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Prevention of Porosity Formation and Other Effects of Gaseous Elements in Iron Castings

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Prevention of Porosity Formation and Other Effects of Gaseous Elements in Iron Castings

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Disclaimer

Any findings, opinions, and conclusions or recommendations expressed in this report are those of the author(s) and do not necessarily reflect the views of the Department of Energy.

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1. EXECUTIVE SUMMARY

Iron foundries have observed porosity primarily as interdendritic porosity in large freezing range alloys such as Ni-Hard I and hypoeutectic high Cr alloys or pinholes and fissure defects in gray and ductile irons. For most iron foundries, porosity problems occur sporadically, but even occasional outbreaks can be costly since even a very small amount of porosity can significantly reduce the mechanical properties of the castings. As a result when porosity is detected, the castings are scrapped and remelted, or when the porosity is undetected, defective parts are shipped to the consumer. Neither case is desirable.

This project was designed to examine various factors contributing to the porosity formation in iron castings. Factors such as solubility of gases in liquid and solid iron alloys, surface tension of liquid iron alloys, and permeability of dendritic structures were investigated in terms of their effect on the porosity formation.

A method was developed to predict how much nitrogen the molten alloy picks up from air after a given amount of holding time for a given melting practice. It was shown that small batches of iron melts in an induction furnace can end up with very high concentration of nitrogen (near solubility limit).

Surface tension of liquid iron alloys was measured as a function of temperature. Effect of minor additions of S, Ti, and Al on the surface tension of liquid iron alloys was investigated. Up to 18% change in surface tension was detected by minor element additions. This translates to the same amount of change in gas pressure required in a bubble of a given size to keep the bubble stable.

A new method was developed to measure the permeability of dendritic structures in situ. The innovative aspect of these experiments, with respect to previous interdendritic permeability measurements, was the fact that the dendritic structure was allowed to form in situ and was not cooled and re-heated for permeability tests.

A permeability model was developed and tested using the results of the permeability experiments. The permeability model for flow parallel to the columnar dendrites predicted the experimental permeability results closely when the liquid volume fraction data from equilibrium calculations were used.

The permeability gradient model was constructed in order to test the impact of interdendritic channel constriction on the flow of liquid through the mushy zone of a casting. The model examines two different regimes: (i) Dendritic solidification regime where the permeability is dominated by changes in liquid volume fraction and dendrite arm spacing, and (ii) Eutectic

solidification regime where the permeability is dominated by changes in viscosity of eutectic mixture. It is assumed that the eutectic mixture behaves like a slurry whose viscosity increases with increasing solid fraction. It is envisioned that this model can be developed into a tool that can be very useful for metal casters.

2. INTRODUCTION

Porosity may occur in metal castings in different forms: macroscopic and/or microscopic holes, round or stringy holes, bulk and/or near surface holes. Even when they are small and few, pores can cause a significant reduction in the strength of castings. As a result when porosity is detected, the castings are scrapped and remelted, or when the porosity is undetected, defective parts are shipped to the consumer. Neither case is desirable. Using defective castings as scrap and remelting them costs the metal casting industry millions of dollars in labor, energy use, and other supplies. This is also costly to the environment because of the increase in energy use and the resulting emissions from the melting and casting processes. Supplying end users with defective castings damages the reputation of the metal casting industry and may result in losses in market share. Furthermore, unexpected failure of defective castings may cause damage to end-user facilities and in some cases, severe injury to workers and/or loss of life.

Most porosity in iron castings is a result of the combination of solidification shrinkage and a decrease in the solubility of gases during solidification. It is essential for foundries to learn the mechanisms of porosity formation in their iron castings. Also, it is essential to establish a quantitative relationship among the factors affecting porosity formation. It is also important to have this relationship in a form that can be applied to predict porosity formation in a production environment.

For this purpose, a model has been proposed for alloys that solidify in a dendritic fashion. At this point the model assumes a unidirectional solidification. This model employs temperatures of liquid and mold, physical properties of liquid, solid, and mold, and some thermodynamic data to predict porosity formation. Once it is set up for a certain alloy and mold, then all the input needed is the temperature of liquid and mold at the time of pour. The model calculates the permeability gradient through the mushy zone and thus the resulting pressure drop developed by dendritic network. If the pressure drop is larger than head pressures in the casting, the model predicts porosity.

During the development of this model, experiments were performed to measure permeability of the dendritic structure of Ni-Hard alloy to interdendritic liquid between liquidus and solidus. In addition to the in situ permeability measurements, the microstructure of the Ni-Hard alloy at the permeability test temperature was characterized using quench experiments.

Surface tension of liquid iron alloys, nitrogen entry and solubility in the white iron alloys were studied. A model was developed to predict amount of nitrogen pick up from the atmosphere during melting practice. Another model was developed to predict amount of nitrogen gas evolution during solidification as a function of temperature and nitrogen concentration in liquid.

Better understanding of the factors leading to porosity can enhance economic competitiveness and reduce the environmental impact of the metal casting industry by reducing losses during production. It also has a potential of reducing energy consumption by reducing the scrap rate. In addition, a reduction in the unexpected and catastrophic failure of unsound castings will lead to a decrease in the number of accidents, and their resulting injuries, to end users.

3. BACKGROUND

In castings, porosity formation is generally the result of excessive gas content in the liquid alloy, or solidification shrinkage, or a combination of both.

Due to a decrease in the solubility of gases during freezing, gases dissolved in a molten alloy are rejected from the solid to the liquid, resulting in an increase in the gas concentration in the remaining liquid. As a result, the last liquid to solidify can have a relatively high dissolved gas content and exceed the limit of solubility. Dissolved gases in molten irons may come from various sources, but charge materials containing high amounts of nitrogen, oxygen, and hydrogen, and organic mold binders decomposing during pouring are the most common sources [Bates, Hernandez, Naik].

Volume contraction during solidification creates shrinkage in castings. Some of the factors contributing to shrinkage are the density differences of liquid and solid, the viscosity of the liquid, the solidification range, the solidification rate, and the permeability of the mushy zone [Piwonka, Coble, Fang, Sigworth].

Since the pioneering work of Chvorinov, Pellini, and Taylor et.al. on solidification shrinkage, there have been a number of studies to understand the mechanisms of gas and shrinkage porosity formation and to develop models to predict porosity formation, particularly in Al alloys. Using hydrodynamic principles, several workers [Fang, Campbell 1967, Campbell 1968, Minakawa, Li] developed models to predict shrinkage which correlated well with experimental data in some cases. Davies and Niyama et. al. investigated the effect of casting size and temperature gradient in castings on shrinkage porosity. There has also been a thermodynamic approach to the porosity problem. Several authors [Kubo, Poirier] calculated the effect of the segregation of gases in the liquid on porosity formation. These studies have yielded useful information on topics such as the level of gas pressure required to form gas porosity in a few alloys under various conditions.

The formation of pores in a casting is affected by the pressures exerted by solidification shrinkage (P_s), the increasing gas concentration in the remaining liquid due to reduced solubility in the solid (P_g), the surface tension between gas and liquid (P), the metallostatic head on the casting (P_h), and the environment (P_{ext}). Using these pressures, a condition can be written for a casting that is porosity free:

$$P_g + P_s < P_{ext} + P + P_h \quad (3.1)$$

Equation 3.1 is a general equation and can be rewritten for more specific cases. For example, for early stages of solidification in castings when feeding is not restricted, assuming that the casting is risered properly, the shrinkage pressure term, P_s , is zero so the equation becomes

$$P_g < P_{ext} + P_i + P_h \quad (3.2)$$

This equation is also more suitable for alloys with a short freezing range such as eutectic alloys. On the other hand, for the late stages of solidification when feeding is restricted by dendritic growth in alloys with a long freezing range, even though there is a suitable riser on the casting, Equation 3.1 can be rewritten as

$$P_g + P_i < P_{ext} + P_h \quad (3.3)$$

where P_i is the pressure drop in the liquid in interdendritic region due to the fact that the dendritic network becomes an obstacle to liquid flow. The pressure drop term can be expressed as

$$P_i = P_h - P_i \quad (3.4)$$

where P_i is the pressure in the liquid in the interdendritic region.

4. EXPERIMENTAL PROCEDURE

4.1 Survey of Porosity Defects in Castings

Numerous foundries were contacted to obtain castings with gas defects in order to develop a random survey of the types of defects found in the industry. Both sponsor members and foundries at large were contacted. A total of 42 castings were collected from twelve foundry organizations. The group of defective castings included castings poured from gray cast iron, ductile iron, Type I NiHard and High-Cr white cast iron alloys.

A variety of defects were observed in these castings including both exogenous gas defects and indigenous gas defects. Many of the castings had similar types of defects. There were three types of defects that were most predominant. They included mold gas, nitrogen and hydrogen gas defects, and carbon monoxide reaction products. Typical examples of these three types of defects are presented in here to illustrate the defect features. The 42 individual reports are available on request for those who wish to study them.

4.2 Experimental Materials

The experimental materials used in this project were provided by Texaloy Foundry (Ni-Hard white iron), Durametal (high Cr white iron), and Daimler-Chrysler (gray and ductile iron). Chemical compositions were determined using X-ray fluorescence, wet chemistry, inductively-coupled plasma, atomic absorption, and combustion methods (Leco C, S, O, N analyzers).

Differential thermal analysis (DTA) was performed to determine solidification reaction temperatures for each alloy on an instrument fitted with a pair of matched alumina crucibles with tantalum lids. One crucible contained the sample, with a mass of between 50 and 100 mg, while the other crucible was empty. After evacuation of the furnace chamber, a flow of 1.67 cm³/s of high purity argon was maintained throughout the experiment. Specimens were heated to approximately 50C above their liquidus temperature at 5C/min, allowed to equilibrate for 5 min, and then cooled at 5C/min to 700C. The temperature difference between the crucibles was monitored during heating and cooling. Heat taken up or given off during the analysis was plotted, after normalizing for the sample weight.

Densities of the materials were measured using the Archimedes principle.

