglu, Handiak, and Gruzleski [62] studied the correlation between density and hydrogen level measured by the reliable modern technique which is the Telegas instrument. Their results, Fig. 2.8, show good correlation between density

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and hydrogen concentration in Sr-modified and unmodified A356 alloy. At the same time, they applied the quantification method as proposed by Rosenthal and Lipson [59], and found a reasonable agreement with the experimental results. However, these experiments were limited in that only a few samples were studied within a narrow range of hydrogen levels. Crucible design, and the effect of inclusions were not considered. No authors have considered the nature of the correction factor used in hydrogen level determination in any detail, despite the fact that it is the key factor in estimation of hydrogen concentration from density results.



Figure 2.8 The correlation between density and hydrogen concentration in untreated and Sr-modified A356 alloy [62].

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Recently, LaOrchan, Mulazimoglu and Gruzleski [63] studied the relationship between density and the hydrogen content over a wider range of hydrogen concentrations, 0.07-0.35 ml./100 g. Al., as well as the effect of various combinations of melt treatments (modification and grain refinement) in A356 and 413. They found a good correlation in all combinations of melt treatment in A356 as shown in Fig. 2.9. However, their data show a large scatter which may be due to differences in melt cleanliness and the influence of solidification shrinkage. When they attempted to correct the calculated hydrogen levels from sample density, they found that a constant correction factor did not apply over a wide range of hydrogen. Instead, they found that the correction factor is hydrogen level dependent according to C.F. = $5.5 \exp(-6[H_C]_R)$, as shown in Fig. 2.9. The nature of this phenomenon is not yet well understood.

At the same time, these authors showed that their simple method did not work for the short freezing range alloy, 413, due to lack of repeatability in sample density. In this alloy macroshrinkage is very significant in determining the sample appearance and density. This effect of macroshrinkage is clearly seen in the two reduced pressure samples of Fig. 2.10. These two samples were poured within a few minutes of each other from the same melt. Shell formation occurred over the top surface of the sample on the left side of the photograph resulting in a massive cavity. The sample on the right froze with an open surface for a longer time and contains dispersed porosity. Both samples have the same hydrogen concentration, but the densities are very different.

Obviously, the solidification pattern of the melt in the crucible is important to explain the phenomena occurring in this test. Since the standard non risered crucible used in this test had a very thin wall thickness, the heat flow which controls the solid/liquid interface location can dissipate in all directions and results in shell formation. All gas and shrinkage cavities are then trapped within the sample and large central shrinkage cavities occur. On other occasions, the sample surface may not freeze over first, and dispersed porosity can form throughout the entire body of the sample. LaOrchan, Mulazimoglu and Gruzleski [63] then suggested in their paper that a riser should be added to the RPT sample.





- a) untreated with constant correction factor,
- b) modified with constant correction factor,
- c) untreated with H_2 dependent correction factor,
- d) modified with H_2 dependent correction factor.



Figure 2.10 Appearance of sectioned RPT sample of 413 alloy.

Risering not only controls solidification shrinkage but also improves heat flow repeatability and eliminates shell formation over the top of the sample. Moreover, risering yields a constant volume sample which in turns allows the sample weight to be directly related to its density. This leads to a more convenient way to quantify the hydrogen. With the constant volume sample, it is not necessary to directly measure the density. The sample needs only to be weighed, and the pore volume can then be determined from a known equation.

It should be clear at this point that there is a real possibility to make the RPT fully quantitative. It has been shown to be possible in a long freezing range alloy, such as A356, but there is considerable scattering of the data. For short freezing range alloys, shrinkage and lack of repeatability of the solidification pattern may be improved by risering along with a proper mold design. This can be done by modifying the crucible to meet the following requirements:

- i) minimize the shrinkage problem to ensure that porosity is due solely to gas.
- ii) avoid shell formation and keep the free liquid surface exposed to the reduced pressure as long as possible in order to magnify the pore size, and to maintain feeding of the sample.

Quantification of the gas content from the reduced pressure sample density is possible provided three important pieces of information are present;

- i) the hydrogen loss into the system,
- ii) the effect of inclusions on the density-hydrogen content correlation of the test,
- iii) accurate value of $[H_c]_A$ in which shrinkage does not play a role.

2.3 Objectives.

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In summary, it is possible to lay out the objectives of this research as follows,

- to develop a truly quantitative reduced pressure test to measure melt hydrogen in a variety of aluminum casting alloys.
- ii) to design a constant volume sample for this reduced pressure test which will be inexpensive and which will allow the test to be used on both short and long freezing range alloys.
- iii) to determine the effect of melt cleanliness on the response of the reduced pressure test.
- iv) to develop the mathematical relationships between sample density and true melt hydrogen.

v) to explore the fundamental nature of the above relationships.

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vi) to develop operating procedures for use of this quantitative reduced pressure test.

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Chapter 3 Materials and Experimental Procedures

As mentioned earlier a quantitative RPT should employ a risered constant volume sample in order to compensate for shrinkage effects and improve heat flow repeatability. Therefore the first phase of the project involved the design of a suitable constant volume sample. The materials, equipment and experimental procedures related to the testing of this constant volume sample will be discussed in this chapter.

3.1 Alloys and Melt Treatment Procedures.

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The materials selected for study in this work were 356, 357, 319 and 413 alloys. These are alloys which are widely used in the North American foundry industry. Their compositions as obtained from spectrometer analysis, and some of their typical applications are shown in Table 3.1. To perform an experiment about 10 kg. of alloy was melted in a silicon carbide crucible in an electric resistance furnace. Various hydrogen levels were obtained by degassing and regassing. The melt was degassed below 0.1 ml./100 g.Al. by bubbling prepurified nitrogen gas into the melt using a perforated graphite tube. Regassing was carried out by slowly inserting moistened paper into the melt.

Alioys		J	Elements, v	vt.%	Typical applications		
	Si	Cu	Fe	Mg	Zn		
319	5.96	3.3	0.21	0.01	0.07	engine parts, oil tanks	
356	7.31	0.07	0.22	0.42	< 0.02	flywheel castings, airframe castings	
357	7.02	0.035	0.066	0.51	0.03	pressure-tight applications	
413	11.90	0.02	1.13	0.03	0.05	marine and food equipment applications	

Table 3.1 Chemical composition of the alloys used and some typical applications.

There are two melt treatment processes that are widely applied in order to improve the mechanical properties of cast Al-Si alloys; namely, modification and grain refinement. Through the modification process, the acicular silicon can be transformed to a fibrous shape resulting in noticeable improvement in elongation and strength [64]. Grain refinement is employed in order to reduce the grain size which is believed to improve the mechanical properties [65]. Since these two processes are widely used, it was deemed necessary to study the effect of these two parameters on the RPT. In order to study such effects, the melt was modified and grain refined using the following procedures.

To modify the silicon phase, 90% Sr-10% Al master alloy was added to obtain 0.02 wt.pct. retained Sr for 319, 356, and 357 alloys; and 0.05 wt.pct. Sr for the 413 alloy. The melt was held for at least 30 minutes to allow complete dissolution of the master alloy.

Grain refinement was obtained using commercial alloy 5Ti-1B-Al. The master alloys were added before degassing, and the amount of titanium was targeted at 0.1 wt.pct. in the melt which is the composition at which the grain refiner is reported to yield optimum performance [66].

3.2 Hydrogen Measurement.

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Hydrogen levels in the melt were measured by a recirculating gas technique whose reliability has already been established [16-23]. Two types of hydrogen measurement units were employed in this work, namely TELEGASTM and A/SCANTM. The TELEGASTM instrument, developed by ALCOA, was used in conjunction with newly developed A/SCANTM probes. This method had been shown in an independent study [67] to yield accurate results, and has the advantage that the probe life is longer than that of the ceramic probe of the TELEGASTM instrument. The A/SCANTM instrument, developed by ALCOA, used in this work was model F which is designed for the measurement of hydrogen in aluminum foundry alloys.

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The reason behind the employment of these two hydrogen measurement units is related to the probe being used. As the number of measurements increases, particles tend to clog the probe and lower hydrogen measurement results. The effects of a clogged probe on measured hydrogen are clearly shown in Fig. 3.1. Hydrogen readings as a function of measuring time were taken from the same probe in a melt of nearly the same hydrogen level. A probe at a second measurement gave a hydrogen level of 0.151 ml./100 g.Al. However, after the twelveth measurement, the hydrogen measured was 53% less. After the fifteenth measurement the probe failed completely resulting in an unreasonably low hydrogen level. When the probe was replaced the measured hydrogen was 0.147 ml./100 g.Al. which is almost the same level as that obtained from the previous probe at the second measurement. This is the most common scenario found with this type of probe.



Figure 3.1 Typical reading profile of Alscan probe. The probe at the second reading is in good condition, whereas at the twelveth reading the probe is clogged. At the 15^{th} reading, the probe failed completely.

It can be shown mathematically that the characteristics of the probe change as the number of measurements increases. In this technique, hydrogen in the melt diffuses through the ceramic probe into the carrier gas as shown in the schematic of Fig. 3.2. Hydrogen dissolved in the melt diffuses to the measuring system via a probe of a distance

"L". The concentration of hydrogen at the melt-probe interface can be assumed constant at all times since the probe is stirred in the melt. The hydrogen diffused into the measuring system increases as a function of time until it is in equilibrium with hydrogen dissolved in the melt. Based on this unsteady state mass transfer, the concentration of hydrogen diffused into the system as a function of time can be calculated as;

$$C^{t} = C^{\infty} + (C^{0} - C^{\infty}) \operatorname{erf}\left(\frac{L}{2\sqrt{Dt}}\right)$$
(3.1)

where

 C^{t} = concentration of hydrogen at time = t, mol.,

 C^{α} = concentration of hydrogen at time = α , mol.,

 C^0 = concentration of hydrogen at time = 0, mol.,

L = diffusion path, cm.,

t = time, s.

 $D = diffusivity of hydrogen in the probe, cm.^2/s.$

Based on this equation and coupled with the raw data of measured hydrogen level versus time, a non-linear regression analysis can be performed in order to determine the diffusion path, L, of hydrogen into the measuring system. Calculated diffusion paths as obtained from the data given in Fig. 3.2. are 0.51 cm. and 16.33 cm. for the probe at the second and tenth measurement respectively. It is clear that the diffusion path of the probe at the tenth measurement is 3000 % higher than at the second measurement. Since, in reality, the dimensions of the probe do not change, the increase in diffusion path in this case represents the difficulty of diffusion of hydrogen into the measuring system, ie. a clogged probe.

The two hydrogen measurement units were used to check each other. Of two simultaneous readings, the highest value was always selected. In the case that the difference of the readings was more than 0.04 ml./100 g.Al., the probe that gave the lower value was replaced. Each probe was used for not more than 10 readings nor not more than four insertions into the melt, whichever came first.



Figure 3.2 Schematic diagram of the gas recirculation technique.

Table 3.2 Typical readings compared to the standard readings as obtained from the calibration process.

% H ₂ in the standard gas mixtures	Readings obtained from the instrument	Standard readings	% error
0.5%	21.0		
	21.5		
	22.0		
	avg. = 21.5	22.0	2.27
2.0%	77.0		
	78.0		
	78.5		
	avg. = 77.8	81.0	3.91
4.0%	35.5		
	35.5		
	36.0		{
	avg. = 35.7	37.0	3.51



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The instruments were calibrated every two months against standard samples of pure dry nitrogen containing certified percentages of hydrogen in order to insure the accuracy of the measurement. Three measurements were taken with each of the three standard gas mixtures which are 0.5%, 2.0% and 4.0% hydrogen. The readings were always found to be within $\pm 5\%$ of the standard readings. Table 3.2 summarizes typical readings obtained from the calibration process compared to the standard readings.



Figure 3.3 A schematic diagram of the reduced pressure test apparatus.

3.3 Density Measurement.

The apparent density of the RPT samples was measured by the Archimedes principle of weighing the sample in air and water. Once the mass of the sample measured in air and water was known, the apparent density was calculated by applying the equation: Apparent Density = $\frac{Mass \text{ in air}}{Mass \text{ in air } - Mass \text{ in water}} \times Density \text{ of water}$ (3.2)

The density of water, at the measuring temperature, was taken from published values [68]. For all in-water measurements, a minor amount of Teepol 610^T was added to a distilled water bath to reduce the surface tension between the sample surface and water.