4.3 Nitrogen Solubility Measurements

Solubility of nitrogen in cast iron alloys was measured in both liquid and solid state. For the measurements in the liquid state, starting materials were in the form of cylindrical ingots with a diameter of 5 cm and a height of 5 cm. Measurements were made on the low carbon Type I Ni-Hard, high carbon Type I Ni-Hard, high chromium white iron, gray iron, and ductile iron compositions. All as-received ingots used in this study were pre-melted in vacuum (approximately 2×10^{-4} Torr) to ensure a low content of gaseous elements. The vacuum treatment lowered the N content of the Ni-Hard I ingots below 0.002 wt% and that of the high Cr ingots to about 0.02 wt%.

In the solubility measurements, the previously vacuum-melted ingots were remelted in the induction furnace in a pressurized chamber. The melt was held for 20 minutes at 1 atm Ar+N₂ mixture (0.78 atm N₂) at various temperatures. Variation of the holding temperature was $\pm 2^\circ\text{C}$. At the end of the holding period, power to the induction coil was shut off, and simultaneously, the gas pressure was raised to 1.34 atm to prevent nitrogen leaving the sample. From previous experience, it is known that kinetics of nitrogen entry is very slow when there is no stirring of the melt. Therefore, it is not expected that the ingot picked up more nitrogen before solidification occurred. Total nitrogen was determined using a Leco gas analyzer.

Solubility of nitrogen in the solid state was measured using very thin cylindrical samples in a tube furnace designed to attain low partial pressures of oxygen. High purity (99.999%) nitrogen gas was passed through an oxygen scrubber before it was transported into the furnace tube. An oxygen meter continuously monitored the gas coming out of the furnace tube. The oxygen concentration in the tube atmosphere was maintained below 1×10^9 ppm to prevent oxide formation on the surface of specimens. 1 mm thick and 5 cm long samples were electro-discharge machined from the ingots. They were ultrasonically cleaned in soap water. Their surfaces were ground using 600 grit paper to remove the oxide layer. Two pins were placed in separate boats and positioned in the center of the furnace tube next to a thermocouple. Nitrogen gas flow was started after sealing the tube. Before heating up, it was made sure that the oxygen partial pressure was below a certain level. This usually took a day of flowing nitrogen through the furnace tube. An over pressure of two inches of water was maintained in the tube during the experiments. Then the furnace was heated to the holding temperature. Holding temperatures of 800°C, 900°C, 1000°C, and 1100°C were used. The samples were held at these temperatures for 100 hours. At the end of the holding period, one of the samples was quenched by pulling the boat to the cold end of the tube with the help of a pull device that was devised to work without breaking the seal thus without disturbing the tube atmosphere. The other sample was allowed to cool slowly with the furnace. Once the tube cools down near room temperature, the seal was broken and samples were taken out and analyzed for nitrogen and oxygen immediately. A Leco N and O analyzer was used to determine the amount of nitrogen and oxygen in the samples. Three samples per specimen were tested. In most tests, the oxygen concentrations were less than

1 ppm indicating that oxygen was below the detection limit of the instrument. When a significant amount of oxygen (>10 ppm) was detected, the samples were discarded.

4.4. Nitrogen Absorption Experiments

The following procedure was used to determine the rate of nitrogen absorption from air into molten white irons during induction melting. A 1.5 kg charge of previously vacuum melted material was placed in an alumina crucible (15.2 cm high and 8.3 cm dia) in a vacuum induction furnace and remelted under vacuum. Once the temperature was stabilized to a desired range by adjusting the power, the furnace chamber was filled with high purity argon (99.999%Ar) and opened to the atmosphere. As soon as the chamber was opened, exposing the melt to air, samples were drawn from the molten bath using quartz tubes with 3 mm ID and a suction bulb. The quartz tubes partially filled with molten metal were immediately quenched in water. Sampling was done frequently (every ½ to 1 minute) for the first five minutes after the chamber was opened to air. Later, sampling was performed every 2-3 minutes.

The temperature of the molten metal was determined using a dip-stick style S-type thermocouple immediately after each chemistry sample was taken. In several experiments, a flow (~30 ml/min) of high purity argon gas was placed over the melt to form an argon blanket to simulate a foundry practice. When the high Cr white iron was melted, a piece of Fiberfrax[®] was also used to cover the top of the crucible to make the argon blanket more effective. The cover was opened periodically for sampling and temperature taking. Later, the samples were cleaned and broken into small pieces for analysis in a Leco gas analyzer for nitrogen, oxygen, and carbon content. Three analyses were carried out for each sample when sufficient material was available.

4.5 Surface Tension Measurements

Sessile drop experiments [White, Ellefson, Anson] were conducted on three alloys: NiHard white iron, high Cr white irons, and gray iron. Samples of 16 mm dia by 6 mm height (~ 10 grams) were placed on a polished sapphire disc in the center of a tube furnace. A vacuum (~200 millitorr) was established in the furnace prior to heating. The furnace was heated to 1375 °C. Images of the sample were captured using an Eastman Kodak MDS100 software package. Images were subsequently analyzed using an Optima 6.5 image analysis software package. A custom macro was created to facilitate measurement of the critical dimensions.

Surface tensions were calculated using the Dorsey equation, given by

$$\sigma = g\rho A^2$$

where σ is the surface tension, g is the acceleration due to gravity, ρ is the density, and A^2 is given by

$$A^2 = X^2 \left(\frac{0.052}{f} - 0.12268 + 0.0481f \right)$$

where

$$f = \frac{H45}{X90} - 0.4142$$

with H45 and X90 being taken from the image measurements in pixels.

The Dorsey equation calls for the density of the liquid. This datum is not readily available. For this iteration, the solid density of both alloys was used. Most metals expand about 4% on melting, and the variation in density with temperature is not likely to be significant with iron alloys over this temperature range. However, it was assumed that the effect of this simplification is that calculated surface tensions are a few percent higher, and that this effect becomes slightly more pronounced as temperatures increase.

Densities were measured using a micromeritics autopycnometer 1320. The measured densities were NiHard $7.788 \pm .007$ g/cm³, and for the high Cr white cast iron 7.583 ± 0.002 g/cm³.

4.6 Interdendritic Flow Experiments

The correlation of specimen temperature with velocity of eutectic flow rate was studied for the flow of the NiHard eutectic composition through its established austenitic dendrites. In order to reproduce, as closely as possible the progress and cooling of metal during casting, a process was devised where the Ni-Hard sample could be melted and then allowed to cool as in a casting. When the Ni-Hard sample approached the melting temperature (1178°C) of its eutectic component, a charge of liquid eutectic alloy was allowed to flow through the “porous” dendritic structure of the mostly frozen Ni-Hard sample. The progress of the eutectic liquid, as it passed through the semi-solid NiHard sample, was noted and used to determine the velocity of the interdendritic flow for the experiment.

To enable this sequence of events, a two-chambered, quartz crucible, Figure 4.6.1, was built. The lower chamber was charged with the Ni-Hard sample, the upper with a sample of the

eutectic alloy. The floor of each chamber consisted of a removable plate of quartz. The lower chamber also included quartz pegs to prevent the mostly frozen Ni-Hard sample from falling out during the flow experiment.

Preparation for the interdendritic flow experiments began with the measuring of the dimensions of the two-chambered crucible. The dimensions of the cross-section of the crucible were recorded as were the positions of the Ni-Hard retaining pegs (Figure 4.6.1). Next, the bottom plate (“gate”) was inserted and held in place by a tungsten spring. Following this, charges of Ni-Hard and the eutectic alloy were weighed and the Ni-Hard charge was placed in the lower chamber. The upper gate was then installed, supported by another spring, and the upper chamber was charged with the eutectic alloy.

At the temperatures at which the flow experiments occurred, the metal in the crucible and the ceramic holder used to keep the crucible vertical in the furnace became incandescent, preventing the viewer from distinguishing and tracking the progress of the position of the eutectic liquid in the upper chamber during flow. A single-ended quartz tube, tall enough to be discernible above the crucible and holder, was floated on top of the eutectic charge. The charged crucible was then placed in a ceramic holder.

These experiments were carried out in a tube furnace. A flow of argon (99.999 % purity) was maintained in the tube to prevent oxidation. To the crucible gates was attached a rod which extended, through a seal, to the outside of the furnace, allowing the experimenter to manipulate the gates. This assembly was placed in contact with three thermocouples, which extended to the approximate midpoint of the furnace tube. This final assembly, comprising an end-cap of the tube-furnace, the thermocouple sheaths and the manipulating-rod, as well as the crucible in its ceramic holder, was slid into the furnace tube until it pressed against retaining rods extending from the furnace’s other end-cap. The furnace tube was then sealed and filled with Ar at low positive pressure. This gas flowed, from front to back, through the tube during all phases of the experimental run. Figure 4.6.2 shows a schematic of the experimental setup.

The furnace initially heated the crucible and its charges to 1360 °C, the temperature at which the Ni-Hard alloy was molten, and then free-cooled to the flow experiment temperature. At this temperature (approaching the melting point of the eutectic fluid) the experimenter used the quartz manipulating-rod to pull the gates from their positions in the IDF crucible. The top gate opened first, allowing the eutectic charge to fall and settle atop the semi-solid Ni-Hard plug. The bottom gate was then opened to allow flow through the porous dendritic plug. The progress of the marker as the eutectic fluid flowed around the dendrites, was observed and recorded using a digital camera, fitted with a filter, which peered through a port in the other end-cap of the furnace. The change in position of the marker telegraphed the progress of the liquid flowing through the porous dendritic plug. The flow continued until the marker came to rest on the

surface of the porous plug. In order to take into account the dynamic structure of the porous dendritic plug, this flow experiment was conducted either immediately on reaching the desired temperature or after a pause of as long as 30 minutes, during which the experiment's temperature remained constant.

Video-recorded images showing the marker's progress were measured to determine the change in position over time. This gave the velocity of the marker, and so, of the eutectic fluid passing through the porous dendritic plug. Pictured in Figure 4.6.3 is a sample of the recorded images measured to determine flow velocity.

The position measurements were plotted and a line fit to them to determine the magnitude and character of the velocity, u , (see Equation 4.6.1 rewritten here) of the marker, and so of the eutectic fluid through the dendrite network.

$$u = \frac{K}{\mu} \left(\frac{dP}{dx} \right) \quad (4.6.1)$$

The slope of the line defines the velocity value for the experiment. The pressure drop through the porous dendritic n, dP/dx , was taken as the average drop across the plug ($\square P/L$). The value for this pressure drop was taken after analyzing the forces present at each end of the plug throughout the experiment. The forces taken into account were the weight, density and volume of eutectic fluid both above and below the dendritic plug, the weight of the marker, and the force exerted by surface tension both above and below the plug. The permeability of the porous dendritic plug was then calculated algebraically through D'Arcy's equation (equation 4.6.1).

4.7 Quench Experiments

To recreate the microstructure present at the time of fluid flow in the Interdendritic Flow experiments, a NiHard specimen was taken through a heating and cooling history mimicking that experienced in the IDF experiments. This mimic was carried out using a furnace through which a specimen was moved over time through the temperatures occurring in the IDF chamber as the IDF specimen approached the flow-experiment temperature. At the temperature and time flow was allowed, the mimic specimen was quenched to preserve the microstructure existing at that point. Figure 4.7.1 shows the temperature history of a mimic specimen compared to that of the IDF specimen. The mimic experiments were designated IDFQ – IDF Quenched.

Figure 4.7.2 shows the arrangement used to perform the IDFQ experiments. A vertical tube furnace contained a tube open on both ends which allowed a specimen to be heated and then dropped to a quench bath below. A boom, mounted on a ball-screw which in turn was mounted on a tower, extended over the furnace and held the specimen in the tube via a chain. The boom and sample were raised and lowered by the ball screw which was controlled by a stepper motor. To attain the correct cooling curve, the physical temperature profile of the vertical furnace was recorded, and a set of velocity commands programmed into the stepper motor. The software program, LabView[®], was used to transmit these commands to the stepper motor.

The specimens for IDFQ were contained in an Ar-filled quartz capsule. As is shown in figure 4.7.2, the capsule was attached to a chain hanging from the boom. Also extending down from the boom was a thermocouple probe. The tip of this probe was positioned so that it was level with the NiHard specimen in the capsule. Figure 4.7.3 shows a photograph of the quartz capsule.

The center-to-center spacings of both primary and secondary dendrites were measured using photomicrographs. Results are discussed in chapter 5.6.

Average dendrite arm spacing was measured by hand, using printed copies of photomicrographs of the quenched samples. It should be noted that these quench experiments produced equiaxed structures. Therefore, some of the adjacent primary dendrite arms were not absolutely parallel. Average values over the length of the measured arms were recorded for these spacings.

5. RESULTS

5.1 Survey Of Porosity Defects In Iron Castings

A list of the foundries that contributed castings with defects is shown in Table 5.1.1. The defective castings are listed in Table 5.1.2 along with the identification of the alloy, the type of defect, and a brief description of the cause of the defect, when possible.

A variety of defects were observed in these castings including both exogenous gas defects and indigenous gas defects. Many of the castings had similar types of defects. There were three types of defects that were most predominant. They included mold gas, nitrogen and hydrogen gas defects, and carbon monoxide reaction products. Typical examples of these three types of defects are presented here to illustrate the defect features. The 42 individual reports are available on request for those who wish to study them.

5.1.1. Mold Gas Defect

The example casting with the mold gas defects contains multiple irregular shaped pores on the surface and subsurface with discoloration from oxidation. The photographs in Figure 5.1.1 illustrates the defects on the surface of the casting. Metallographic sections were obtained from the defect regions and the photomicrographs in Figure 5.1.2 and Figure 5.1.3 illustrate the porosity voids in cross section. The surface pores can be round but surfaces are irregular and exhibit an oxide skin that is rough textured. It was surmised that the defects were caused by mold gas or core out-gassing caused by improper sand mixture, improper curing, low permeability and/or insufficient venting of the mold cavity.

5.1.2. Nitrogen & Hydrogen Defects

The example casting with nitrogen/hydrogen gas defects also contained pores at the surface of the casting. The photographs in Figure 5.1.4 illustrate the defects on the surface of the casting. Metallographic sections were obtained from the defect regions and the photomicrographs in Figures 5.1.5 through 5.1.8 illustrate the porosity voids in cross section. Both nitrogen and hydrogen produce rounded pores that are either on the surface or immediately subsurface. The pores can form as individual pores or in clusters particularly at hot spots like inside corners.

Nitrogen can be interdendritic particularly in high alloy “hard” white iron castings. In graphitic iron castings the pores can be lined with a graphite film and possibly an oxide film. The texture of the film is generally smooth. The graphite in the base metal structure will be contiguous with the pore. Hydrogen by contrast will have a smooth textured graphite film lining the pore without oxides and the graphite in the structure will be absent in the metal adjacent to the pore.

The source of nitrogen can be both indigenous and exogenous. Indigenous nitrogen sources can include the charge materials and/or nitrogen in the air after long holding times at the pouring temperature. Exogenous nitrogen sources can be from improperly cured cores and core resins.

Sources of hydrogen can also be both indigenous and exogenous but, in both instances, the source is moisture from wet ladles wet furnace refractory, leaking tuyeres and/or high sand moisture.

5.1.3. Carbon Monoxide Reaction Defects

Two examples of carbon monoxide gas defects are presented. These castings also contained pores at the surface of the casting. In the first example, the photograph in Figure 5.1.9 illustrates the defects on the surface of the casting. The surface appearance of the porosity voids can be smooth or irregular. Oftentimes, foreign material is associated with the porosity.

Metallographic sections were obtained from the defect regions and the photomicrographs in Figures 5.1.10 and 5.1.11a illustrate the porosity voids in cross section. Usually the porosity void displays an irregular profile with foreign substances deposited on the cavity surface. The foreign material can be sand, slag from the melting furnace, slag from a mold addition such as inoculant or treatment alloy, or slag from turbulence in the gating system. A high density of manganese sulfide or iron sulfide particles in the immediate vicinity can also be seen.

The defect region was probed in a scanning electron microscope (SEM) to identify the composition of the foreign constituents on the defect cavity wall. Energy dispersive X-ray spectrometry (EDS) was used to characterize the chemical makeup of the inclusions. EDS spectra are shown in Figures 5.1.11b and 5.1.12. They illustrate that the inclusions consisted of sand grains and a slag-like constituent rich in elements associated with the inoculant.

The defects in the second example of carbon monoxide gas defects are documented in Figures 5.1.13 and 5.1.14. The defect is similar but not identical. The slag inclusion in this example is rich in S rather than the elements associated with the inoculant.

The cause for carbon monoxide reaction porosity is related to the formation and attachment of non-metallic inclusions at the cast surface. These inclusions are associated with complex combinations of iron composition, pouring temperature and an oxygen source such as the atmosphere, sand or other oxides such as oxidation of mold additions or even oxidation of the flowing metal (turbulence) during mold filling.

5.1.4 Summary Remarks

The sources for the hydrogen gas in cast iron need better definition. The literature does not give a clear indication of the amount of moisture that can be tolerated.

More work is needed to determine the cause for carbon monoxide reactions. Clearly, slag and oxide inclusions are always present to some extent. It seems likely that the occurrence of defects is related to the compositions of the slag, iron alloy and inoculants.

Table 5.1.1. Foundries that participated to the survey

- Maca Supply Company
- Texaloy Foundry Company, Inc.
- United Machine & Foundry
- Grede Foundries
- Citation Corporation
- AB & I, Inc.
- John Deere Foundry
- M & H Valve Company
- Brillion Iron Works
- Kurdziel Iron of Rothbury, Inc.
- DaimlerChrysler Corporation
- Durabar, Division of Wells Manufacturing

Table 5.1.2. List of Internal Reports on Castings with Defects

Report No.	Foundry Source	Iron Type	Gas Type	Root Cause
41439-1	A	Ductile	Indigenous O ₂	Trapped In Liquid-Evolved During Solidification
41439-2	B	White	Carbon Monoxide Oxide	Reaction Between C in Iron and O in Slag/Sand
41439-3	B	White	Carbon Monoxide Oxide	Reaction Between C in Iron and O in Slag/Sand
41439-4	C	White	Indigenous O ₂	Too Long Of a Hold Time After Melting
41439-5	C	White	Indigenous O ₂	Too Long Of a Hold Time After Melting
41439-6	C	White	Indigenous O ₂	Too Long Of a Hold Time After Melting
41439-7	D	Ductile	Hydrogen	Moisture
41439-8	E	Ductile	?	"Blow" Insufficient Venting or Sand Permeability
41439-9	F	Gray	Hydrogen/Nitrogen	"Hot Spot" Gas Rejected to Last Liquid To Solidify
41439-10	E	Ductile	?	"Blow" Insufficient Venting or Sand Permeability
41439-11	G	Gray	Hydrogen	Moisture
41439-12	G	Gray	Hydrogen	Moisture
41439-13	G	Gray	Hydrogen	Moisture
41439-14	H	Gray	H ₂ /CO	Moisture And Metal Slag Reaction
41439-15	I	Gray	Carbon Monoxide Oxide	Slag/Iron Reaction-Slag Contained Inoculant
41439-16	I	Gray	Carbon Monoxide Oxide	Slag/Iron Reaction-Slag Contained Inoculant
41439-17	J	Gray	Carbon Monoxide Oxide	Iron/Mold/Slag Reactions, Excess MnS & FeS
41439-18	J	Gray	Carbon Monoxide Oxide	Iron/Mold/Slag Reactions, Excess MnS & FeS
41439-19	J	Gray	Carbon Monoxide Oxide	Iron/Mold/Slag Reaction
41439-20	J	Gray	Carbon Monoxide Oxide	Liquid Iron/Slag Reaction, Excess MnS, and FeS
41439-21	J	Gray	Carbon Monoxide Oxide	Iron/Mold/Slag Reactions, Excess MnS & FeS
41439-22	J	Gray	Carbon Monoxide Oxide	Iron/Mold/Slag Reaction
41439-23	J	Gray	Carbon Monoxide Oxide	Iron/Mold/Slag Reactions, Excess MnS
41439-24	J	Gray	Hydrogen	Moisture
41439-25	D	Ductile	Hydrogen	Moisture
41439-26	F	Gray	Not Applicable	Trapped Sand And Slag
41439-27	F	Gray	Not Applicable	Trapped Sand And Slag
41439-28	K	Gray	Carbon Monoxide Oxide	Iron/Mold/Slag Reaction
41439-29	L	Gray	Hydrogen	Moisture
41439-30	M	Gray	Not Applicable	Trapped Sand And Slag
41439-31	N	Gray	Hydrogen	Moisture
41439-32	N	Gray	Not Applicable	Trapped Sand And Slag
41439-33	N	Gray	Not Applicable	Trapped Sand And Slag
41439-34	O	Gray	Hydrogen	Moisture
41439-35	P	Ductile	Carbon Monoxide Oxide	Slag Reaction With Floated Graphite
41439-36	Q	White	Nitrogen	Too Long Of a Hold Time After Melting
41439-37	Q	White	Nitrogen	Too Long Of a Hold Time After Melting
41439-38	B	White	Nitrogen	Too Long Of a Hold Time After Melting
41439-39	R	Hi Si Ductile	Carbon Monoxide Oxide	Slag/Iron Reaction-Slag Contained Inoculant
41439-40	S	Ductile	Hydrogen	Moisture
41439-41	T	Ductile	Hydrogen	Moisture
41439-42	U	Gray	Not Applicable	Cold Shut

5.2 Characterization Of Experimental Materials

5.2.1 Chemical Composition

Chemical composition of experimental cast irons is given in Table 5.2.1.1. The techniques used to determine the elements were also indicated in the table.