To ensure accurate measurement, the apparatus was tested by evaluating the density of cold rolled pure aluminum and comparing the result with the known value [68]. It was found that the measured density agreed to within ± 1 % of the published value, as summarized in Table 3.3.

3.4 Reduced Pressure Test.

The reduced pressure test system used in this research, like other systems widely used on the foundry floor, consisted of a vacuum pump, a reduced pressure chamber, crucible, pressure gauge, timer, and a valve to adjust the pressure. A schematic of the reduced pressure test system is shown in Fig. 3.3. The chamber pressure used in most of the experiments was 8.41 kPa.(27.5 in. of Hg).

Immediately after the hydrogen concentration was measured by the TELEGASTM or AlSCANTM, about 0.3 kg. of the metal from the melt was poured into a preheated crucible in the reduced pressure chamber. The sample in the chamber was allowed to solidify for about 360 seconds at the test pressure, and the sample density was then determined by the Archimedes principle as previously described.

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Sample No.	Measured density of cold rolled pure aluminum, g./cc.	serror from published value (2.70 g./cc.)
	2.68	
1	2.68	
1	2.69	
	2.69	
	2.70	
-	avg. = 2.69	0.44
	2.68	
÷.	2.69	
2	2.69	
	2.70	
	2.70	
	avg. = 2.69	0.44

Table 3.3 The comparison between measured density of cold rolled pure aluminum with the published value.

3.5 Inclusion Experiments.

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It has already been mentioned that inclusions are an important factor promoting pore formation. A sample containing a high number of inclusions tends to yield more porosity than a sample of lower inclusion content, and hence has a lower density. In order to study the effects of the amount of inclusions on the sample density, two experimental procedures were carried out in this work. The first procedure was to add inclusions to the melt, while the second was to remove inclusions from the melt.

Inclusions were added to the melt by many processes. These included blowing the melt with moist air and alumina powder, adding secondary (scrap) alloy, and stirring the melt with a graphite tube.

In order to remove inclusions from the melt, two processes was carried out. For the first, the melt was purged by high purity chlorine gas via a perforated graphite tube.

This technique has been recommended by many researchers [69-70] to be very effective in inclusion removal.

Another attempt to remove inclusions was made using the apparatus as shown in Fig. 3.4. The principle of this apparatus was to remove inclusion by filtration. The apparatus was designed to sit on top of the RPT chamber pressure. The reservoir (7) made from insulating material serves to hold the melt prior to the filtering process. Once a desired amount of liquid metal is poured into the reservoir, and the vacuum pump turned on, liquid metal is sucked through the foam filter (6) into the mold (3) located in the vacuum chamber. Unfortunately, it was found that the samples obtained by this technique contained more porosity than those obtained by the normal procedure, as shown in Fig. 3.5. It is believed that the holes in the foam filter break the liquid metal flow into small streams of liquid, thus increasing the surface to volume ratio. This increase in the melt surface enhances the possibility of oxidation at the surface, hence increasing the number of alumina inclusions. Moreover, melt flow rate through the filter is relatively fast which in turns reduces the efficiency of the filter [71]. Inclusion removal by this technique was found to be inadequate and the approach was abandoned.

3.6 Thermal Analysis.

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Thermal analysis was carried out in order to record temperature and solidification time in the melt. The results were used to determine the solidification time of the RPT sample. The data obtained was also coupled with the mathematical model to calculate the temperature profile within the melt. The temperature recordings were done with a precision temperature computer board. Commercial data acquisition software was used to process the data. The sampling was performed in a low noise mode with the temperature reading averaged over 0.017 ms. throughout the complete solidification process. The thermocouples used were type K of 8.5×10^4 m. diameter, and the thermocouple accuracy was estimated by the manufacturer to be ± 1.1 K.
MATERIALS AND EXPERIMENTAL PROCEDURES



Figure 3.4 Filtering unit as applied on top of the RPT chamber.



Figure 3.5 The amount of porosity in filtered sample (right) compared to that in a nonfiltered sample (left).

3.7 Plant Tests.

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Plant tests were carried out in order to assess the ability of the newly designed mold and riser to measure the melt hydrogen concentration under real operating conditions. For hydrogen measurement, the AlSCAN[¬] model F was used to obtain the hydrogen level prior to the RPT sampling process. A brand new probe was always used in order to assure the accuracy of the reading. The RPT sampling process was carried out immediately after the hydrogen content in the melt has been measured by AlSCAN[¬]. The sampling procedure was similar to that described previously in section 3.5.

The plants selected for this work were;

- 1. Shellcast Foundries Inc.
 - 10645 Lamoureux Ave.

Montreal, PQ. H1G 5L4

2. Robert Mitchell Inc.

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Montreal, PQ. H4L 3K5

- 3. Grenville Castings Ltd.
 - Merrickville, ONT KOG 1N0

These foundries were chosen as they cast a variety of aluminum alloys using different techniques, ie. sand casting, investment casting, etc.

Chapter 4. Mold and Riser Design

This chapter deals with designing of the mold and riser for a constant volume sample. The important design criteria and the outcome will be presented first. After the design work was completed, an extensive testing program was carried out in order to evaluate the test parameters for sensitivity and repeatability. These include chamber pressure, chamber temperature, pouring temperature, and mold temperature. All of these results will be discussed in this chapter.

4.1 Mold and Riser Design.

4.1.1 Mold Design.

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Mold and riser design were aimed at maintaining the advantage features of this test (ie. fast, simple and inexpensive) with the addition of good sensitivity and accuracy for the RPT. The criteria used to fulfill such requirements were as follows:

- i) The mold must be reusable in order to keep the test inexpensive. A permanent steel mold was selected in this case.
- For simplicity, the shape of the permanent mold should allow easy removal of the sample. For this purpose, a V-shape mold was chosen.
- iii) For speed, the size of the specimen should be small enough to solidify in an appropriate time without sacrificing the test sensitivity.
- iv) If the speed is not important, the test sensitivity can be improved by using a mold that yields a longer solidification time, ie. larger pores. The solidification time can be controlled by adjusting the mold wall thickness and the size of the mold.
 Once a steel mold had been selected for this test, the next parameter considered

was the shape of the mold. A V-shape was selected since it provides test simplicity and also enhances the feeding due to its ability to promote a directional solidification pattern. It was found that a narrowed bottom V-shape mold provides less porosity than does a wide bottom V-shape mold as shown in Fig. 4.1. This is due to a difference in solidification time. The melt in a narrowed bottom V-shape mold solidifies faster than the melt in a wide bottom V-shape mold with the result that the test is less sensitive in the narrowed bottom V-shape mold. The effect of the sample shape on the sensitivity of the RPT is clearly shown in Fig. 4.2. In order to differentiate the hydrogen level from 0.1 to 0.15 ml./100 g.Al., the density difference in a wide bottom mold is 0.04 g./cc. compared to 0.02 g./cc. for a narrowed bottom mold, ie. there is a 50% difference.



Figure 4.1 Porosity as obtained from wide bottom V-shape mold (right) and narrow bottom V-shape mold (left).

As a speed criterion, a solidification time of about 5 min. was selected in this work for two reasons. The first is that the overall time for the test should be roughly about 10 min. which is comparable to that of a leading hydrogen measurement technique, ie. AISCAN. Secondly the test should yield a reasonable sensitivity. It was shown by



previous work [63] that the sensitivity of the test sample solidified in 5 min. is about ± 0.05 ml./100 g.Al.

Figure 4.2 The effect of mold shape on the RPT sensitivity. (\Box) represents the density and hydrogen relationship of a wide bottom V-shape mold, whereas (\blacktriangle) represents that of narrow bottom V-shape mold.



Unit : cm.



The size of the mold previously used [63] provided a basis for designing of the mold in this work. A short and wide bottom V-shape mold of about 82 ml. in volume, which requires a solidification time of about 5 min., was chosen, as shown in Fig.4.3. In order to optimize the test sensitivity, the wall thickness of the steel permanent mold was kept to a minimum to reduce the cooling rate, ie. to promote a large pore size, and yet to be strong enough to withstand thermal deformation. A wall thickness of 0.6 mm. was determined to be optimum.

4.1.2 Riser Design.

The design proposed by Sulinski and Lipson [60] and Church and Herrick [72] provided a basis for our approach to use a riser to concentrate all solidification shrinkage. The final design (Fig. 4.4) consists of a removable and disposable riser mold fabricated from CO_2 -bonded silica sand. Some important design criteria used were as follows:



Figure 4.4 Riser and permanent steel mold parts of the constant volume risered mold for the RPT.

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- i) Minimize the shrinkage level to ensure that porosity is due solely to hydrogen gas.
- Avoid solid shell formation to keep the free surface liquid exposed to the reduced pressure as long as possible in order to magnify the porosity.

To avoid volumetric shrinkage in the specimen, feeding during the solidification of the sample should be provided by choosing a proper size of a riser. A riser size of 6 cm. diameter by 3 cm. high, fabricated from silica sand (135 mesh size) and sodium silicate binder (5%), was selected.



Figure 4.5 The solidification pattern of aluminum in the mold and riser. The hottest spot is always located in the middle of sand riser which ensures the feeding and repeatable solidification pattern.

The solidification pattern of the melt in the mold at various solidification times can be seen in Fig. 4.5. The temperature profile at a particular solidification time is obtained from numerical solution of heat transfer governed by the equation:

$$\rho C \frac{\partial T}{\partial t} = k(\nabla^2 T) \tag{4.1}$$

where

 ρ = density of the alloy, kg./m³,

C = specific heat of the alloy, J/kg.K,

T = temperature, K.,

t = time, s.,

k = thermal conductivity of the alloy, W/m.K.

The boundary condition applied in this calculation was obtained from experimental thermal analysis, ie. by determining known temperatures. The cooling curve obtained by calculation agreed well with the cooling curve obtained experimentally, as shown in Fig. 4.6. It is clearly seen that the solidification pattern in the mold maintains its V-shape until the end of solidification. This ensures fluid feeding to the mold, and elimination of volumetric shrinkage. The pattern also confirms that the riser will act as a hot spot which in turn improves heat flow repeatability and eliminates solid shell formation over the top of the sample. The effect of a riser on elimination shrinkage can be clearly seen in Fig. 4.7.

It was found that the same riser (6 cm. in diameter and 3 cm. height) provides adequate feeding for all alloys. However, for a given riser size, the dimensions of the neck were found to be a critical parameter which affected the sensitivity of the test. A sample with a large riser neck contained less porosity than one with a smaller riser neck as seen in Fig. 4.8. The reason for this is that a large riser neck may provide a generous path for gas escape from the melt and allow too much feeding which may suppress the nucleation and growth of the pores. .e =



Figure 4.6 The cooling curve obtained from the calculation (---) compared to that from the experimental results(------).



Figure 4.7 RPT sample obtained from the newly designed mold showing the elimination of macroshrinkage.

MOLD AND RISER DESIGN

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In order to determine the optimum riser neck size, several RPT samples having different neck diameters from 3 cm. to 1.25 cm. were cast from melts of 319, 356, and 413 alloys. These samples were cut and polished to examine the shrinkage distribution. Figs. 4.9 and 4.10 show the polished samples with varying neck size for 356 and 413 alloys, respectively. It was observed that a minimum neck diameter of about 1.75 cm. is necessary for 413 (short freezing range alloy) to produce a shrinkage free specimen (Fig. 4.10, sample B).

A much smaller neck size (Fig. 4.9, sample A) is, however, required for long freezing range alloys such as 319, and 356. This difference in neck size is probably due to the difference in solidification characteristics of short freezing and long freezing range alloys. Short freezing range alloys such as eutectic alloys are shell freezing alloys in which feeding of the shrinkage is mainly through a central channel. A generous riser neck is therefore essential to provide enough liquid to feed this concentrated shrinkage in the specimen portion of the RPT samples. On the other hand, long freezing range

MOLD AND RISER DESIGN



Figure 4.9 Effect of riser neck size on the porosity and shrinkage distribution in samples of 356 alloy. The neck diameters of the samples from right to left are 1.25, 1.75, 2.75 and 3 cm.



Figure 4.10 Effect of riser neck size on the porosity and shrinkage distribution in samples of 413 alloy. The neck diameters of the samples from right to left are 1.25, 1.75, 2.75 and 3 cm.

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alloys have a mushy mode of solidification, and much of the feeding at the neck is by mass feeding which occurs continuously at the neck until the end of solidification in the mold. The final design of the sand riser is shown in Fig. 4.11.