Table 5.2.1.1. Chemical composition (wt%) of cast irons used in the experiments.

	Ni-Hard A	Ni-Hard B	High Cr WCI	Gray Iron	Ductile Iron
C ¹	2.56	2.58	2.36	3.43	3.77
Cr ^{2,3}	2.55	2.62	26.2	0.37	0.37
Ni ³	4.48	4.29		0.27	0.27
Mn ³	0.56	0.54	0.64	0.41	0.30
Si ³	0.42	0.61	0.46	2.24	2.37
Mo ³	0.59	0.62	0.45	0.01	0.01
Cu ³	0.044	0.099	0.053	0.61	0.41
Al ⁴	0.0038		0.0020	0.0030	0.0220
Ti ^{2,4,5}	0.0090	0.0030	0.0050	0.0060	0.0068
S ¹	0.0096	0.0220	0.0205	0.0235	0.0029
N ¹	0.0138	0.0113	0.0478	0.0056	0.0044
O ¹	0.0019	0.0009	0.0212	0.0091	0.0031
P ³	0.019	0.029	0.014	0.070	0.031
Mg ⁴					0.0830
1 Leco gas 2 Wet chemistry 3 X-ray fluorescence (wave length dispersive analysis) 4 Atomic absorption 5 Inductively coupled plasma (ICP)					

A higher carbon version of the Ni-Hard cast iron was also produced adding one weight percent carbon to Ni-Hard A in a vacuum induction furnace.

5.2.2. Differential Thermal Analysis

Differential thermal analysis curves at temperatures near the melting / solidification reactions are shown in Figures 5.2.2.1-5 for the cast irons used in the experiments. Ni-Hard A alloy starts melting at about 1140°C and becomes completely molten at 1335°C upon heating (Figure 5.2.2.1). Upon cooling, the same alloy begins to form austenite dendrites at 1317°C and starts the

eutectic reaction ($L \rightarrow \gamma + M_3C$) at 1129°C. The higher carbon version of the same alloy shows an onset of the melting reaction at 1130°C and becomes completely molten at 1247°C upon heating (Figure 5.2.2.2). The onset of the austenite formation occurs at 1224°C and that of the eutectic reaction at 1129°C upon cooling.

Melting of the high Cr white iron starts at 1270°C and ends at about 1335°C during heating (Figure 5.2.2.3). Upon cooling, the onset of the first solidification reaction is at 1306°C. At 1300°C, austenite dendrites start forming. Finally, the solidification ends with the eutectic reaction ($L \rightarrow \gamma + M_7C_3$) which starts at 1276°C.

The gray cast iron used in this work begins melting at 1140°C and becomes completely molten at 1215°C (Figure 5.2.2.4). During cooling, solidification starts at 1210°C. The onset of eutectic reaction is at 1157°C.

The ductile cast iron demonstrates one reaction only both during heating and cooling (Figure 5.2.2.5). The onset of melting during heating is at 1140°C and the onset of the eutectic reaction during cooling is at 1161°C.

5.2.3. Equilibrium Calculations of Solidification Reactions

Results of the equilibrium calculations using the Scheil method performed by means of Thermo-Calc[®] software and the TCFE3 steel database are shown in Figures 5.2.3.1-4 for all materials used in this work. There is considerable agreement between the calculations and the experimental DTA results in terms of types of solidification reactions and the reaction temperatures.

5.3 Solubility And Absorption Of Nitrogen In Cast Irons

5.3.1. Absorption of Nitrogen

The increase in nitrogen content of the molten alloy when it is exposed to air is plotted as a function of time in Figures 5.3.1.1 and 5.3.1.2 for the Ni-Hard and high Cr white iron alloys, respectively. The maximum solubility and the rate of increase in the nitrogen content rose with increasing temperature of the melt. It is shown that nitrogen entry into the molten iron alloys had two different regimes at each temperature as a function of time: An initial fast rate and a subsequent slower rate.

At 1660°C, nitrogen entered the molten Ni-Hard alloy at a linear rate of 0.0092 wt% per minute for approximately the first four minutes of exposure. After that, the rate slowed significantly. The average oxygen content in the molten Ni-Hard alloy was 0.0065 wt% during the exposure.

At 1365°C, the initial rate of nitrogen entry into the Ni-Hard alloy was slower than that at the higher temperature. The linear rate was 0.0025 wt% per minute for the first 20 minutes of exposure at this temperature. The average oxygen content in the molten Ni-Hard alloy was 0.0052 wt% during the experiment at 1365°C.

When an argon gas flow was maintained over the surface of the molten Ni-Hard alloy, which was held at 1424°C in the induction furnace, the initial rate of nitrogen entry was 0.0024 wt% per minute for the first three minutes of exposure. After the first three minutes, the rate of nitrogen entry decreased significantly. Although the holding temperature was 59°C higher in this case, the initial linear rate was lower than (or very near) that at 1365°C because of a lowered nitrogen partial pressure over the melt due to argon flow. The argon flow reduced the level of nitrogen contained in the molten alloy when the second regime, i.e. slower rate, was attained; it was reduced from 0.04 wt% to 0.01 wt%. No cover was used on top of the crucible in this particular experiment at 1424°C. The average oxygen content in the molten Ni-Hard was 0.005 wt% during the experiment.

Similar trends were observed with the high Cr white iron composition (Figure 5.3.1.2). The flow of argon gas was maintained over the molten high Cr white iron at both holding temperatures. At 1435°C, the linear rate of nitrogen entry into the molten high Cr white iron was 0.0017 wt% per minute for the first 30 minutes of exposure. This resulted in a nitrogen content of approximately 0.08 wt% in the molten high Cr white iron. After this point, the rate of increase was very slow. The average oxygen content in the molten high Cr white iron was 0.0062 wt% during the experiment.

At a higher temperature of 1567°C, the molten high Cr white iron reached a nitrogen content of 0.17 wt% within approximately 20 minutes of exposure at a nitrogen entry rate of 0.0069 wt% per minute. Then the rate of entry slowed down. The average oxygen content in the molten high Cr white iron was 0.0079 wt% during the exposure at 1567°C.

Carbon loss due to oxidation of the molten Ni-Hard alloy during the same experiments was recorded and is shown in Figure 5.3.1.3. At all three temperatures, there was a significant carbon loss from the melt. Oxidation of carbon from molten Ni-Hard white iron was faster at 1660°C than it was at 1365°C.

5.3.2. Solubility of Nitrogen in Liquid Iron Alloys

Figure 5.3.2.1 shows the variation in maximum dissolved nitrogen content of the molten iron alloys at 0.78 atm N₂ partial pressure as a function of temperature. In this case, the nitrogen content of the ingots approximates the amount of nitrogen in the molten alloys, because

solidification took place at a pressure which was higher than the holding pressure of the melt. It is assumed that no significant change in the nitrogen content of the alloys took place during solidification. This assumption is based on previous experience as explained in the experimental procedure. The nitrogen content of the molten Ni-Hard alloy (2.5 wt% C) increased linearly with increasing temperature from about 0.0372 wt% at 1385°C to 0.0403 wt% at 1535°C. Nitrogen content of the 3.5 wt% carbon containing molten Ni-Hard alloy was considerably lower. This alloy contained less than 0.02 wt% N at all four temperatures investigated. Furthermore, a change in temperature did not have any effect on the solubility of nitrogen.

Molten high Cr white iron had one order of magnitude higher nitrogen solubility than the molten Ni-Hard alloys. The solubility of nitrogen in the molten high Cr composition increased with decreasing temperature.

Gray and ductile irons had lower nitrogen solubilities with slight increases in solubility with increasing temperature.

The average oxygen content in the ingots was 0.0022 wt% and did not vary significantly with temperature.

5.3.3. Solubility of Nitrogen in Solid Ni-Hard

Solubility of nitrogen in solid NiHard alloy was determined. It was found that the N solubility decreases with increasing temperature between 800°C and 1100°C according to:

$$[N] = \frac{24}{T} - 0.0052 \quad (5.3.3.1)$$

where [N] is nitrogen content in weight percent and T is temperature in K. Figure 5.3.3.1 shows the variation of N content of solid Ni-Hard with temperature.

5.4 Surface Tension

In all three liquid alloys (Ni-Hard WCI, High Cr WCI, and Gray cast iron), increasing temperature resulted in a decrease in surface tension. This is in agreement with the few existing studies [Hernandez, Naik, Jimbo]. The effect of impurities in liquid iron alloys on surface tension was also studied. Small amounts of sulfur and titanium had significant effects on the surface tension of liquid NiHard alloy. As shown in Figure 5.4.1, surface tension increased about

16% by increasing the sulfur content from 0.0095 to 0.0190 weight percent. The increase appears to be linear at temperatures between 1330°C and 1450°C. Addition of Ti, on the other hand, decreased the surface tension of liquid NiHard (Figure 5.4.2). This time the relationship was not linear and the change was less steep with only a 12% drop as Ti increased from 0.01 wt% Ti to 0.04 wt%. At higher Ti contents, the decrease in surface tension was less significant.

Effect of the same impurity elements (S and Ti) on surface tension was different in the liquid high Cr white iron composition. As shown in Figure 5.4.3, increasing S lowered the surface tension of liquid High Cr WCI in a linear fashion. The decrease in the surface tension was about 18% as the S content increased from 0.017 wt% to 0.042 wt%. The addition of Ti also lowered the surface tension, albeit in a non-linear fashion (Figure 5.4.4). Unlike the surface tension of liquid NiHard, the surface tension of liquid high Cr WCI changed slowly at low Ti concentrations and the decrease was more significant at higher Ti contents.

The surface tension of liquid gray iron was studied as a function of temperature and aluminum content as shown in Figure 5.4.5. Like the other compositions, the surface tension of liquid gray iron decreased with increasing temperature. This was observed at all Al levels studied. Rate of decrease was about 2.5 mJ/m²K at low Al level of 0.01 wt%. The rate of decrease went up to 3.3 mJ/m²K at 0.17 wt% Al. In general, the surface tension of liquid gray iron increased with increasing Al content.

An increase of about 300 mJ/m² in surface tension of a liquid alloy with compositional change or temperature change requires about 20% increase in gas pressure in a bubble of a given size to keep the bubble stable. Otherwise the bubble would collapse under the force of surface tension.

Effect of Ti addition on the solidification range of the white iron alloys was investigated using differential thermal analysis (DTA). Figure 5.4.6 demonstrates effect of Ti content on the solidification reactions during cooling. While the eutectic temperature is not affected by the addition of Ti, the liquidus is shifted to higher temperatures. This behavior is not clearly established in the Ni-Hard alloy as shown in Figure 5.4.7.

5.5 Interdendritic Flow

The eutectic flow velocity and the velocity-derived permeability of the dendritic plug are shown in Figures 5.5.1 and 5.5.2. The velocity of the eutectic fluid through the dendritic plug was seen to increase with temperature of the experimental system. This increase in velocity for higher temperatures was even more marked in the experiments which soaked the system at the flow temperature before allowing flow. These results follow the accepted relationship between dendrite density and coarseness. The cooling rate for the experiments is constant. During cooling, dendrites are nucleating and growing. When cooling is halted and the system held at a

constant temperature, nucleation for that temperature has largely completed and dendrite growth and coarsening now are the primary change occurring in the system. The coarsening of dendrites increases the permeability of a given structure by decreasing the average surface to volume ratio of the dendrites. Temperature shows an effect here in the rapidity of isothermal coarsening. The higher temperatures show evidence of greater coarsening and so greater increases in permeability given the same amount of time.

The linear relationship between the marker position and time (i.e., constant velocity) as shown in Figure 5.5.3 imply the constancy of both the pressure drop across the plug and the viscosity of the eutectic fluid over the time during the flow experiment. The pressure difference was modeled mathematically, using the density of the eutectic fluid, the surface tension results of related sessile-drop experiments with the eutectic alloy, the recorded heights of the liquid column over the dendritic plug and the weight of the marker. The force balance shown in Figure 5.5.4 was used to determine the pressure drop across the dendritic plug.

A dominant force was found to be the surface tension on the pendant of liquid that emerges from the bottom of the plug during experiments. This force grows from zero, when the pendant is just appearing to a maximum at the point where the pendant is closest to hemispherical in shape. Beyond this point, the pendant is experiencing plastic deformation and finally necking. To eliminate the regions where the pressure drop would be decreasing (as the pendant approached the hemispherical shape), the change in height of the marker was calculated as a function of the changing volume of the emerging pendant. The pendant volume was modeled by calculating the volume of spherical sections which would include the current pendant shape. Data points associated with the change in height required to fill this hemisphere were taken into account in pressure-drop calculations. An acceleration of the flow at the end of most of the experiments was explained by the characteristic increase in fluid flow during drop necking [Shin]. Position data from this acceleration point were also ignored to enable calculations with a constant pressure drop. The resulting permeability assumes a constant pressure drop across the plug, which holds both pendant surface tension and meniscus surface tension both at maximum.

Surface tension affects not only the forces involved in the IDF experiment, it also affects the shape of the dendritic plug and the eutectic column. The dendritic plug is thickest in the middle and thinnest at the corners. However, the change in thickness is slight until the corners of the plug are reached. Maximum difference in thickness is approximately 20%. The area of greatest thinning is, essentially, the difference in area of the crucible cross section and a circle inscribed in it (~27%). The average thickness of a corner is approximately 83%. Because the meniscus of the eutectic column is similar in curvature to that of the dendritic plug, the pressure at any point on the surface of the plug is essentially the same. The combination of equal pressure and unequal thickness leads to a probable higher velocity ($\leq 17\%$) of flow at the corners than at the middle of the plug. Since, however, the area experiencing this velocity difference and the

velocity difference itself are small, it was decided that an average thickness of the plug would be representative for the determination of permeability.

Finally, in order to show that the flow of eutectic liquid was occurring through the dendritic structure, and not around the dendritic plug between the plug and the wall of the quartz cell, an experiment was performed using 304 stainless steel as plug. It was shown that level of eutectic liquid did not change when the stainless steel plug was used. There was no flow through the plug due to lack of interdendritic space in 304 stainless steel, and neither was there any flow at the interface of the stainless steel and the quartz wall. A cross section of the 304 SS and the eutectic in the quartz cell is shown in Figure 5.5.5.

In another experiment to show the uniformity of the flow, a liquid composition which differed markedly from the eutectic composition and therefore was not near chemical equilibrium with the dendrites was allowed to flow through the dendritic structure of the Ni-Hard alloy plug. Because of the non-equilibrium case, there was a reaction between the liquid and the surface of dendrites. This reaction zone was delineated using picric etching and observed under an optical microscope as shown in Figure 5.5.6. Uniform thickness of the reaction zone suggests that the flow was uniform throughout the dendritic structure with no preferred path.

5.6 Quench Experiment Results

Figure 5.6.1 shows the average cooling rate of about 10 °C per minute of cooling rates attained in the IDFQ furnace. For structure investigations of the IDF experiments, the same approximate cooling rate was used to approach each quench temperature. Note, also, the range of cooling rates used to reach 1200 °C. These rates were used in the cooling rate study mentioned in chapter 4.7.

The primary and secondary dendrite arm spacing measured from IDFQ specimens are compared in Figure 5.6.2 to data cited by Flemings [5.6.1].

The liquid fraction at quench was determined using image analysis software (Figure 5.6.3). Samples were deeply etched to enhance the differentiation of dendritic and interdendritic structures. This enabled determination of solid fraction without requiring erosion or smoothing of the image electronically. Figure 5.6.4 shows a typical image used for this solid fraction determination.

5.7 Porosity Formation Model

This model surmises the formation of porosity voids in castings is a function of the ability of liquid to fill voids in the densest region of the mushy zone. The voids in the mushy zone occur

on shrinkage as the final interdendritic liquid freezes. A minimum volumetric flow rate of liquid must be achieved to fill these voids before final solidification of this liquid prevents flow. This minimum necessary flow rate is proportional to the progress, over time, of the freezing front as the casting solidifies – the “flow rate of solid”. The proportional constant is the ratio of the solid density of eutectic to its liquid density. Adequate flow rate of liquid into the areas of the mushy zone closest to the final solidification front is possible only as long as the pressure driving it through the mushy zone matches or exceeds the pressure drop which would occur at the minimum necessary flow rate.

The pressure drop across the mushy zone is a function of the resistance to flow of the dendritic structure formed there. The closeness of packing of parts of this dendritic structure is not constant across the mushy zone, but increases as one approaches the final solidification front. Therefore, the resistance to flow of a given length of mushy zone varies with its position within the mushy zone. Regions closest to the final solidification front will offer the greatest resistance. However, the ability of liquid to flow is already attenuated before these regions are encountered. This attenuation must be taken into account to prevent overestimating the minimum closeness of dendrite packing which would make porosity likely. This minimum necessary flow model, therefore, examines flow of eutectic liquid through a permeability gradient. The permeability of the dendritic regions of the mushy zone is smallest nearest the solidification front of the casting. As distance from this front increases, so does the permeability of the dendritic region at that distance. The rate of change of permeability through the mushy zone is a function of the temperature profile of the mushy zone as well as the local cooling rates in this zone.

The model describing the solidification of NiHard at the final stages of freezing is examined through the following scenario:

At a temperature approaching the freezing temperature of the NiHard eutectic composition, dendrites are assumed to have formed a fixed structure. This dendritic structure, considered static here, is not uniform. As mentioned above, as one travels up-temperature from the frozen front of eutectic, the permeability of the dendritic regions which have formed along that temperature gradient increases – a permeability gradient exists across the mushy zone.

Resistance to fluid flow is modeled, as in previous studies of interdendritic flow, by the D’arcy equation for average flow rate through porous media:

$$Q = \frac{KA}{\mu} \left(\frac{dP}{dx} \right) \quad (5.7.1)$$

where Q is the volumetric fluid flow rate normal to the plane of solidification, K is the permeability of the porous medium, A is the cross sectional area of the porous region, μ is the fluid's viscosity and dP/dx is the pressure differential in direction of flow across the porous medium. Examining flow through a finite element of constant permeability, equation (5.7.1) can be written as

$$Q = \frac{KA}{\mu} \left(\frac{\Delta P}{\Delta x} \right) \quad (5.7.2)$$

where $\Delta P/\Delta x$ is the finite pressure drop across the finite element.

Holding the volume flow rate constant at the minimum necessary flow rate, the pressure necessary to maintain that flow, and assuming constant viscosity of fluid in the finite element, the pressure drop across an element would vary with the permeability of that element as

$$\Delta P_i = \frac{Q\mu(\Delta x)_i}{K_i A} \quad (5.7.3)$$

so that

$$\sum_{i=1}^n \Delta P_i = \sum_{i=1}^n \frac{(\Delta x)_i}{K_i} \left(\frac{Q\mu_i}{A} \right) \quad (5.7.4)$$

gives the pressure drop across the permeability gradient.