*1 Neck Size for 356 and 319 Alloys *2 Neck Size for 413 Alloy 7.5 6.0 1.75^{2} 1.25^{1} 5.5



Figure 4.11 Dimensions of sand riser.

The next important step was to test if the designed mold and riser were able to yield a good relationship between sample density or sample weight and the hydrogen level in a variety of commonly used alloys. It will be shown in the following chapter that this mold and riser design is workable even with 413 alloy.

One drawback of the sand riser is that it is not reusable, and some effort was made to design a more permanent riser system. The material selected was Fiberfrax Duraboard made from alumina-silica fibers and binders. This material was chosen because of its insulating properties and high strength. The insulation delays solidification time in the sample which will enhance the porosity formation process, hence improving the test sensitivity. The important advantage of using this high strength insulator is that it can be used as a semi-permanent riser. It was found that a riser made from this material can be reused at least 20 times.

The final design of this riser is shown in Figure 4.12. The riser is smaller than the sand riser, but yields a solidification time two minutes longer than the sand riser. Although, this slows down the testing process, an advantage of this riser is that the same neck size was applicable for both 356 and 413 alloys.



Figure 4.12 Dimensions of Fiberfrax Duraboard riser.

With the Fiberfrax riser the test sensitivity in both 356 and 413 was slightly improved as shown in Fig. 4.13. However, the reproducibility of the test using the Fiberfrax riser was poor. At a particular hydrogen level, 0.155 ml./100 g. Al., the deviation of density of the Fiberfrax riser sample was relatively high (0.08 g./cc.) whereas the deviation of the sand riser sample was less than 0.05 g./cc. Using these values to predict the hydrogen level, the deviation of the Fiberfrax riser sample leads to an error of ± 0.075 ml./100 g. Al. whereas that of the sand riser sample is only ± 0.05 ml./100 g. Al. It was therefore decided to conduct all further experimental work with the sand riser.

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Figure 4.13 The effect of fiberfrax $[\Box]$ and sand $[\blacksquare]$ riser on the test sensitivity and reproducibility.

4.2 Constant Volume Sample.

A major objective of this work was to design a mold that yields a constant volume sample in order to simplify the test procedure. That is, with a constant volume sample, the user need not measure the density of the sample. Only the weight is required, and this can be related to a simple hydrogen level equation.

In order to determine that the mold in fact yields a constant volume, the following procedures were undertaken. Several samples were taken at different hydrogen levels. The density of the samples was measured, and this used to calculated the sample volume. The density, weight, and volumes of 356 alloy samples drawn from various hydrogen levels are summarized in Table 4.1

It is clearly shown that this mold yields an accepted constant volume with a standard deviation of only ± 0.29 ml. Similar results were also obtained from 319, 357 and 413 alloys with standard deviations of ± 0.53 , ± 0.36 , and ± 0.27 ml. respectively.

Sample weight, g.	Density, g./cc.	Hydrogen level, cc./100 g.Al.	Volume, cc.
217.83	2.662	0.110	81.840
213.88	2.603	0.170	82.180
214.1	2.611	0.170	81.990
204.42	2.463	0.240	83.010
203.95	2.468	0.240	82.650
213.11	2.583	0.190	82.520
213.29	2.592	0.190	82.290
217.81	2.674	0.070	81.450
218.25	2.673	0.070	81.640
216.01	2.632	0.130	82.070
216.17	2.636	0.130	82.020
213.81	2.584	0.190	82.750
212.15	2.584	0.190	82.100
215.67	2.617	0.150	82.400
214.77	2.624	0.150	81.860
218.89	2.660	0.083	82.289
217.88	2.670	0.083	81.603
212.26	2.587	0.132	82.050
211.74	2.567	0.132	82.500
209.15	2.546	0.271	82.140
208.53	2.538	0.271	82.170
206.2	2.496	0.233	82,610
219.24	2.658	0.097	82.481
218.44	2.638	0.097	82.790
218.17	2.640	0.122	82.650
217.88	2.641	0.122	82.502
209.51	2.551	0.191	82.140
205.58	2.502	0.191	82.170
		Average volume, cc.	82.277
		Standard deviation, cc.	±0.287

Table 4.1 Reproducibility of sample volume in 356 alloy.

Based on this constant volume, it can be seen from Fig. 4.14 that the sample weight is directly related to the sample density, and hence the hydrogen level, and the simplicity of the test is clearly demonstrated.



Figure 4.14 The relationship of sample weight and density.

4.3 Parameters Affecting Test Sensitivity and Reproducibility.

There are three important parameters that could affect the test sensitivity and reproducibility. They are cooling rate, pressure acting on the melt and inclusions. Cooling rate is generally known to be a parameter that affects porosity size [53,57], and hence the sample density. The parameters related to the cooling rate could be the temperature of pouring, the mold temperature, and the chamber temperature. Higher pouring temperature results in longer solidification time. This is also true for mold and chamber temperature. During solidification which take places in a partial vacuum, gas phase convection may not have a significant effect on extracting heat out of the mold. On the other hand, radiation may have a significant effect since the rate of extracting heat

out of the system is proportional to the temperature to the fourth power.

In order to stabilize in the melt, porosity must have an internal pressure equal to or greater than the pressure acting on the melt, P_{ex} . The smaller P_{ex} , the easier bubbles can form.

The effect of inclusions was clearly demonstrated in a previous chapter to have a significant effect on porosity formation. This topic will also be discussed in detail in the following sections.

4.3.1 Pouring Temperature.

This experiment was conducted on alloy 413 at a hydrogen level of 0.2 ml./100 g.Al. A difference of ± 25 K from 973 K was selected since this is a normal temperature range found on the foundry floor. The mean density of the samples poured at 948 K, 973 K, and 998 K was 2.56, 2.57, and 2.56 g./cc., respectively. The difference is less than 1% which leads to an error of only ± 0.001 ml./100 g.Al. This is probably because the cooling rate at an early stage is very fast especially when the melt is in contact with the mold. The temperatures of the melt under such conditions may drop down to the same level at almost the same time.

This is also true for a long freezing range alloy such as 356. In this case, the pouring temperatures were 973, 998, and 1023 K, and the mean densities of the samples were nearly the same at 2.55, 2.54, 2.54 g./cc., respectively, as shown in Fig. 4.15. The deviation of the sample density leads to an error of only ± 0.001 ml./100 g.Al. It can be concluded therefore that pouring temperature does not have any significant effect on the sensitivity of the test.

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Figure 4.15 The effect of pouring temperature on the reproducibility of the RPT sample density. a) in 356 alloy and b) in 413 alloy.

4.3.2 Mold Temperature.

For the experiment on the effect of mold temperature, one mold was preheated on the top of a furnace for 1 min. to bring the mold temperature to about 373 K while another was left at room temperature. The mean densities obtained from the hot mold, and the cold mold in 356 alloy were equal at 2.53 g./cc. In 413 alloy, the mean densities were 2.53 and 2.54 g./cc. for the hot and cold mold respectively, which is not a significant difference when using these values to predict the hydrogen level. The error obtained from the density deviation is only ± 0.001 ml./100 g.Al. Since the mold is so thin, a cold mold may absorb heat from the melt and reach the same temperature as a hot mold in a very short period of time. The effects of mold temperature on sample densities are shown in Fig. 4.16.

4.3.3 Chamber Temperature.

The chamber temperature was measured at the center of the chamber prior to pouring. As the temperature in the chamber increased from 308-358 K, it was found that there was no significant change in the sample density. In a 356 alloy with a hydrogen level of 0.131 ml./100 g.Al., the variation in sample density was only ± 0.01 g./cc. In 413 alloy the sample density varied by only ± 0.01 g./cc. These results are shown in Fig. 4.17. The deviation of the sample density leads to an error of ± 0.005 for both alloys. This indicates that the effect of radiation is not important in the reduced pressure chamber.

4.3.4 Chamber Pressure.

In order to study the effect of this parameter, the following procedure was used. RPT samples from four to five different hydrogen levels were drawn. At each hydrogen

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Figure 4.16 The effect of mold temperature on the reproducibility of the RPT sample density. a) in 356 alloy and b) in 413 alloy.

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Figure 4.17 The effect of chamber temperature on the reproducibility of the RPT sample density a) in 356 alloy and b) in 413 alloy.



Figure 4.18 The effect of chamber pressure on the sensitivity of the RPT in 356 alloy.

level, the sample was solidified under three different chamber pressures, 21.99, 8.41 and 1.72 kPr (0.217, 0.083, and 0.017 atm.), and the relationship between sample density and hydrogen level t different chamber pressures was established.

For 356 alloy, Fig. 4.18, it is clearly shown that the chamber pressure has a strong effect on the test sensitivity. As the chamber pressure decreases, the slope of the density vs. hydrogen curve increases. This results in a larger difference between the sample density at the low and high ends of the hydrogen scale. At a chamber pressure of 1.72 kPa., the largest difference in sample density is about 0.3 g./cc. while it is only 0.1 g./cc. for a sample solidified at 21.99 kPa. Thus it is much easier to detect the hydrogen level in a sample solidified at lower chamber pressure than at high chamber pressures.

However, the reproducibility of the test at low chamber pressure is not as promising as is its effect on the test sensitivity. At a particular hydrogen level, the standard deviation of density of a sample drawn at 1.72 kPa is relatively high, about ± 0.034 g./cc., whereas the deviation at 21.99 kPa. is only ± 0.008 g./cc., Fig. 4.19.

If these experimental data are used to predict the hydrogen level, such deviations of the sample density can lead to an error of ± 0.15 , ± 0.05 and ± 0.03 ml./100 g.Al. for samples solidified at 1.72, 8.41 and 21.99 kPa respectively. The chamber pressure at 8.41 kPa was determined to yield the optimum sensitivity and reproducibility.

Similar results were also found in the short freezing range alloy, 413. The sensitivity of the test increases as the chamber pressure decreases. The largest difference in the sample density is about 0.1 g./cc. at 1.72 kPa while the smallest difference in the sample density obtained at 21.99 kPa is only 0.03 g./cc., as shown in Fig. 4.20.

The effect of chamber pressure on the reproducibility of the test in 413 alloy can be seen in Fig. 4.21. It is clear that the deviation of the density increases significantly as the chamber pressure decreases. The standard deviations of the density are ± 0.028 , ± 0.013 , and ± 0.008 g./cc. for samples solidified at 1.72, 8.41 and 21.99 kPa respectively. If these density and hydrogen relationship are used to predict the hydrogen level in the melt, the deviation of the density as shown in Fig. 4.20 could lead to errors of roughly ± 0.1 , ± 0.05 , and ± 0.03 ml./100 g.Al. respectively.



Figure 4.19 The effect of the chamber pressures on the reproducibility of the RPT in 356 alloy.

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Figure 4.20 The effect of chamber pressure on the sensitivity of the RPT in 413 alloy.



Figure 4.21 The effect of chamber pressure on the reproducibility of the RPT in 413 alloy.

It is also clearly shown in Fig.4.19 and 4.21 that as the chamber pressure increases, the mean density of the sample drawn at a particular chamber pressure also increases. For example, in 356 alloy (Fig. 4.19), the mean density of the sample increases from 2.45 to 2.56 as the chamber pressure increases from 1.72 to 21.99 kPa. It is therefore important to control the chamber pressure at a constant level in order to avoid a reproducibility problem. For a selected chamber pressure of 8.41 kPa, the chamber pressure should be kept constant within ± 1.72 kPa in order to keep the deviation of the sample density to within ± 0.03 g./cc.

Since the chamber pressure exerts a strong effect on the reproducibility of the test, pressure measurement must be taken care of very carefully. A pressure gauge that is very sensitive to atmospheric pressure, i.e. mechanical pressure gauges, must be checked against the atmospheric pressure before the gauge is applied. This is because atmospheric pressure is subject to change every day. The most suitable pressure gauge for this test should be the pressure gauge that gives absolute pressure, i.e. the McLeod gauge.

4.4 The Effect of Melt Cleanliness.

Since, as discussed previously, the RPT is sensitive to the amount of inclusions in the melt, this work was extended to study the effect of melt cleanliness on the relationship between the RPT sample density and the hydrogen content. The tests which were carried out in 356 and 413 alloy, will be discussed separately.

4.4.1 356 Alloy.

The objective of this test was to study the density-hydrogen relationship as affected by three levels of melt cleanliness; normal, dirty and clean. A clean melt was prepared by purging a chlorine-based gas into the melt, while dirtied melt was prepared by the process discussed in Chapter Three. The effect of the three levels of melt



cleanliness on the density-hydrogen relationship is shown in Fig. 4.22.

Figure 4.21 The effect of melt cleanliness on the sensitivity of the density-hydrogen curve of 356 alloy.

It must be mentioned here that it is a difficult task to control the amount of inclusions right after melt cleansing since the oxidation can take place during a natural regassing process. Moreover, during the hydrogen measurement process, the probe must be stirred which in turn introduces inclusions into the melt very easily. As a result, it can be seen that the density and hydrogen relationship of the clean melt does not show a significant change from the normal one. The density-hydrogen curve of the clean melt is a bit flatter than that of the normal. On the other hand, the dirtied melt tends to have a steeper density-hydrogen curve than the normal melt. The slopes of the density-hydrogen curves are -0.921, -1.131, and 1.561 g.cc.⁻¹/ml.(100 g.Al)⁻¹ for clean, normal and dirtied melts, respectively. An increase in the amount of inclusions tends to increase the RPT sensitivity because more inclusions provide easier pore formation.

4.4.2 413 Alloy.

Since there was little difference between clean and normal melts for the 356 alloy, only two levels of melt cleanliness, i.e. normal and dirty melt, were studied in the 413 alloy. The effect of melt cleanliness on the density-hydrogen level relationship is shown in Fig. 4.23. The results from this alloy were similar to those observed in the 356 alloy. A dirtied melt produces a somewhat steeper density-hydrogen curve than that of the normal. The slopes of the density-hydrogen curves were found to be -0.987 and -1.326 g.cc.⁻¹/ml.(100 g.Al)⁻¹ for normal and dirty melts, respectively. Again an increase in the amount of inclusions results in an increase in the sensitivity of the density-hydrogen curves.



Figure 4.23 The effect of melt cleanliness on the sensitivity of density-hydrogen curve in 413 alloy.

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Chapter 5 Quantitative Reduced Pressure Test.

At this stage of the work it was deemed important to test if the designed mold and riser could yield a good relationship between sample density or weight and the hydrogen level in a variety of commonly used alloys. The mold and riser were tested for the four alloys some of which were long and some of which were short freezing range alloys. The results will be discussed in these two groups.

5.1 The Density-Hydrogen and Weight-Hydrogen Relationship.

5.1.1 Long Freezing Range Alloys.

5.1.1.1 319 Alloy.

Figs. 5.1 and 5.2 present the density-hydrogen and weight-hydrogen results for 319 alloy. Of note is the good linear relationship between density, weight and true hydrogen for hydrogen concentrations varying from 0.07-0.28 ml./100 g.Al. The empirically derived relations of density-hydrogen and weight-hydrogen are:

$$D_a = A \times H_2 + B \tag{5.1}$$

and

$$W_a = A \times K_2 + B \tag{5.2}$$

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where

 H_2 = dissolved hydrogen concentration, ml./100 g.Al., D_a = apparent density, g./cc., W_{a} = weight in air, g.,

A and B are constants.

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Figure 5.1 Sample density and hydrogen relationship of 319 alloy for various melt treatments; a) untreated, b) grain refined, and c) modified.

The slopes (A), intercepts (B) and the correlation coefficients of the curves as affected by various melt treatments are listed in Table 5.1.



Figure 5.2 Sample weight and hydrogen relationship of 319 alloy for various melt treatments; a) untreated, b) grain refined, and c) modified.

	Melt treatments	А	в	R ²
Density-Hydrogen	Untreated	-1.191	2.829.	0.80
Relationship	Grain Refined	-1.194	2.840	0.79
	Modified	-1.780	2.873	0.70
Weight-Hydrogen	Untreated	-88.419	231.822	0.74
Relationship	Grain Refined	-94.799	233.486	0.77
	Modified	-148.689	237.061	0.75

Table 5.1 The slopes, intercepts, and coefficients of correlation of density-hydrogen and weight-hydrogen curves of various melt treatments for 319 alloy.

Densities in modified samples are the most sensitive to hydrogen in the melt with the result that this curve has the highest slope. The influence of hydrogen on the densities of untreated samples is less, and the slope of this curve is flatter than in the other cases. The effect of hydrogen on the densities of untreated samples is very close to that on grain refined samples with the slopes of the density-hydrogen curves being -1.191, -1.194 and 1.780 g.cc⁻¹/ml.(100 g.Al)⁻¹ for the untreated, grain refined and modified alloys, respectively. This implies that, at the same hydrogen level, there is more porosity in the modified alloy and less porosity in the untreated alloy. The effect of melt treatments on the amount of porosity at similar hydrogen levels can be seen in Fig.5.3.

Melt treatment had a similar effect on the relationship between the sample weight and hydrogen level. This is understandable since the sample weight is directly related to the sample density, as shown in the previous chapter. The slopes of the weight-hydrogen curves were found to be -88.419, -94.799, and -148.689 g./ml.(100 g.Al)⁻¹ for the untreated, grain refined and modified samples respectively.

Fig. 5.4 shows sectioned RPT samples taken from melts containing hydrogen levels of 0.19 ml./100 g.Al.(sample A) and 0.07 ml./100 g.Al.(sample B). As can be seen in Fig. 5.4, the degree of porosity increases as the hydrogen content rises. An increase in hydrogen level from 0.07 to 0.20 ml./100 g.Al. results in about a 10 g. difference in the weight of RPT samples. Such a difference is easily measured and can be employed directly to monitor processes such as degassing.

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QUANTITATIVE REDUCED PRESSURE TEST



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Figure 5.3 The effect of melt treatment on the amount of porosity at similar hydrogen levels; left-untreated, middle-grain refined, and right-modified.



Figure 5.4 Sectioned RPT samples showing degree of porosity as the hydrogen content rises; left-0.19 ml./100 g.A1., and right-0.07 ml./100 g.A1.

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A good relationship between density and a wide range of hydrogen concentrations in the melt exists in every melt treatment process. The coefficients of correlation of this relationship are ranging from 0.70-0.80. A similar result was also obtained on the relationship between the sample weight and hydrogen level with correlation coefficients of 0.74-0.77.

5.1.1.2 356 Alloy.

الا حيا Figs. 5.5 and 5.6 illustrate the density-hydrogen and weight-hydrogen relations observed for 356 alloy with various melt treatments processes. A good linear relationship between density-hydrogen and weight-hydrogen was again observed. The slopes and correlation coefficients of these relationships, as affected by melt treatment are listed in Table 5.2. These results confirm the earlier results that the experimental data fit the linear model very closely for hydrogen concentrations in the range 0.05-0.35 ml./100 g.Al. It is interesting to note that the slope of the density-hydrogen curve obtained from the new mold in 356 alloy is noticeably steeper than that reported in previous works [63]. This may be due to the increase in the solidification time of the sample and the elimination of shrinkage, which is a predominant factor in determining the density of the nonrisered samples at low hydrogen levels (<0.15 ml./100 g.Al.).

Table 5.2 The slopes, intercepts, and coefficients of correlation of density-hydrogen and weight-hydrogen curves of various melt treatments for 356 alloy.

	Melt treatments	A	В	R ²
Density-Hydrogen Relationship	Untreated	-0.988	2.756	0.77
	Grain Refined	-1.098	2.737	0.76
	Modified	-1.641	2.809	0.80
Weight-Hydrogen Relationship	Untreated	-78.284	226.166	0.75
	Grain Refined	-88.270	225.025	0.75
	Modified	-133.537	231.084	0.80

QUANTITATIVE REDUCED PRESSURE TEST



Figure 5.5 Sample density and hydrogen relationship of 356 alloy for various melt treatments process; a) untreated, b) grain refined, and c) modified.

QUANTITATIVE REDUCED PRESSURE TEST



Figure 5.6 Sample weight and hydrogen relationship of 356 alloy for various melt treatments; a) untreated, b) grain refined, and c) modified.

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The effect of modification on the relationship between the density of the RPT samples and hydrogen concentration in the melt is similar to that in 319 alloy. The slope of the density-hydrogen curve in the modified alloy is the steepest, -1.641 g.cc⁻¹/ml.(100 g.Al)⁻¹ Grain refinement was found to slightly increase porosity in the sample as shown by a steeper slope, -1.098 g.cc⁻¹/ml.(100 g.Al)⁻¹, than that of the untreated alloy, -0.988 g.cc⁻¹/ml.(100 g.Al)⁻¹.

The effect of melt treatment on the relationship between the sample weight and hydrogen in the melt is similar to that on the sample density and hydrogen concentration in the melt. The slope was found to increase from -78.284 g./ml.(100 g.Al)⁻¹ in the untreated sample to -88.270 g./ml.(100 g.Al)⁻¹ in the grain refined sample, and to -133.537 g./ml.(100 g.Al)⁻¹ in the modified sample. The change in the sample weight was about 25 g. as the hydrogen content was decreased from 0.35 to 0.06 ml./100 g.Al.

Excellent correlation coefficients of the density-hydrogen relationship were also observed in this alloy. The correlation coefficients were found to be 0.77, 0.80, and 0.76 for the untreated, modified and grain refined alloy respectively. Similar results were also found in the weight-hydrogen relationship where the correlation coefficients were 0.75, 0.81 and 0.75 for untreated, modified and grain refined respectively.

5.1.1.3 357 Alloy.

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The characteristics of the density-hydrogen and weight-hydrogen relationships in 357 alloy are similar to those of 356 alloy because of the similarity in their chemical compositions. These alloys differ only in their magnesium level and as a result they possess the same solidification characteristics, ie. length of mushy zone, feedability, etc.

Figs.5.7 and 5.8 show the results for density-hydrogen and weight-hydrogen relations for 357 alloy while Table 5.3 summarizes the effects of melt treatment on the slopes of the density-hydrogen and weight-hydrogen curves. The coefficients of correlation of these curves are also listed in this table.


Figure 5.7 Sample density and hydrogen relationship of 357 alloy for various melt treatments; a) untreated, b) grain refined, and c) modified.

QUANTITATIVE REDUCED PRESSURE TEST



Figure 5.8 Sample weight and hydrogen relationship of 357 alloy for various melt treatments; a) untreated, b) grain refined, and c) modified.

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	Melt treatments	A	В	R ²
Density-Hydrogen	Untreated	-1.020	2.731	0.82
Relationship	Grain Refined	-1.161	2.766	0.79
	Modified	-1.537	2.802	0.79
Weight-Hydrogen	Untreated	-83.641	224.812	0.77
Relationship	Grain Refined	-90.893	227.117	0.78
	Modified	-121.926	230.164	0.77

Table 5.3 The slopes, intercepts, and coefficients of correlation of density-hydrogen and weight-hydrogen curves of various melt treatments for 357 alloy.

Modification shows the strongest influence on the formation of porosity in this alloy. Grain refinement in this case was also found to increase the amount of porosity in the melt, but the effect was less than that of modification. The slopes of the density-hydrogen curves are -1.020, -1.161, and -1.537 g.cc⁻¹/ml.(100 g.Al)⁻¹ for the untreated, grain refined, and modified alloy respectively. Melt treatment produced a similar effect on the weight-hydrogen relationship. The slopes were found to be -83.641, -90.893, and -121.926 g./ml.(100 g.Al)⁻¹ for the untreated, grain refined, and modified respectively.

As expected, good linear relationships between density, weight and the hydrogen content for all of the long freezing range alloys were found. This is due to the presence of a long dendritic mushy zone, which helps trap hydrogen pores. The higher slope of the density-hydrogen curve for 319 indicates that this alloy is more susceptible to hydrogen porosity than 356 and 357. Again, this is likely due to the extended freezing range in 319 alloy, which is 10°C longer than in 356 and 357 alloy.

The influence of Sr-modification on inducing the formation of porosity has been observed by many researchers [73-76]. The hypotheses behind this observation are that modification may 1.) reduce the surface tension of the melt, 2.) increase the length of mushy zone, 3.) reduce the solubility of hydrogen in liquid or solid aluminum, and 4.) increase the inclusion content. Some of these hypotheses have recently been verified by Emadi and Gruzleski [47].

The pores are generally present in the grain boundaries and interdendritic regions where hydrogen and inclusions are rejected and pushed by the solidification process. These conditions provide a suitable atmosphere for pore formation. For a given volume, a grain refined alloy generates more boundaries than an untreated alloy because of an increase in the number of nucleation sites. Inclusions are also finely distributed by these small and plentiful crystals which in turn provide more chance to nucleate pores. These phenomena may result in more porosity in grain refined alloys than in the untreated ones.