The permeability of a porous medium can be determined through D'arcy's equation when values for ΔP , Q , μ , and Δx can be observed. Experiments for determining permeability by measuring these values are described below.

Permeability of a structure can also be determined by observing the structure of the porous medium. Previous studies have modeled the porous structure of columnar dendrites using the Hagen-Poiseuille equation which describes the flow rate of fluid through a bundle of capillary tubes [Streat, Santos]:

$$Q = \frac{n\pi r^4}{8\mu} \frac{\Delta P}{L\tau} \quad (5.7.5)$$

Where n is the number of capillaries per unit area, r is the average radius of the capillaries, L is the length of capillaries, and τ is the tortuosity factor. In dendritic structures, the capillaries in equation (5.7.5) are the interdendritic channels through the structure. The progression from equation (5.7.5) to a structurally-based equation for permeability given by Santos and Melo is repeated below in equations (5.7.6) through (5.7.15).

The effective length of the channel capillaries in a dendritic structure is defined as

$$L_e = L\tau \quad (5.7.6)$$

The volume fraction of liquid (g_L) is given by

$$g_L = \frac{n\pi r^2 L_e}{AL} \quad (5.7.7)$$

Combining equations (5.7.6) and (5.7.7)

$$g_L = \frac{n\pi r^2 \tau}{A} \quad (5.7.8)$$

and

$$r^4 = \frac{A^2 g_L^2}{(n\pi\tau)^2} \quad (5.7.9)$$

Substituting equation (5.7.9) into equation (5.7.5)

$$Q = \left(\frac{A g_L^2}{8n\pi\tau^3} \right) A \left(\frac{\Delta P}{\mu L} \right) \quad (5.7.10)$$

The similarity between equations (5.7.10) and (5.7.2) gives

$$K = \frac{Ag_L^2}{8n\pi\tau^3} \quad (5.7.11)$$

Next, consider flow through a columnar dendrite structure as shown in Figure 5.7.1.

For flow parallel to the axis of the primary dendrite arms, the cross sectional channel area presented to the liquid flow is approximately

$$A_i = \lambda_1^2 \quad (5.7.12)$$

For flow normal to the axis of the primary dendrite arms

$$A_i = \lambda_1\lambda_2 \quad (5.7.13)$$

The number of channels per unit area (n) is given by

$$n = \frac{A}{A_i} \quad (5.7.14)$$

Substituting equation (5.7.14) into (5.7.11) gives, for flow parallel to the primary dendrite arms,

$$K = \frac{g_L^2 \lambda_1^2}{8\pi\tau^3} \quad (5.7.15)$$

and

$$K = \frac{g_L^2 \lambda_1 \lambda_2}{8\pi\tau^3} \quad (5.7.16)$$

for flow normal to the primary arms.

It has been proposed that the tortuosity term might be described as in equations (5.7.17 through 5.7.19) [Santos] by a series of the form

$$\tau = \sum_{k=0}^i \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L^k} \quad (5.7.17)$$

The series' most predictive of experimental results for permeability, using equation (5.7.17) in (5.7.15) and (5.7.16) are, for flow parallel to primary arms, when $i = 3$

$$\tau = 1 + \left(\frac{\lambda_2}{\lambda_1} \right) + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L} + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L^2} + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L^3} \quad (5.7.18)$$

and for flow normal to primary dendrite arms, when $i = 2$ [Santos].

$$\tau = 1 + \left(\frac{\lambda_2}{\lambda_1} \right) + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L} + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L^2} \quad (5.7.19)$$

Combining equations (5.7.15) and (5.7.18), produces a dendritic permeability equation described by liquid fraction and dendrite arm spacing, exclusively

$$K = \frac{g_L^2 \lambda_1^2}{8\pi \left(1 + \left(\frac{\lambda_2}{\lambda_1} \right) + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L} + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L^2} + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L^3} \right)^3} \quad (5.7.20)$$

Equation (5.7.20) most correctly describes the permeability of a dendritic structure oriented to place the primary dendrite arms parallel to the axis of fluid flow through the structure. Equation (5.7.21), below, describes flow through a dendritic structure presenting its primary arms normal to the axis of fluid flow:

$$K = \frac{g_L^2 \lambda_1 \lambda_2}{8\pi \left(1 + \left(\frac{\lambda_2}{\lambda_1} \right) + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L} + \left(\frac{\lambda_2}{\lambda_1} \right)^{g_L^2} \right)^3} \quad (5.7.21)$$

As the permeability of the dendritic structure depends on dendrite arm spacing and liquid fraction, dendrite arm spacing depends on cooling rate and temperature. Flemings has shown that dendrite arm spacing can be calculated from the average cooling rate during solidification of the casting, observing that

primary dendrite arm spacing depends on the product of thermal gradient $[(G)]$ and growth rate $[(R)]$ Note the product GR has the units of cooling rate. . . , and experimental results are often expressed in this way. . . . Secondary dendrite arm spacings also depend directly on cooling rate. . . . Relationships found between dendrite arm spacing $[(d)]$ and thermal variables have the form

$$d = b(GR)^{-n} \quad (5.7.22)$$

where the exponent n is in the range of $1/3$ to $1/2$ for secondary spacings and generally very close to $1/2$ for primary spacings.[Flemings]

Applying equation (5.7.22) to (5.7.21) and (5.7.20), b and n_p are used in predicting primary arm spacing, while c and n_s are used for the equation dealing with secondary arm spacing. So

$$\lambda_1 = b(GR)^{-n_p} = b(\Delta T_t)^{-n_p} \quad (5.7.23)$$

$$\lambda_2 = c(GR)^{-n_s} = c(\Delta T_t)^{-n_s} \quad (5.7.24)$$

where ΔT_t is the change in temperature over time (cooling rate). Thus

$$K_{parallel} = \frac{g_L^2 (b(\Delta T_t)^{-n_p})^2}{8\pi \left(1 + \left(\frac{c(\Delta T_t)^{-n_s}}{b(\Delta T_t)^{-n_p}} \right) + \left(\frac{c(\Delta T_t)^{-n_s}}{b(\Delta T_t)^{-n_p}} \right)^{g_L} + \left(\frac{c(\Delta T_t)^{-n_s}}{b(\Delta T_t)^{-n_p}} \right)^{g_L^2} + \left(\frac{c(\Delta T_t)^{-n_s}}{b(\Delta T_t)^{-n_p}} \right)^{g_L^3} \right)^3} \quad (5.7.25)$$

and

$$K_{normal} = \frac{g_L^2 (b(\Delta T_t)^{-n_p}) (c(\Delta T_t)^{-n_s})}{8\pi \left(1 + \left(\frac{c(\Delta T_t)^{-n_s}}{b(\Delta T_t)^{-n_p}} \right) + \left(\frac{c(\Delta T_t)^{-n_s}}{b(\Delta T_t)^{-n_p}} \right)^{g_L} + \left(\frac{c(\Delta T_t)^{-n_s}}{b(\Delta T_t)^{-n_p}} \right)^{g_L^2} \right)^3} \quad (5.7.26)$$

Applying the Model

This model is applied to a set of finite elements, the size of which is inversely proportional to the steepness of the temperature gradient in the casting region being modeled. Figure 5.7.2 shows the temperature profile of a NiHard casting as calculated using the error function as in equation 5.7.27 [Flemings].

$$T = erf \frac{x}{2\sqrt{\alpha_s t}} (T_m - T_0) + T_0 \quad (5.7.27)$$

D'Arcy's equation describes the bulk behavior of a liquid passing through a porous structure. The representative volume of porous structure for this treatment is "...the volume above which the fluctuations in the void volume in the porous [structure] are negligible. This is the case when the element [being treated in the D'arcy equation] contains a sufficient number of pores and solid features... for example, when the length scale of the elementary volume is at least one order of magnitude greater than the pore scale"[Bejan]. With the pore size as defined in figure 5.7.1, measuring a maximum of about sixty microns, the minimum size necessary for the representative elementary volume is six hundred microns on a side. The element size used in this work is one thousand microns on a side.

Cooling rate (ΔT_t) for examination of the model in this work was calculated as the average linear difference in temperature of a given element over the time required for the element's temperature to change from the NiHard liquidus temperature of 1335 °C to its temperature at the time when the coolest element had reached 1127 °C which is the end of eutectic solidification.

Liquid volume fraction (g_L) was determined using functions derived from a Scheil calculation performed in ThermoCalc[®] for the Ni-Hard composition. Two functions were fit to the discontinuous curve portions shown in Figure 5.7.3, these functions were input to the model to give liquid volume fractions associated with average element temperatures input into the model.

The controlling flow rate was determined from the volumetric freezing rate for the interdendritic fluid.

$$Q_s = \frac{g_L(\Delta T_t)}{\Delta T_f} \quad (5.7.28)$$

where Q_s is the “solid flow rate” – the rate at which the interdendritic volume becomes filled with solid eutectic material, and ΔT_f is the temperature change over which the eutectic freezes (note, only binary alloys have a single temperature at which its eutectic forms). The numerator is multiplied by a unity volume. The minimum necessary volumetric flow rate is taken as Q_s in the finite element closest to the eutectic solidification temperature.

The necessary volumetric flow rate for liquid is proportional to the minimum necessary solid volumetric flow rate by the density ratio of solid to liquid.

$$Q = Q_s \frac{\rho_s}{\rho_l} \quad (5.7.29)$$

The minimum necessary velocity is that required to achieve the minimum necessary volumetric flow rate through an area smaller, proportional to the liquid fraction of a given element, than the cross sectional area of the element. This recognizes the equality of area and volumetric fractions in multiphase structures. In elements with low liquid volume fractions (i.e., low liquid area fractions) the constant necessary volume flow rate is achieved by relatively high flow velocities. As the liquid area fraction rises, the area through which that necessary volume may flow is increased. Thus, with warmer elements, having a larger area fraction of liquid, the necessary flow velocity is lower than with cool elements which have a smaller area through which the liquid must flow at a given volumetric rate.