5.1.2 Short Freezing Range Alloy.

5.1.2.1 413 Alloy.

For an alloy with a macroshrinkage problem, such as 413, risering has been shown to be effective for eliminating the shrinkage and improving the relationship between hydrogen and sample density. Fig. 5.9 clearly shows this improvement of the relationship between true melt hydrogen and sample density obtained from our present work for alloy 413 (Fig.5.9 b.) compared to that from previous vork (Fig. 5.9 a.). A linear relationship between the sample density and the hydrogen content was again observed in this alloy when the risered mold was used.

Melt treatment produced a good relationship between the sample density and hydrogen content only for the grain refined alloy, as shown in Fig. 5.10. Grain refined alloy, again, is more sensitive to hydrogen content than in the untreated alloy. For the modified alloy, Fig. 5.11, the density-hydrogen correlation is much poorer than that found in the other melt treatments, as evidenced by the scattering in the data. The reason for this phenomenon was due to the problem with the Alscan probe. The probe was found to easily malfunction in melts treated with Sr. In this case, the probe tends to clog more quickly as the number of readings increases. The process of probe clogging was not clearly understood and was very inconsistent ie. some probes failed earlier; some failed very late. The inconsistency of the probe was the major contributor to the



scattering of data in this modified 413 alloy.

Figure 5.9 Sample density and hydrogen relationship of untreated 413 alloy; a) previous results [63], and b) present results.



Figure 5.10 Sample density and hydrogen relationship of grain refined 413 alloy.



Figure 5.11 Sample density and hydrogen relationship of modified 413 alloy.

The effect of melt treatment on the weight-hydrogen relations is similar to that on density-hydrogen relations. The change in weight of the RPT samples with hydrogen concentration is shown in Fig. 5.12.

An excellent coefficient of correlation was found in the untreated and grain refined alloy. The coefficients of correlation for the density-hydrogen relationship were 0.80 and 0.72 for the untreated and grain refined alloys, respectively. Similar effects were also found on the weight-hydrogen curve where the correlations were 0.79 and 0.70 for the untreated and grain refined alloys, respectively. The effects of melt treatment on the slopes of the density-hydrogen and weight-hydrogen relationships are summarized in Table 5.4.

Table 5.4 The slopes,	intercepts, an	d coefficients	of correlation o	f density-hydrogen	and
weight-hydrogen curv	es of various	melt treatmen	ts for 413 alloy	•	

	Melt treatments	A	В	R ²
Density-Hydrogen	Untreated	-1.088	2.775	0.80
Relationship	Grain Refined	-1.162	2.765	0.72
Weight-Hydrogen	Untreated	-89.338	227.293	0.79
Relationship	Grain Refined	-95.857	226.875	0.70

5.2 The Accuracy.

Based on development of a consistent relationship between sample density, weight and hydrogen contents as measured by the recirculating gas technique, it is possible to employ this relationship to predict the amount of hydrogen in the melt. Assuming that the hydrogen content measured by the recirculating gas technique is correct, sample density or weight can be related to the hydrogen content by;

$$H_2 = C \times D_a + D \tag{5.3}$$

and,



Figure 5.12 Sample weight and hydrogen relationship of 413 alloy for various melt treatments; a) untreated, and b) grain refined.

$$H_2 = C \times W_a + D \tag{5.4}$$

where C and D are constants.

Even though the correlation coefficients of the curves are good, the method can yield some error in the prediction. This error can be determined statistically by employing a 95% confidence prediction limits technique. A band on the curve of

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hydrogen level-density into which 95% of the total data points lie for untreated 356 alloy is shown in Fig.5.13. At a certain density, the predicted hydrogen level is the point in the middle of this band, and the margin of error is one-half of the difference between the maximum and the minimum hydrogen level of the band at that particular point, ie. Δh in Fig.5.13.



Figure 5.13 A band of 95% prediction limit curve (---) of hydrogen content and density relationship for untreated 356 alloy.

It was observed that scattering of the data increases as the hydrogen level increases. It is therefore important to consider two ranges of hydrogen concentration when determining the margin of error. The first range is the total range from the low to the high end of the hydrogen levels. The second is the range of hydrogen lower than 0.15 ml./100 g.Al. The first range can be used to predict the amount of hydrogen in the melt at expectedly high values, ie. before degassing, while the second range will be used to predict hydrogen at a relatively low value, ie. after degassing, typical of desired hydrogen levels in foundry melts.

For the total hydrogen range (low to high end of hydrogen level), the error in the

prediction of hydrogen level from the sample density and from the sample weight for a variety of alloys is listed in Table 5.5. The error found, when using sample density as a predictor, falls in the range of $\pm 0.041 - \pm 0.060$ ml./100 g.Al. When the sample weight is used as a prediction parameter, the error increases slightly to the range of $\pm 0.040 - \pm 0.067$ ml./100 g.Al. This is due to the accumulated error from the variation in the sample volume.

When the hydrogen level is lower than 0.15 ml./100 g.Al., the error was found to decrease greatly. Table 5.6 shows the error obtained by using sample density for hydrogen prediction. In this case, the error is in the range of $\pm 0.026 - \pm 0.041$ ml./100 g.Al. which is 34% less than that obtained in the previous case. When the sample weight is used, the error increases slightly to the range of $\pm 0.025 - \pm 0.046$ ml./100 g.Al. The improvement in the accuracy in this hydrogen range is mainly due to the improvement in density reproducibility of the samples. The density of the samples drawn within this hydrogen range has a reproducibility of about ± 0.009 g./cc., whereas at higher hydrogen levels, the reproducibility was found to be about ± 0.018 g./cc. Table 5.7 shows typical reproducibility data obtained from two hydrogen levels.

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Alloys	Melt treatments	с	D	R²	error, ml./100 g.Al.
Hydroge	en-Density relations	ship			
319	Untreated	-0.673	1.935	0.80	±0.044
	Grain refined	-0.665	1.920	0.79	±0.052
	Modified	-0.395	1.178	0.70	±0.065
356	Untreated	-0.779	2.184	0.77	±0.062
	Grain refined	-0.695	1.942	0.76	±0.055
	Modified	-0.486	1.398	0.80	±0.062
357	Untreated	-0.803	2.222	0.82	±0.060
	Grain refined	-0.682	1.920	0.79	±0.059
	Modified	-0.514	1.475	0.79	±0.058
413	Untreated	-0.679	1.918	0.85	±0.041
	Grain refined	-0.617	1.742	0.72	±0.050
Hydroge	en-Weight relations	hip			
319	Untreated	-0.008	1.972	0.74	±0.051
	Grain refined	-0.008	1.934	0.77	±0.055
	Modified	-0.005	1.238	0.75	±0.060
356	Untreated	-0.010	2.214	0.75	±0.064
	Grain refined	-0.008	1.956	0.75	±0.060
	Modified	-0.006	1.425	0.81	±0.055
357	Untreated	-0.009	2.108	0.77	±0.067
	Grain refined	-0.009	1.981	0.78	±0.061
	Modified	-0.006	1.498	0.77	±0.061
413	Untreated	-0.009	2.044	0.89	±0.040
	Grain refined	-0.007	1.684	0.70	±0.052

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Table 5.5 The slopes, intercepts, and error of Hydrogen-Density and Hydrogen-Weight for a variety alloys for a total hydrogen range (low to high end hydrogen level).

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Alloys	Melt treatments	с	D	R ²	error, ml./100 g.Al.	
Hydroge	Hydrogen-Density relationship					
319	Untreated	-0.498	1.454	0.65	±0.032	
	Grain refined	-0.583	1.687	0.73	±0.026	
	Modified	-0.319	0.957	0.68	±0.028	
356	Untreated	-0.665	1.868	0.57	±0.039	
	Grain refined	-0.569	1.599	0.73	±0.025	
	Modified	-0.412	1.193	0.70	±0.030	
357	Untreated	-0.707	1.968	0.42	±0.041	
	Grain refined	-0.490	1.402	0.54	±0.035	
	Modified	-0.438	1.267	0.52	±0.039	
413	Untreated	-0.669	1.889	0.52	±0.039	
	Grain refined	-0.478	1.370	0.53	±0.044	
Hydrog	Hydrogen-Weight relationship					
319	Untreated	-0.006	1.504	0.65	±0.032 🦿	
	Grain refined	-0.008	1.893	0.75	±0.025	
	Modified	-0.004	0.974	0.73	±0.026	
356	Untreated	-0.008	1.887	0.54	±0.040	
	Grain refined	-0.007	1.546	0.75	±0.028	
	Modified	-0.005	1.252	0.65	±0.031	
357	Untreated	-0.006	1.484	0.23	±0.046	
	Grain refined	-0.006	1.485	0.52	±0.036	
	Modified	-0.005	1.244	0.46	±0.041	
413	Untreated	-0.008	1.822	0.55	±0.038	
	Grain refined	-0.005	1.277	0.49	±0.046	

Table 5.6 The slopes, intercepts, and error of Hydrogen-Density and Hydrogen-Weight for a variety alloys for a low hydrogen range (< 0.15 ml./100 g.Al.).

H ₂ contents, ml./100 g.Al.	Density, g./cc.	Standard deviation
0.130	2.64 2.63 2.69 2.62 2.61	±0.01
0.216	2.47 2.44 2.43 2.43 2.41	±0.02

Table 5.7 Typical results for density reproducibility at 0.130 and 0.216 ml./100 g.Al.

5.3 Plant Tests.

It was shown earlier that there is a good relationship between the sample density or weight and the true hydrogen level. As a result, the sample density or weight can be used to predict the melt hydrogen content with a certain margin of error, about ± 0.05 ml./100 g.Al. Plant tests were carried out in order to assess the ability of the newly designed mold and riser to measure the melt hydrogen content under real operation conditions.

The tests were carried out in three aluminum casting plants on two major casting alloys, 356 and 413. The results will be discussed separately.

5.3.1 356 Alloy.

Plant tests on this alloy were carried out in Shellcast Foundries Inc. and Robert Mitchell Inc. The results are shown in Fig. 5.14. The 45° solid line is the ideal line on which the experimental points should fall. The RPT results (y-axis) agree fairly well with the recirculating technique (AlScan) at low hydrogen level (<0.15 ml./100 g.Al.) with an error of roughly about $\pm 0.03 \text{ ml./100 g.Al}$. At high hydrogen levels, the prediction by the RPT tended to underestimate the hydrogen by about $\pm 0.05 \text{ ml./100 g.Al}$., the

reason being that the pouring temperature was very high (1053 K) due to difficulty in controlling the temperature of the gas furnace in the plant.



Figure 5.14 Plant results of 356 alloy at Shell Cast Inc. (\bullet) and Robert Mitchell Inc. (\blacksquare).

Of note is that the test at Robert Mitchell Inc., represented by (\blacksquare) in Fig. 5.14, in which the RPT tended to underestimate the hydrogen content in the melt. This may be due to differences in the number of inclusions. The melt prepared by Robert Mitchell was from new ingots which were relatively clean, i.e. fewer inclusions, compared to melts of Shellcast Foundries Inc. which were prepared from roughly 50% new ingot and 50% scrap. A cleaner melt tends to produce less porosity than a dirtied melt resulting in a higher RPT sample density, and hence, lower hydrogen content. Nonetheless, the overall prediction by the RPT is good to within ± 0.05 ml./100 g.Al.

5.3.2 413 Alloy.

The tests on this alloy were carried out in Grenville Castings Ltd. The results are

shown in Table 5.8. It must be pointed out here that the melt temperature was poorly controlled during the test. As a result, it affected the measurement of the recirculating gas technique which, as discussed in Chapter One, is strongly dependent on the melt temperature. The technique requires a constant temperature during the measurement in order to provide a correct value. In this case, the melt temperature changed abruptly during the measurement period thereby affecting the microprocessor and miscalculating the true hydrogen content. Furthermore, the time allowed by the plant for hydrogen measurement was only 10 minutes, purely from economic considerations. This has been shown by Chen and Gruzleski [77] to be insufficient for the machine to provide a correct value.

With respect to the above discussion, it can be seen from Table 5.8 that the RPT technique produced higher values than the recirculating gas technique. The error was found to be in the range of 0 to -0.07 ml./100 g.Al. However, the values obtained from the RPT technique show consistent behavior with respect to the regassing process. As can be seen in Table 5.8, the predicted hydrogen level increased whenever the melt was being regassed. Predicted hydrogen levels increased from 0.13 (at normal stage) to 0.14 and 0.18 ml./100 g.Al. when the melt was regassed by the double addition of an ammonium salt. Furthermore the prediction is repeatable at each hydrogen level and less sensitive to pouring (melt) temperature than the recirculating technique. This test clearly shows that the RPT is more robust than the recirculating technique in terms of speed and melt temperature.

#	Sample Density, g./cc.	Predicted H ₂ contents, ml./100 g.Al.	Measured H ₂ contents, ml./100 g.Al.	error, ml./100 g.Al.	Melt Temperature, K (°C)	Remarks
1	2.48	0.13	0.13	0.00	1125 (752)	Normal
2	2.46	0.13	0.12	-0.01	991 (718)	condition
3	2.43	0.14	0.07	-0.07	974 (701)	Regassing by
4	2.43	0.14	0.10	-0.04	998 (725)	ammonium salt
5	2.32	0.18	0.14	-0.04	989 (716)	Recassing by
6	2.29	0.18	0.18	-0.01	1128 (755)	ammonium salt

Table 5.8 Plant test results of 413 alloy at Grenville Castings Ltd.

Chapter 6 Modeling of Pore Formation.

This chapter presents a mathematical model to predict the density of RPT samples for various hydrogen levels. Some observations on porosity formation for various situations will be discussed which lead to assumptions of the mechanism of pore formation. Finally, the mathematical model will be presented and the results will be shown.

6.1 Some Observations on Porosity Formation.

There are several important experimentally observed phenomena in this experiment with regard to formation of porosity. The first is that most pores form either in the interdendritic regions or between the grains, as shown in Fig. 6.1. At an early state of solidification, this region was a molten pool trapped between equiaxed dendritic crystals which provide an atmosphere suitable for pore formation. It is in this region that hydrogen is rejected at the solidification front due to the difference in hydrogen solubility in the solid and the liquid state. Inclusions which will act as nucleation aids are also pushed into or trapped within this region. The combination of the rejection of hydrogen and the presence of inclusions can easily facilitate the formation of porosity.

For a given melt, ie. the same number of inclusions, the total pore number per unit area (pore density) decreases only slightly as the hydrogen content decreases. Fig. 6.2 shows pore density as measured under a microscope in RPT samples for various hydrogen levels. The difference between the pore density at the low and high ends of the hydrogen level is only 5 pores per cm^2 , ie. only a 15 % difference. This indicates that with the same number of inclusions the possibility for pore nucleation is not a strong function of hydrogen level in RPT samples. However, when the melt is dirtied intentionally by the process described in chapter three, pore density increases

MODELING OF PORE FORMATION



Figure 6.1 Pores form in different areas a) interdendritic region, and b) between the grains (100X).

significantly, as clearly shown in Fig. 6.3. These samples were drawn from the same hydrogen level (0.2 ml./100 g.Al.), and the sample from the dirtied melt (left) has 38 pores per cm² whereas that from the normal melt (right) has only 22 pores per cm².

For a given cooling rate, the pore size was found to depend on the initial hydrogen content. The initial hydrogen content affects the size of porosity by providing more mass for the pore and increasing the probability of pore formation. The higher the gas content, the sooner the gas exceeds the solubility limit of the solid and liquid aluminum, and the melt thus has more chance to interact with nucleation sites to form pores. The effect of the hydrogen content on pore size can be seen in Fig. 6.4.



Figure 6.2 Number of pores per unit area (pore density) in 356 alloy as a function of hydrogen level.



Figure 6.3 Comparison of pore density in dirtied sample (left) and that of normal sample (right).



Figure 6.4 The effect of hydrogen content on pore size. The hydrogen levels are 0.23 and 0.12 ml./100 g.Al. for the sample on the left and right respectively.

6.2 The Mechanism of Pore Formation.

Based on these observations, a mechanism of pore formation can be outlined. As the temperature in the liquid aluminum falls below the liquidus temperature, the primary phase starts to form, resulting in a mushy zone in which a group of dendritic structures combines and forms a molten pool, as shown schematically in Fig. 6.5. As solidification proceeds, hydrogen rejected from the solid accumulates in the liquid phase. Once the amount of hydrogen in the liquid phase exceeds the solubility limit, the molten pool is in a ready state to form pores. However, gas pores can form only when their nucleation process is facilitated. In the absence of nucleation, the hydrogen may remain dissolved in the solid phase or diffuse into a tiny shrinkage void in the interdendritic region. Neither of these processes affects the sample density.

Appropriate sites for pore nucleation are grooves between the secondary dendrite arms as it is in this region where it is difficult for liquid to feed through to compensate



Figure 6.5 Mushy zone and development of molten pool in 356 alloy.

for the volume shrinkage. Inclusions, in this case, can help facilitate nucleation by blocking liquid feeding into the groove between the secondary arm spacing. Of note is that this mechanism does not require wettability of inclusions, hence any inclusion that has a larger size than the secondary arm spacing can help nucleate pores. Once a shrinkage void forms, hydrogen will diffuse into the void and it will start to grow. Thus the initial size of the porosity can be assumed to be equal to the space between the secondary dendrite arms. If pores form early, they will detach from the dendrite arm and finally be trapped between the grains, Fig. 6.6 a. A pore that forms at a later stage of solidification will be trapped between the secondary arms, as shown schematically in Fig. 6.6 b.

In a short freezing range alloy, ie. 413, this mechanism may not be entirely applicable since the equiaxed crystals of the eutectic phase have a round (spherulitic) shape, as shown schematically in Fig. 6.7 a. The formation of isolated melt pools is more difficult because of this shape. A pore that forms early can easily escape from the pool, float to the top of the sample or combine with other pores resulting in larger pores





Figure 6.6 Formation of pores at different stages in 356 alloy. a) pores form at early stage, and b) pores form at later stage.

as shown in Fig. 6.7 b. Nevertheless, the pore that forms at a later stage of solidification will be trapped between the crystals of the eutectic phase (Fig. 6.7 c.).

In all alloys porosity grows continuously as long as hydrogen is rejected from the liquid and solid phases, and the growth process ends when the sample is completely solidified.



Figure 6.7 Mushy zone and formation of pores at different stages in 413 alloy. a) mushy zone, b) pores form at early stage, and c) pores form at later stage.

6.3 The Mathematical Model.

6.3.1 Derivation of the Model.

As mentioned earlier, a mass balance approach can be used to predict the volume of a gas pore. Mass balance dictates that

 $M_{HQ} = f_{S} M_{S} + f_{L} M_{L} + M_{P}$ (6.1)

where

 M_{H0} = initial hydrogen mass in the melt, mol.,

 M_s = maximum hydrogen mass dissolved in the solid, mol.,

 M_L = maximum hydrogen mass dissolved in the liquid, mol., and

 $M_{\rm P}$ = hydrogen mass in the pores, mol.

The term on the left hand side is the initial amount of hydrogen in the liquid, while the first, second and third terms on the right are the amounts of hydrogen in the solid, liquid, and pores, respectively. Since the amount of hydrogen is generally known in terms of volume rather than mass, the above question can be converted to

$$C_{H0} = f_{S} C_{HS} + f_{L} C_{HL} + C_{HP}$$
(6.2)

where f_s is the fraction of solid and f_L is the fraction of liquid. Since we are interested in the total volume of the pores, C_{HP} , equation 6.2 can be rearranged as

$$C_{HP} = C_{H0} - (f_{S} \cdot C_{HS} + (1 - f_{S}) \cdot C_{HL})$$
(6.3)

where f_L is replaced by (1- f_s).

The unit of pore volume, C_{HP} , is generally expressed as ml./100 g.Al. at standard pressure (101325 Pa) and standard temperature (273 K). However, during pore formation, the temperature and pressure of the pores changes as a function of time, which in turn affects the pore volume. This volume at standard pressure and temperature

can be converted to a pure volume of the pores at their formation state by a simple Gas Law calculation as

$$C_{HP} = V_{P'} \frac{P_{P'} T_{sd}}{T_{P'} P_{sd}} = C_{HO} - (f_{S'} C_{HS} + (1 - f_{S}) C_{HL}$$
(6.4)

where V_p is the actual volume of the pores at temperature (T_p) and pressure (P_p) of pore formation. The volume of pores, V_p , can be related to the radius of the pores, r, as

$$V_p = N.\frac{4}{3}.\pi r^3$$
 (6.5)

where N is the number of pores per mm³. By substituting equation 6.4 for V_p and through rearrangement, Eq. 6.3 becomes

$$N.\frac{4}{3}.\pi.r^{3}.\frac{P_{P}T_{std}}{T_{P}P_{std}} = (C_{HO} - f_{S}.C_{HS} - (1-f_{S}).C_{HI})$$
(6.6)

From the above equation, the growth rate of the pores at a particular solidification time can be determined as

$$\frac{d}{dt}\left(N.\frac{4}{3}.\pi.r^{3}.\frac{P_{P}T_{sud}}{T_{P}P_{sud}}\right) = \frac{d}{dt}\left((C_{HO} - f_{S}.C_{HS} - (1 - f_{S}).C_{HL})\right)$$
(6.7)

As discussed previously, the pressure in the pores (P_p) at the moment of their formation is

$$P_p = P_a - P_s + \frac{2\sigma}{r} \tag{6.8}$$

As discussed in chapter two, P_s does not have a significant affect on pore formation and in this case the application of the riser to the mold has shown that macroshrinkage was eliminated. It is therefore reasonable to neglect the shrinkage pressure. Since P_p is a function of pore radius, P_p and r must be solved simultaneously until the end of solidification in order to calculate the pore size correctly. The final derivation of equation 6.7 can then be expressed as

$$\frac{dr}{dt} = \frac{1}{\left(1 - \frac{2.\sigma}{3.r.P_p}\right)} \cdot \left[\frac{T_p \cdot P_{std}}{P_p \cdot T_{std}} \cdot \frac{1}{N.4\pi r^2} \left(\frac{dC_{H0}}{dt} + (C_{HL} - C_{HS}) \cdot \frac{df_S}{dt}\right) + \frac{r}{3.T_p} \frac{dT_p}{dt}\right] (6.9)$$

Since the sample solidifies under a partial vacuum, it is likely that some gas may be lost to the pumping system with the result that the initial amount of hydrogen in the melt is a function of time; hence the derivation of equation 6.7 must include the dC_{H0}/dt term. Equation 6.9 can be solved numerically by a Runge-Kutta method [78], providing that N, dC_{H0}/dt , C_{HL} , C_{HS} , df_s/dt and dT/dt are known. dT/dt and df_s/dt can be determined experimentally by thermal analysis, as discussed by Upadhaya et al [79]. Determination of N, C_{HL} , C_{HS} and dC_{H0}/dt will be discussed in the following sections.

6.3.2 The Determination of Gas Loss to The Vacuum System.

Since the sample solidifies under a partial vacuum, it is likely that some gas may be lost to the pumping system. The change in melt gas content as a function of time due to application of vacuum can be determined numerically by employing the mass transfer equation:

$$\frac{\partial C}{\partial t} = D \nabla^2 C \tag{6.10}$$

where

D = diffusivity of hydrogen in aluminum, cm²/s.,and

C = concentration of hydrogen in aluminum, mole.

Since the melt is contained on the sides and bottom by a steel mold and a sand riser, the boundary condition for this part of the melt can be assumed as an insulation. For the open surface, it is assumed that the hydrogen gas that diffuses out of the melt is immediately taken away by the vacuum system. Therefore, the amount of hydrogen at this boundary is always zero.

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It is generally known that the diffusivity of hydrogen is a function of temperature [80], and as a result the hydrogen concentration calculation must be coupled with the calculation of the temperature profile in the melt as discussed in chapter 4. The physical properties of materials used in this calculation are listed in Table 6.1. The amount of hydrogen as a function of time for various initial hydrogen levels is shown in Fig. 6.8.

	Materials				
Properties	356 Alloy	413 Alloy	Sand		
Density, kg./m ³	2685	2645	1600		
H ₂ solubility limit in solid, ml./100 g.Al.	0.04 for unt grain refined 0.03 for mo	-			
H ₂ solubility limit in liquid, ml./100 g.Al.	0.37	0.25	-		
Thermal conductivity, W/m.K	155.0 103.0		0.6		
Specific heat, J/kg.K	1481 1090		1129		
H ₂ diffusivity, cm ² /s	3.6e-6.exp(- for liquid 1.1e-5.exp(- for solid	-			

Table 6.1 Physical properties of materials used in this calculation.