The change in viscosity of the interdendritic fluid throughout the mushy zone is described by two functions. The function that applies at temperatures from the warmest end of the mushy zone to the beginning of eutectic solidification gives liquid viscosity as dependant only on temperature. This function uses relationships deduced by Chapman between viscosity, an energy parameter and a separation distance between atoms in the fluid. The fluid in Chapman’s work is made up of spherical atoms. Intermolecular forces are the primary aspect of momentum transfer in this fluid. Using this set of assumptions, a correlation curve was generated for liquid metals between temperature and viscosity. The estimation of liquid metal viscosity with respect to temperature

is described in detail in the literature [Geiger]. Using this technique, a viscosity/temperature relationship may be applied to a given metal's temperature profile in a casting. The viscosity/temperature relationship for the cast iron was used and is shown in Figure 5.7.4.

The change in viscosity of the interdendritic liquid in the temperature regime (1127 °C to 1135 °C) is changed with respect to solid fraction. This is because this temperature regime is that through which the interdendritic liquid in NiHard actually freezes. Its effective viscosity is a function of particles entrained in the liquid [Abulnaga]. The relationship between solid fraction entrained in liquid and the factor by which this solid-liquid mixture's viscosity exceeds the pure liquid's viscosity was determined by Thomas and is shown in Figure 5.7.5. In this region, the dendritic permeability is constant throughout and equal to the permeability developed by the eutectic solidification start region.

Porosity is predicted in this model when the head pressure at the liquid end of the mushy zone is less than or equal to the pressure drop (equation (5.7.4)) across the mushy zone, where the pressure drop gives the necessary volumetric flow rate to keep interdendritic volumes filled.

6. DISCUSSION

Nitrogen Pickup During Melting

The results in Figure 5.3.1.1 show that the temperature of the melt influences the kinetics of nitrogen entry significantly. Increasing molten metal temperature increases the rate of nitrogen pickup. On the other hand, these graphs do not show the possible effect of temperature on the solubility of nitrogen in molten white irons with certainty. This is because the nitrogen content of the molten white irons does not reach a steady state due to either the relatively short duration of experiments or because of change in chemical composition of the melt with time (for example, loss of carbon to oxidation and loss of Mn to evaporation and oxidation).

To see the effect of temperature increase on the solubility of nitrogen in the molten iron alloys, one would look at Figure 5.3.2.1. Solubility of nitrogen in the molten 2.56%C Ni-Hard white iron increases linearly with temperature. Evidently, the effect of temperature increase on the solubility of nitrogen in the molten Ni-Hard is not as big as its effect on the kinetics of nitrogen entry into the molten Ni-Hard.

The nitrogen content of the molten Ni-Hard with 2.56%C exposed to air for long times at 1365°C and 1660°C is higher than the solubility of nitrogen for alloys at similar temperatures held under Ar + N₂ gas mixture. For example, after 15 minutes of exposure to air at 1365°C, the nitrogen content of the molten Ni-Hard is 0.041 wt%. On the other hand, the solubility of nitrogen in the same iron at the same temperature is 0.037 wt% (Figure 5.3.2.1). In the same way, after 10 minutes of exposure to air at 1660°C, the nitrogen content of the molten Ni-Hard is 0.045 wt%. On the other hand, the solubility of nitrogen in the same iron at the same temperature can be estimated as 0.043 wt% from Figure 5.3.2.1. At longer holding times, the difference between these values grows larger. The difference can be explained with the oxidation of carbon (Figure 5.3.1.2). At 1365°C after 15 minutes of exposure to air, the molten Ni-Hard loses 0.26 wt% carbon. At 1660°C after 10 minutes of exposure to air, it loses 0.29 wt% carbon. It is well known that solubility of nitrogen in liquid iron alloys increases with decreasing carbon content [Pehlke, Gomersall]. Therefore, in the air exposure experiments, as the molten Ni-Hard I loses carbon with time, its nitrogen content goes up.

This is also shown in Figure 6.1 by the curves predicting the rate of nitrogen absorption by the liquid metal. The curves were plotted using the following rate equation [Gokcen]:

$$\log \frac{N_s - N_o}{N_s - N} = Kt \quad 6.1$$

where N_s is the solubility of nitrogen in the molten alloy at a given temperature, N_o is the nitrogen content of alloy before it was exposed to air, N is the nitrogen content of the alloy at a

given time, t , and K is a constant which contains thermodynamic conditions such as partial pressure of nitrogen available and size of the system. For plotting, an average K was calculated from the nitrogen absorption data for each condition in Figure 5.3.1.1.

The rate curves fit the data of short exposure times reasonably well. However, for the longer exposure times, the data deviate from the rate model. The experiments conducted without the Ar flow resulted in higher nitrogen concentrations in the molten iron alloy than predicted by the model at long exposure times. This also indicates that the solubility of nitrogen increases with time due to oxidation of carbon from the melt.

Air exposure experiments also show that the solubility of nitrogen is much higher in the molten high Cr white iron than that in the molten Ni-Hard white iron. This was confirmed by the N solubility measurements in the molten high Cr white iron (Figure 5.3.2.1). Also, it has been reported that Cr increases the solubility of nitrogen in steels [Pehlke, Rawers, Wada].

The air exposure experiments were designed to show that molten white irons can pick up significant amount of nitrogen from the atmosphere during induction melting. One has to understand that the rates of nitrogen pickup mentioned above are very much dependent on the specific setup of operation. These experiments were conducted in a very small induction furnace in which the molten metal was stirred rather vigorously. These rates will not apply to industrial scale induction melting practices. Because the surface area of the molten metal exposed to air compared to the volume of the molten metal is very much smaller and the induction stirring is slower in large furnaces, the rate of nitrogen pickup at a given temperature will be much smaller. This is shown in Figure 6.2. On the other hand, there are several points that would apply to industrial scale induction melting of white irons: (i) Molten white irons pickup nitrogen from the atmosphere during induction melting. (ii) Increasing superheat increases the rate of nitrogen entry into molten white irons. (iii) Using an argon blanket lowers the rate of nitrogen entry and decreases the final nitrogen content in molten white irons.

Contribution of Nitrogen to Porosity During Solidification

This subject is discussed here with respect to the solidification of the Ni-Hard alloy with the help of Figure 6.3. In this figure, the experimentally determined solubility of nitrogen in the 2.56%C containing Ni-Hard alloy in the solid and liquid state is plotted. It is assumed here that the nitrogen solubility in cementite is negligible and all nitrogen in solid is in austenite. Solubility of nitrogen in the remaining liquid below the liquidus is determined using a method that utilizes available experimental values and equilibrium calculations by means of the Thermo-Calc[®] software. First, the liquid volume fraction (Figure 5.7.3) and the carbon content of the remaining liquid (Figure 6.3) were calculated as a function of temperature between the liquidus and solidus. Then using the experimental nitrogen solubility values for the 2.56% and 3.56% carbon

containing liquid Ni-Hard alloys, a nitrogen solubility line for the remaining liquid was determined. Since the carbon content of the remaining liquid increases as the temperature decreases, the nitrogen solubility of the remaining liquid decreases drastically. The regression line fit to the experimentally determined data for the solid-state solubility of nitrogen was extended over the mushy zone to cover the solubility of nitrogen in the proeutectic austenite dendrites.

If a Ni-Hard alloy with similar composition to the one in Table 5.2.1.1 was poured in a mold and was allowed to solidify, the following scenario can be drawn with the help of the diagram in Figure 6.3. The N content of 0.0138 wt% of the liquid alloy would be constant until the liquid reaches the liquidus temperature. Then, with the formation of austenite dendrites, the nitrogen content of the remaining liquid will increase as the temperature decreases as shown in Figure 6.3. At around 1200°C, the nitrogen content of the remaining liquid will exceed the solubility limit of nitrogen in the remaining liquid. At this point, the excess nitrogen will start to evolve in gas form in the remaining liquid. Since at this temperature, a network of austenite dendrites is already formed, it is very likely that the evolving nitrogen gas will be trapped between the dendrites, thus resulting in porosity.

A similar alloy solidifying with a higher nitrogen content (for example, 0.02 wt% in Figure 6.3) will start nitrogen evolution at a higher temperature. At about 1250°C, the nitrogen content of the remaining liquid will exceed the solubility limit of nitrogen. As a result more nitrogen will evolve in gas form during the solidification of this alloy. On the other hand, at 1250°C, only 25% of the volume of the casting is solid and it may be easier for the nitrogen bubbles to escape.

As shown in Figure 6.3, the highest N concentration in this Ni-Hard composition that will not result in the nitrogen evolution is about 0.0090 wt%. In this case, the nitrogen content of the remaining liquid exceeds the solubility limit of nitrogen in the remaining liquid below the solubility limit of nitrogen in solid. This means that the remaining liquid can solidify without rejecting any nitrogen.

Interdendritic Flow

The experimental data are presented both taking surface tension into account and also, not using surface tension. As seen in figure 6.4, when surface tension is taken into account, the permeabilities are higher at all temperatures. Surface tension, being dominant under the NiHard plug, effectively lowered the determined pressure drop across the plug. In order to retain the constant, observed velocity with this lowered pressure drop the permeability of the plug must be greater than calculated without surface tension.

The experimental data used to determine the pressure drop across the NiHard filter were the mass of the marker, the NiHard, and the eutectic, as well as the cross sectional area of the crucible. These were combined to give volume and thicknesses of material involved in the experiment. After cooling, the NiHard filter was measured for an average thickness. The meniscus evident on both the NiHard plug and post-flow eutectic were used to take into account the possibility of surface tension being a significant contributor to the magnitude of pressure drop across the NiHard plug during eutectic flow.

The permeability model discussed in chapter 5.7 was applied to predict the results of the interdendritic flow experiments. The results are plotted in Figure 6.4. This model predicted the permeability for columnar dendritic structure in two orientations relative to fluid flow: parallel to primary dendrite arms and perpendicular to those arms. The model required inputs of liquid volume fraction at a given temperature, and the cooling rate of the specimen. The cooling rate was directly obtained from the IDF experiments. The liquid volume fraction was obtained either from the equilibrium calculations using Thermo-Calc[®] software (see Figure 5.7.3), or the quench experiments which were performed in parallel with the IDF experiments.