6.3.3 The Number of Nucleation Sites, N.

As we have observed, the pore density in the RPT samples (number of pores per unit area) does not change as a function of hydrogen level. It is then assumed that pore density is constant for all hydrogen levels. The pore density is determined experimentally by counting the number of pores over a given area. It must be pointed out here that the model assumes that once the hydrogen content exceeds the solubility limit in solid and liquid aluminum, the pores form instantly. Thus, pore density in this case was measured on the sample that provides such conditions, ie. the dirtiest melt. For 356 alloy, the



Figure 6.8 Hydrogen content in the melt is gradually reduced due to gas lost to the pumping system.

sample used to determine the number of nucleation sites was the dirtied sample solidified at an initial hydrogen level of 0.20 ml./100 g.Al. However, for the case of 356 grain refined alloy, it was found that most of the sample had a lower pore density but larger pores than found in the untreated case, as shown in Fig. 6.9. It is believed that in this case the pores formed in the melt pool break the mesh of small equiaxed crystals, and combine with other pores, resulting in a lower pore density but a larger pore size, as shown schematically in Fig. 6.10. The number of nucleation sites for the grain refined alloy is then less than that of the untreated alloy.

For the shell freezing 413 alloy, pores formed at an earlier stage of solidification may easily detach from the pool and combine with other pores making a count of nucleation sites difficult. The sample used for this alloy was the sample solidified from an initial hydrogen concentration of 0.17 ml./100 g.Al. Pores formed in this sample were easily detected and counted under a low magnification microscope. In this case, grain refinement did not exert a significant effect on the pore density or pore size in the sample, perhaps due to the planar interface of the eutectic phase which minimizes pore entrapment within the melt pool.

The numbers of nucleation sites determined in this way for the various alloys and melt treatments are listed in Table 6.2

Table 6.2 Number of nucleation site per cm^3 . for various melt treatments in 356 and 413 alloy.

Melt treatment	Alloys		
	356	413	
Untreated	160	150	
Sr-modified	160	_	
Grain refined	120	150	



Figure 6.9 Comparison of pore size and pore density between untreated sample (left) and grain refined sample (right).



Figure 6.10 Formation of pores in grain refined alloy (a) compared to that of untreated alloy (b).

6.3.4 The Solubility Limit of Hydrogen in Solid and Liquid Aluminum.

The solubility limits of hydrogen in the solid and liquid phases of Al-Si alloys have been well established by many authors [1,10,27]. These authors have shown that at equilibrium the solubility of hydrogen in the liquid and solid vary with temperature and amount of alloying elements. However, such an equilibrium state requires at least 5 to 10 min. [1] to be reached for a particular temperature, and it is reasonable to assume that the nature of the RPT precludes equilibrium from being reached. It is then assumed that the solubility limit in the liquid is constant. Since the melt cools very quickly to the liquidus temperature and the temperature then slowly declines as the phase transformation takes place, the solubility limit in the liquid is taken as that at the liquidus temperature. This results in the solubility limits of 0.37 and 0.25 ml./100 g.Al. for 356 and 413 alloy respectively [1].

For the solubility limit of hydrogen in solid 356 alloy, it has been shown experimentally by Tynelius [53] that the value is 0.04 ml./100 g.Al. for untreated alloy.

However, for modified 356 alloy, the solubility limit was found by the same author to be 0.03 ml./100 g.Al.

For 413 alloy, the solubility limit of hydrogen in the solid is not known, and it is then assumed that this value is equal to that in the 356 alloy.

6.3.5 The Algorithm for Calculation.

The algorithm for calculation of pore radius is outlined in Fig. 6.11. The program starts by reading the time, temperature, and fraction of solid data of the RPT sample which was determined separately, and then reading time and hydrogen content calculated sepearately from this program. Once these data are stored, the condition for pore formation is determined when the following equation is satisfied,

$$C_{HP} > C_{HO} - f_{S'}C_{HS} - (1 - f_{S}).C_{HL}$$
 (6.11)

It is then assumed that the molten pools (of which the number is equal to pore density, N) are formed and a nucleation site in each molten pool is presented, so that pores can form in each pool. From the time that equation 6.11 is satisfied until the end of the solidification time, the radius of pores can be calculated by the Runge-Kutta method. The density of the RPT sample can be then be determined by the equation;

$$Density = \frac{100}{\left(\frac{100}{\rho_{th}}\right) + N.\frac{4}{3}\pi r^3}$$
(6.12)

where ρ_{th} is the theoretical density of the alloys.

The calculation is based on the volume of gas per 100 g. of alloy. The term in the lower left is the volume of aluminum while the one on the right is the volume of pore.

The program is written in C code and is presented in appendix 6.1.

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Figure 6.11 Algorithm of the model.

6.4 Results and Discussion.

Since mathematical modeling is a time consuming task, this study is limited only to two important alloys namely; 356 and 413. The characteristics of the density-hydrogen curve of 356, 357 and 319 are similar, and so the study of 356 may well represent the behavior of other two alloys. Alloy 413 has a unique solidification characteristic, ie. its short freezing range, and it was therefore deemed important to study this alloy. The results for these two alloys will be discussed accordingly.

6.4.1 356 alloy.

6.4.1.1 Pore Radius.

Fig. 6.12 shows the calculated pore size as well as the change in the temperature as a function of time in 356 alloy for various hydrogen levels. The pores grow rapidly in the beginning and slow down later because at first the rates of change of the fraction of solid, temperature and hydrogen content in the melt are high but near the end of solidification these three terms diminish, and slow down the growth rate of the porosity.

The increase in pore diameter with increasing hydrogen level is as expected. A major effect of the initial amount of hydrogen is on the starting point of pore formation; the higher the gas content, the earlier the gas pores can form.

Fig. 6.13 gives a comparison between the calculated pore radius with the average pore size obtained experimentally. The results agree fairly well for the samples of high hydrogen levels, ie. greater than 0.15 ml./100 g.Al. The calculation overestimates pore radius at low hydrogen levels because most of the pores are trapped in the secondary arm spacing rather than forming and combining in the molten pool, and under these conditions the dendritic structure will play an important role in determining pore size.



Figure 6.12 Development of pore radii in 356 untreated alloy for various hydrogen levels; at 0.1, 0.2 and 0.3 ml./100 g.Al.

The effect of grain refinement was to reduce the pore density, and to cause the pore size to be larger. The development of the pore radius in untreated and grain refined samples is shown in Fig. 6.14. which clearly shows that the smaller the pore density, the higher the pore size.

For the modified alloy, the parameters affected are the solubility limit in the solid and the surface tension of the liquid-gas phase. The results show that the gas pores can form earlier resulting in a larger pore size. Development of pore radius as affected by modification compared to that in the untreated alloy is given in Fig. 6.15.

The pore radius in the grain refined and modified alloys as calculated by the mathematical model agrees very well with the average pore radius obtained from experiment, as shown in Fig. 6.13. but there is a tendency to overestimate pore radius at low hydrogen concentration.



Figure 6.13 Calculated pore radii (\bullet) of 356 alloy compared to those of experimental results (\bigcirc) for various melt treatments; a) untreated, b) grain refined and c) modified.



..... Grain refined ----- Untreated

Figure 6.14 Development of pore radii in grain refined 356 alloy (---) as compared to those of untreated alloy (---) for variety of hydrogen levels; 0.1, 0.2, and 0.3 ml./100 g.Al.





Figure 6.15 Development of pore radii in modified 356 alloy (---) as compared to those of untreated alloy (---) for variety of hydrogen levels; 0.1, 0.2 and 0.3 ml./1C0 g.Al.

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6.4.1.2 RPT Sample Density.

Once the pore radius is known, the RPT sample density can be calculated. The calculated sample density for various melt treatments is compared with experimental data in Fig. 6.16. It is clearly seen that the results match the experimental data very well.

6.4.2 413 Alloy.

6.4.2.1 Pore Radius.

The growth behavior of the pore radius in 413 alloy is similar to that in 356 alloy. The pores grow rapidly at first and slow down later due to the rapid change of temperature and the fraction of solid. As the hydrogen content increases, pores can grow earlier which in turn increases the pore size, Fig. 6.17.

The calculated pore radii in untreated and grain refined alloy agree very well with the experimental results, but at lower levels of hydrogen, the model overestimates pore size due to the fact that most pores are trapped in the eutectic phase, as shown in Fig. 6.18. Grain refinement does not affect pore density in this alloy, and the results are similar for both the untreated and grain refined alloys.

6.4.2.2 RPT Sample Density.

The calculated sample density as compared with experimental results is shown in Fig. 6.19. It is clearly illustrated that the predictions agree well with the experimental results. This indicates that the mass balance approach functions, provided that the number of nucleation sites is known.

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MODELING OF PORE FORMATION

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Figure 6.16 Calculated density (\bullet) compared to the experimentals results (\bigcirc) in 356 alloy for various melt treatments; a) untreated, b) grain refined, and c) modified.



Figure 6.17 Development of pore radii in 413 alloy for various hydrogen levels; 0.1, 0.2 and 0.3 ml./100 g.Al.

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Figure 6.18 Calculated pore radii (\bullet) of 413 alloy compared to those of experimental results (O) for various melt treatments; a) untreated, and b) grain refined.

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Figure 6.19 Calculated densities (\bullet) of 413 alloy compared to those of experimental results (\bigcirc) for various melt treatments; a) untreated, and b) grain refined.

6.4.3 The Effect of Melt Cleanliness.

Inclusions in the melt can be minimized by many techniques, such as filtering or purging by chlorine based gas. These techniques could affect the inclusions in the melt in two ways. The first is that the number of inclusions in the melt is minimized but the size distribution remains the same, ie. there may still remain a small number of inclusions that can provide nucleation sites for pores. The second is that the inclusions are completely eliminated and the nucleation sites removed.

For the first case, the porosity can form at an early state since there are nucleation sites available, but only in small number. In this case, the calculation predicts that the size of pores will be larger than the normal case where there are more nucleation sites. The effect of the number of nucleation sites on the development of pore radius can be seen in Fig. 6.20. The calculation was carried out for a hydrogen level of 0.25 ml./100 g.Al. and the number of nucleation sites was chosen as 160 and 80 per cm³. of 356 alloy. It can be seen that pores start forming at the same time, but that the pores are larger in the melt with a smaller number of nucleation sites than in the melt with a higher number of nucleation sites. Experimental evidence for this is presented in Fig. 6.21. These two samples were taken at the same hydrogen level but with different amounts of inclusions. The sample on the left was filtered by a 30 ppi foam filter prior to casting while the one on the right was cast under normal conditions. It is clearly seen that the pore size of the cleaner melt, ie. fewer inclusions, is larger than that of the normal melt.

An increase in pore radius due to a reduction in the number of nucleation sites also affects the calculated sample density as shown in Fig. 6.20. The density of the sample with a smaller number of nucleation sites is slightly less than that of the sample with the higher number of nucleation sites.

When nucleation sites are not available, pores cannot form, resulting in a higher sample density. Or, if pores do form late in solidification they tend to be small and typical of a melt with a lower hydrogen content. Such RPT samples will have a higher density than is typical for their hydrogen concentration.

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Figure 6.20 Development of pore radii for various cases;

Normal case - pores can form instantly from abundant nucleation sites, Case 1 - pores can form instantly from fewer nucleation sites, Case 2 - pores can form later from fewer nucleation sites.



Figure 6.21 The effect of number of nucleation sites on the size of porosity; filtered sample (left), normal conditions sample (right).

These phenomena are shown numerically in Fig. 6.20. The calculation was carried out for a melt with hydrogen of 0.25 ml./100 g.Al. and with two levels of nucleation sites, 80 and 160 sites per cm³. The melt with 160 sites per cm³, is in a typical case where there are abundant active nuclei that can provide sites for pore formation. For the melt with 80 sites per cm³., two conditions were assumed. The first condition is that pores can form immediately once the hydrogen level exceeds the solubility limit, ie. there are fewer nucleation siges but all of them are effective. The second condition is that nucleation is retarded due to the requirements of energy to overcome the nucleation barrier. It can be seen from Fig. 6.20 that for the normal and the first cases, pores form at the same time, but the pore size in the melt with lower nucleation sites is larger. For the second case, pores were assumed to form 40 seconds later than in the first two cases and it was found that the pore size in this case was still higher than that of the normal case, but lower than that of the first case. The effect of these pore radii on the density of the sample are summarized in Table 6.3. where it is clear that the sample density of the first case is lower than the normal case. However, for the second case, the sample density is higher than the normal. This second case describes well the effect of melt cleanliness on the sample density where the number of nucleation sites in the melt is reduced both in number and in size.

Cases	No. of Nucleation sites, cm ³ .	Radius, mm.	Density, g./cc.
Normal	160	0.528	2.443
Case 1 🕾	80	0.689	2.420
Case 2	80	0.618	2.488

Table 6.3 Radii and densities of RPT samples for various cases.

6.4.4 Validity of the Model

Since the amount of gas loss due to the vacuum system cannot be verified, the calculation was then extended to the situation where gas loss does not take place, ie. solidification at atmospheric pressure. Calculation under these conditions can verify the validity of the model for, if the model predicts the sample density correctly, this implies that the calculation of gas loss is also correct. The calculation was carried out for two alloys 356 and 413 of the same casting shape as the RPT sample. All the variables used in this calculation were the same as those used for the RPT sample calculations except for omission of the dC_{HO}/dt term. The results are shown in Table 6.4. which demonstrates clearly that the calculation matches the experimental data very well indicating the validity of the gas loss calculation.

Hydrogen level, ml./100 g.Al.	Alloys				
	356		413		
	Calculated density, g./cc.	Experimental density, g./cc.	Calculated density, g./cc.	Experimental density, g./cc.	
0.121	2.67	2.68	2.65	2.66	
0.175	2.66	2.66	2.64	2.65	
0.254	2.64	2.64	2.63	2.64	
0.342	2.62	2.63	2.62	2.63	

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Table 6.4 Calculated density of the RPT sample compared to the density as obtained from the experimental results.

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Chapter 7 Conclusions and Future Work.

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7.1 Conclusions.

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Based on the results and discussion of the previous chapters, the major conclusions that can be drawn are as follows:

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- 1. A constant volume RPT sample can be used to quantify the amount of hydrogen in liquid aluminum for various types of alloys including 319, 356, 357, and 413, with a reasonable margin of error. As the sample has a constant volume, either the sample weight or density can be used to quantify the hydrogen content. The simplest measuring technique is to use the sample weight. The error as measured by this technique is in the range of ±0.025-0.049 ml./100 g.Al. if the sample weight is used, and in the range of ±0.025-0.047 ml./100 g.Al. if the sample density is used.
- 2. Inclusions and chamber pressure significantly affect the test sensitivity and reproducibility. The higher the chamber pressure, the better the test sensitivity but the poorer the test reproducibility. An optimum chamber pressure was found to be 8.41 kPa. The higher the number of inclusions, the better the test sensitivity.
- 3. A simple mathematical model based on a mass balance approach can be used to calculate pore size and sample density accurately for various types of alloys and different melt treatments.

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7.2 Recommendation for Future Work.

The following areas for further work are suggested in order to extend the present studies.

- Study in detail the effect of the amount of inclusions on the reproducibility of the RPT.
- 2. Extend the test to other casting alloys.
- 3. Redesign the riser to employ a reusable material such as a ceramic or steel sheet to make the analysis cost cheaper.
- 4. Improve the test speed by redesigning the mold to solidify more quickly.
- Improve the test sensitivity in the lower range of hydrogen levels (<0.15 ml./100 g.Al.). This can be done by reducing the chamber pressure and/or redesigning the mold.
- 6. Since the major key to the success of the model to predict the sample density is the number of pores or nucleation sites, it would be interesting to determine the number of nucleation sites theoretically.
- 7. Incorporate the model into a mathematical model that can predict the temperature profile and fraction of solid. This will result in a complete model that can predict the microstructure, the mechanical properties, and the amount of porosity in the RPT sample.
- 8. Since it was shown in the model that the effect of Sr-modification on decreasing the hydrogen solubility in the solid phase plays a major role in increasing the porosity of the sample, experimental investigation of this effect would be interesting.

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Statement of Originality

The specific original contributions made in this work can be summarized as follows:

- For the first time, a constant volume sample mold and riser were designed for the RPT, and the hydrogen content predicted by this method was related to actual melt hydrogen by a recirculating gas technique.
- The RPT with the newly designed mold and riser have been used to predict with confidence the hydrogen contents in various casting alloys (319, 356, 357, and 413) and different melt treatments, ie. grain refined and modified.
- 3. For the first time, the parameters that affect the test sensitivity and reproducibility, ie. chamber pressure, chamber temperature, mold temperature and the number of inclusions have been studied in detail.
- 4. A simple mathematical model based on a mass balance approach has been develped to predict the sample density correctly provided that the number of pores in the solid is known. This model has shown that the solubility limit of hydrogen dissolved in solid aluminum may be another parameter that strongly affects the formation of porosity in 356 modified alloy.

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Appendix 6.1 Computer Code for the Mathematical Model.

The following is the computer code for the mathematical model explained in Chapter 6. The code was written in C-language and can be compiled and run under the commercial software Microsoft Turbo-C.

#include <stdio.h>
#include <math.h>

void main()

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```
{ float r,r0,ss,D,nu,Pa,gamma,tlast,chp,chs,chl,fh,dr,dC,dT,dFs,ti,Ti,pi,dummy[760];
FILE *fpt,*fdat;
float time[760],T[760],Fs[760],t[760],TT[760],FFs[760],ch0[760],cch0[760];
char outdat[20];
int i,j,m,cnt;
float calr(),calT(),calF(),calC();
```

/* Physical Properties */

r0=0.00719/2;/*cm.*/ chl=0.37; chs=0.04; pi=3.1416; nu=160*(100/2.685); gamma=0.79;

```
/* Read time, temperature, and fraction of solid */
    fdat=fopen("fsr356.dat","r");
    i=0;
    do { i=i+1;
        fscanf(fdat,"%f %f %f\n",&time[i],&T[i],&Fs[i]);
        T[i]=T[i]+273.15;
    } while (Fs[i]!=1.0);
    fclose(fdat);
    tlast=time[i];
```

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```
/* Read time, and C<sub>H0</sub> */
            fdat = fopen("ct35610.dat", "r");
            i=0;
            do { i=i+1;
                 fscanf(fdat, "%f %f %f %f %f\n",&dummy[i],&ch0[i],&dummy[i],&dummy[i]);
                 ch0[i]=ch0[i]*83015.11;
                \} while (i!=350); 
            fclose(fdat);
            t[1]=0;TT[1]=T[1];FFs[1]=Fs[1];cch0[1]=ch0[1];
            for (i=2; i < =698; i++)
            \{ t[i]=t[i-1]+0.5;
                FFs[i]=calF(t[i],time,Fs);
                TT[i] = calT(t[i], time, T);
                cch0[i] = calC(t[i], time, ch0);
             }
            t[699] = time[350]; TT[699] = T[350]; FFs[699] = Fs[350]; cch0[699] = ch0[350];
     /* Check if C_{HP} > C_{H0} - Fs.C<sub>Hs</sub> - (1-Fs).C<sub>HL</sub> */
            for(i=1;i < =699;i++)
             { chp=cch0[i]-FFs[i]*chs-(1-FFs[i])*chl;
              if(chp > 0)
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                { j=i;
                 cnt=0:
                 fdat=fopen("rg35630.prn", "w");
                 do
                  {
                           dT = (TT[j]-TT[j-1])/(t[j]-t[j-1]);
                           dFs = (FFs[j]-FFs[j-1])/(t[j]-t[j-1]);
                           dC = (cch0[j]-cch0[j-1])/(t[j]-t[j-1]);
                           ti=t[i];
                           Ti = TT[j];
                           r = calr(r0, ti, Ti, dT, dFs, dC);
                           r0=r:
                           Pa=0.083+2*gamma/(r0*0.01*101325);
                           printf("t = \%.1f sec. Pa = \%.3f atm. r = \%.4f
     mm.\n",t[j],Pa,r0*10);
                           fprintf(fdat, "%f %f\n",t[j],r0*10);
                           j = j + 1;
                  } while(t[j-1]!=tlast);
                D = 100/((100/2.685) + (nu*4*pi*pow(r0,3)/3));
                Pa=0.083+2*gamma/(r0*0.01*101325);
                printf("D = %.3f g./cc. Pa = %.3f r = %.2f \mum.\n",D,Pa,r0*1e4);
                /*fprintf(fdat,"%f %f %f\n",D,r*10,Pa);*/
                fclose(fdat);
```

```
break;
          }
        }
}
float calr(r0,ti,Ti,dT,dFs,dC)
float r0,ti,Ti,dT,dFs,dC;
{ double dx,x;
 int neq,k,ncall;
 float n,y[2];
 void runge();
       dx = 0.0001;
       neq = 1;
       n = 0.5/dx;
       k=n;
       y[1]=r0;
       x = ti;
       runge(neq,x,y,ncall,k,dx,Ti,dT,dFs,dC);
       return(y[1]);
}
void runge (neq,x,y,ncall,k,dx,Ti,dT,dFs,dC)
int neq,k,ncall;
double x,dx;
float y[2], Ti, dT, dFs, dC;
{int i,j,count;
 float rti,funt();
 float t1[5],t2[5],t3[5],t4[5],ys[5],yss[5];
 rti=x;
 count=0;
 for (i=0; i < k; i++)
     { for (j=1;j < =neq;j++)
           { t1[j]=funt(rti,x,y[j],Ti,dT,dFs,dC);
            ys[j]=y[j]+0.5*dx*t1[j];
       for (j=1; j < =neq; j++)
           { t2[j]=funt(rti,x,y[j],Ti,dT,dFs,dC);
            yss[j] = y[j] + 0.5*dx*t2[j];
           }
       x = x + 0.5 * dx;
```

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```
for (j=1; j < =neq; j++)
         { t3[j] = funt(rti,x,y[j],Ti,dT,dFs,dC);
           ysss[j] = y[j] + dx * t3[j];
         }
     x = x + 0.5 * dx;
     for (j=1; j < =neq; j++)
         { t4[j]=funt(rti,x,y[j],Ti,dT,dFs,dC);
           y[j]=y[j]+(dx/6)*(t1[j]+2*(t2[j]+t3[j])+t4[j]);
         }
     count = count + 1;
     if(count = = ncall) count = 0;
     }
}
float funt (fti,x,yy,Ti,dCdFs,dC)
float fti,x,yy,Ti,dT,dFs,dC;
{ float fh,ff,ff1,ff2,ff3,ff4,ss,gamma,Pa,ttemp,nu,chl,chs,pi;
       ttemp = Ti + ((x-fti)*dT);
       pi = 3.1416;
       nu = 120*(100/2.685);
       gamma = 0.79;
       chl = 0.37;
       chs = 0.04;
       Pa=0.083+2*gamma/(yy*1e-2*101325);
       ff1 = 1/(1-(2*gamma/(3*Pa*yy*101325*1e6)));
       ff2 = ttemp*(chl-chs)*dFs/(Pa*273*nu*4*pi*yy*yy);
       ff3 = yy*dT/(3*ttemp);
       ff4=dC/(nu*4*pi*yy*yy);
       ff = ff1*(ff2+ff3)+ff4;
       return(ff);
}
float calT(a,time,T)
float a,time[760],T[760];
{ int m;
 float st, bt, stemp, btemp, x;
 x = 0;
 for (m=1;m < =350;m++)
 \{ if(time[m] > a) \}
   { bt=time[m];
    st=time[m-1];
    btemp = T[m];
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stemp = T[m-1];
    x=stemp+((btemp-stemp)*(a-st)/(bt-st));
    break;
   }
 }
 return(x);
}
float calF(a,time,Fs)
float a, time[760], Fs[760];
{ int m;
 float st, bt, stemp, btemp, x;
 x = 0;
 for (m=1;m < =350;m++)
  { if(time[m]>a)
   { bt=time[m];
     st=time[m-1];
     btemp=Fs[m];
     stemp=Fs[m-1];
     x = stemp+((btemp-stemp)*(a-st)/(bt-st));
     break;
   }
  }
  return(x);
}
float calC(a,time,ch0)
float a, time[760], ch0[760];
{ int m;
  float st, bt, stemp, btemp, x;
  x = 0;
  for (m=1;m < =350;m++)
  \{ if(time[m] > a) \}
    { bt=time[m];
     st=time[m-1];
     btemp=ch0[m];
     stemp=ch0[m-1];
     x = stemp + ((btemp-stemp)*(a-st)/(bt-st));
     break;
    }
  }
  return(x);
 }
```