The model for flow parallel to the columnar dendrites predicted the experimental permeability results closely when the liquid volume fraction data from the equilibrium calculations were used. When the same data were used for the model predicting the permeability with flow perpendicular to the columnar dendrites, the predictions were lower than the observed permeability by a factor of about 0.5. The liquid volume fractions measured on the samples from the quench experiments. In this case, the predicted permeability for both parallel and perpendicular flow was considerably lower than the observed permeability. Image analysis results for the liquid volume fraction were about ten percent lower than the equilibrium values calculated using Thermo-Calc[®].

Application of Permeability Gradient Model

The permeability gradient model was constructed in order to test the impact of interdendritic channel constriction on the flow of liquid through the mushy zone of a casting. The model examines two different regimes: (i) Dendritic solidification regime where the permeability is dominated by changes in liquid volume fraction and dendrite arm spacing, and (ii) Eutectic solidification regime where the permeability is dominated by changes in viscosity of eutectic mixture. It is assumed that the eutectic mixture behaves like a slurry whose viscosity increases with increasing solid fraction. It was hypothesized that the strongest impact would be seen at the coolest, most solid end of the mushy zone and its impact multiplied by the length through which permeability of the dendritic structure was close to the minimum.

The primary avenue for control of the model was through the temperature profile examined. This profile could be changed by looking at the casting temperatures at different times, or by changing the temperature at the cooling end, or a combination of these two. Throughout a mushy zone of any length, the closeness of the packing of the included dendritic structures would give permeabilities ranging from nearly zero to highly permeable structures. It was hypothesized that this range of permeabilities would have a stronger affect on fluid flow when the mushy zone was longer. Then, even relatively permeable areas of the mushy zone would, by virtue of their length, make a significant contribution to the pressure drop resulting from a given volumetric flow rate of liquid.

To test the model, temperature and time values were taken to $T_0 = 1000\text{ }^\circ\text{C}$ and $t = 600\text{ sec.}$, respectively. The temperature profile predicted for this combination of parameters is shown in Figure 6.5. The liquid fraction (Figure 6.6) varied smoothly from the liquidus, 1300°C , to eutectic solidification start point at 1135°C . Starting at 1135°C , one third of the volume of mushy zone, the liquid eutectic, freezes over a temperature range of 9°C . Figure 6.6 shows that, given the constant cooling rate, the solidification rate of the eutectic portion of the mushy zone is significantly larger than the preceding dendritic solidification rate.

D'arcy's equation was applied to the portion of the mushy zone where the solid fraction had reached at least 0.50. It was assumed that below this solid fraction, the effect of the dendrites that have formed would be minimal compared to the effect above this solid fraction. With decreasing liquid fraction in the mushy zone, linear fluid velocity increases as shown in Figure 6.7 although volumetric velocity of the liquid remains constant. The increase in the linear velocity of the interdendritic liquid takes place until the temperature reaches the eutectic solidification start temperature where the dendrites stop growing. From this point on, we assume a constant dendritic structure with a constant permeability as shown in Figure 6.8. At this point, the linear velocity of the interdendritic liquid also becomes constant. The pressure drop below this temperature is assumed to be because of the increase in viscosity of the eutectic liquid mixture.

The liquid eutectic mixture is treated like a slurry. As the temperature decreases from the eutectic start temperature to the temperature where the system is completely solid, the viscosity of the liquid eutectic mixture increases. This increase is assumed to follow the relationship [Abulnaga] between the slurry viscosity and solid fraction in the liquid as shown in Figure 5.7.5. The pressure drop in the dendritic solidification zone and the eutectic solidification zone is shown in Figure 6.9.

Under the above temperature conditions, the model is predicting that a pressure head of 56 cm is required to have no porosity in the solidified structure. A large portion of the pressure drop in the

mushy zone is taking place at the cold end of the mushy zone where the eutectic solidification ends. This is the region where the viscosity of the eutectic slurry increases abruptly. If we accept that porosity will form in this region and do not worry about filling this porosity with liquid, the pressure head required to feed the next element is 1.6 cm. Furthermore, the pressure head required to feed the element that is located where the eutectic solidification starts is 0.85 cm. This would be the case of a binary alloy which solidifies in a dendritic fashion with some eutectic content. Since such an alloy completes freezing with a eutectic solidification reaction at one constant temperature, this model would consider the pressure drop due to dendritic solidification only.

Challenges for the In-Situ Measurement of Permeability

The newest aspect of these experiments, with respect to previous interdendritic permeability measurements was the fact that the dendritic structure was allowed to form in situ and was not cooled and re-heated for permeability tests. The primary difficulty with this in-situ method was the necessity of holding molten materials separate during melting and formation of the mushy structure while retaining the ability to release the eutectic onto the mushy structure at a chosen time. A system was required that would hold the liquid materials at high temperature without leaking. The fact that iron does not wet well to quartz was a key factor in the quartz crucible's ability to hold the material. Keeping the separation plates (gates) of the crucible firmly enough closed was achieved at the cost of ability to open those gates. Also, maintaining the correct alignment of the gates with respect to the crucible as it was opened was crucial to prevent the crucible or gate breaking. Since there was also some reaction between the quartz and metallic material contained, which roughened the walls of the crucible and the gates, the crucibles of failed tests (i.e. when gates could not be opened) could not be reused for future tests.

The design of the crucibles went through many permutations before finally settling on springs to be used to hold the gates in place. These springs were made of tungsten and were also single-use items. A system of stiffness testing for newly made springs would likely have resulted in more successful tests for interdendritic flow. High purity argon was blown at low velocity through the furnace to prevent oxidation of the specimen. This was also critical for the survival of the tungsten springs.

The progress of the eutectic liquid through the dendritic structure was recorded on a camera for later measurement. A high-resolution, digital video recorder made this possible. The main requirement here was to prevent the bright incandescence of the furnace blinding the camera's sensors. This was easily accomplished by attaching tinted glass in front of the lens. Position measurements were made on a digital screen and size relationships calibrated for permeability calculations.

For the size of the crucible, we were limited with the diameter of the furnace tube. The whole system can be made larger if a larger diameter furnace tube is used. Advantages of the larger system would be to have a larger head pressure on the eutectic liquid, a smaller meniscus to liquid height ratio, and more data points due to longer flow time. Also, a larger system can be easier to manipulate.

Overall, this was a workable system that steadily improved in robustness as experimentation continued.

7. ACCOMPLISHMENTS

Experiments

1. A new method to measure permeability of dendritic structures in situ
2. A new method to measure nitrogen solubility in liquid alloys

Models

1. A kinetic model predicting amount of nitrogen entry into molten alloy during a melting process as a function of holding time and temperature.
2. A thermodynamic model predicting amount of nitrogen evolution during solidification as a function of nitrogen concentration of liquid alloy and temperature.
3. A model predicting porosity formation during dendritic solidification

Publications to date

1. Liquid Metal Feeding Through Dendritic Region in Ni-Hard White Iron, D. Oryshchyn, O.N. Dogan, *AFS Transactions*, Paper No.05-115, (2005).
2. Nitrogen Absorption from Air by Molten Alloy White Irons, O.N. Dogan and J.S. Dunning, *Proceedings of the 65th World Foundry Congress*, 20-24 October 2002, Gyeongju, S. Korea, pp.45-52, (2002).
3. Nitrogen Pickup from Atmosphere by Molten White Irons, O.N. Dogan and J.S. Dunning, *AFS Transactions*, Paper No. 02-131 (2002).

8. CONCLUSIONS

Surface tension of liquid iron alloys (Ni-Hard white iron, high Cr white iron, and gray iron compositions) was determined using sessile drop test. Effect of S, Ti, and Al additions on the surface tension was investigated. In all tests, the surface tension of liquid iron alloys decreased with increasing test temperature.

While sulfur addition up to 0.019 wt% increased surface tension of liquid Ni-Hard alloy, additions up to 0.041 wt% S decreased the surface tension of the liquid high Cr white iron alloy. Titanium additions up to 0.15 wt% decreased the surface tension of both liquid Ni-Hard and high Cr white iron alloys. Aluminum addition up to 0.18 wt% increased the surface tension of liquid gray iron.

Considering that the Ti additions increase the solidification range of white irons and also reduce the surface tension of the liquid white irons, it is not recommended that it is used for nitrogen and oxygen scavenger during melting of these irons. Both increasing solidification range and reducing surface tension promote porosity formation.

To determine the amount of nitrogen entry in to white iron alloy during melting, a kinetic equation was employed. It was shown that significant amount of nitrogen can enter the liquid iron alloys from the air during induction melting.

Solubility of nitrogen in liquid Ni-Hard alloy, high Cr white iron, and gray iron was determined. Solubility of nitrogen in the high Cr white iron is an order of magnitude higher than that of the Ni-Hard alloy. An increase in carbon content of the Ni-Hard alloy from 2.5 wt% to 3.5 wt% decreased the solubility of nitrogen from about 0.04 wt% to 0.02 wt%. The solubility of nitrogen in both the liquid ductile and gray irons was about 0.01 wt%.

A model was established to determine the amount of nitrogen evolution in the mushy zone during solidification as a function of nitrogen content of the liquid Ni-Hard alloy. The model predicts that to solidify without evolving nitrogen, the maximum nitrogen content of the liquid Ni-Hard composition is 0.009 wt%.

A new method was developed to measure the permeability of dendritic structures in situ. The newest aspect of these experiments, with respect to previous interdendritic permeability measurements was the fact that the dendritic structure was allowed to form in situ and was not cooled and re-heated for permeability tests.

The permeability model for flow parallel to the columnar dendrites predicted the experimental permeability results closely when the liquid volume fraction data from the equilibrium

calculations were used. When the same data were used for the model predicting the permeability with flow perpendicular to the columnar dendrites, the predictions were lower than the observed permeability by a factor of about 0.5.

The permeability gradient model was constructed in order to test the impact of interdendritic channel constriction on the flow of liquid through the mushy zone of a casting. The model examines two different regimes: (i) Dendritic solidification regime where the permeability is dominated by changes in liquid volume fraction and dendrite arm spacing, and (ii) Eutectic solidification regime where the permeability is dominated by changes in viscosity of eutectic mixture. It is assumed that the eutectic mixture behaves like a slurry whose viscosity increases with increasing solid fraction.

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