EVALUATION OF THE EFFECT OF TUNGSTEN AND BORON ADDITIONS ON THE
MICROSTRUCTURE AND SOLIDIFICATION CRACKING SUSCEPTIBILITY OF
FE-MN-C FILLER METALS

THESIS

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ABSTRACT

High manganese steels are potential candidates for use in cryogenic applications as they exhibit desirable low temperature properties and are a cost-effective alternative to high-Ni steels (i.e. 9%Ni steel, Type 304L) and Invar alloys. Their cryogenic properties are derived from the austenite stabilizing ability of manganese. A potential use for these steels is in the fabrication of liquefied natural gas (LNG) storage tanks. The demand for natural gas is expected to increase 65% by the year 2040 and thus the need for cost-effective materials to replace conventionally used high-Ni alloys during construction of storage and transportation tanks is relevant. When fabricating these LNG tanks, welding is a critical procedure and thus the weldability of these high manganese steels must be evaluated. In this study, the effect of tungsten (W) and boron (B) additions on the microstructure and solidification cracking susceptibility of Fe-Mn-C filler metals was evaluated.

Five compositions with tungsten additions up to 4.7 wt% and boron additions up to 27 ppm have been evaluated. Susceptibility to solidification cracking of these filler metals was determined using the Cast Pin Tear Test (CPTT). Solidification simulations were conducted using the Scheil approximation within Thermo-Calc™ and actual solidification temperature range measurements were conducted using the Single-Sensor Differential Thermal Analysis (SS-DTA™) technique. Metallurgical characterization was...
carried out using both optical microscopy, and scanning electron microscopy. The objective of this study was to determine the optimum range of tungsten and boron additions within the compositional range of interest that provides adequate resistance to weld solidification cracking.

Results from Scheil simulations indicated only slight variations in the solidification temperature range (STR) among the alloys tested. The simulations showed that W additions lowered the liquidus temperature and subsequently the STR while B expanded the STR, which is attributed to its strong partitioning effect. Using SS DTA, the measured STR for each composition was larger than the Scheil simulations but demonstrated similar trends. Boron appeared to have the most influential effect on the expansion of the STR in these alloys due to segregation.

To assess the solidification cracking susceptibility, two rounds of CPT testing were performed to verify the lower cracking threshold (LCT) and rank the alloys. Both rounds of CPTT results ranked the Base composition (no W or B) as the least susceptible to cracking while the Low W/High B alloy exhibited the highest susceptibility to solidification cracking. A trend from CPTT results showed that higher W additions to both low and high B compositions resulted in a slight increase in resistance to solidification cracking susceptibility. All compositions had LCT values below 1.0 in., indicating that these alloys would be susceptible to solidification cracking, based on previously tested Ni-base alloys using the CPTT. Thus, additions of W to the low B alloys resulted in an increase in cracking resistance.
Characterization of CPTT and button samples showed that each filler metal composition exhibited primary austenite solidification with no evidence of martensite (α’ or ε) or other primary phases. The CPTT specimens exhibited fracture surface morphologies that were characteristic of solidification cracking. Three secondary phases were identified: Titanium nitrides, manganese sulfides, and titanium sulfides/carbosulfides. No boron rich constituents were found during this investigation and more advanced characterization techniques would be needed to evaluate the segregation behavior of boron. There was no evidence of backfilling in any of the CPTT samples examined that could potentially lead to crack healing. The formation of titanium sulfide/carbosulfide during solidification expanded the solidification temperature range and contributed to the overall poor resistance to solidification cracking exhibited in these alloys.

In general, it was determined that the Fe-Mn-C filler metals investigated in this study would be susceptible to solidification cracking under moderate restraint conditions. The presence of boron and sulfur, even at relatively low levels (≤ 50ppm), promoted an increase in solidification cracking susceptibility. No combination of W and B additions was able to provide adequate resistance to weld solidification cracking. Boron appeared to have the most dominant effect on cracking susceptibility while tungsten had a minor positive contribution. This conclusion was reached based on the findings from the CPTT results, solidification analysis, and metallurgical characterization of these filler metals.
DEDICATION

This work is dedicated to my loving wife, Alexys Lenzo, my family, and my friends whom have supported and encouraged me throughout my life.
ACKNOWLEDGEMENT

I would like to acknowledge my graduate research advisor, Dr. John Lippold, for his support and guidance throughout my research here at The Ohio State University. I would also like to thank Ed Pfeifer and Ken Copley for help when troubleshooting laboratory testing equipment and support in conducting my research at the Edison Joining Technology Center. I would also like to acknowledge sponsor, POSCO, for providing materials, funding, and support on this research project over the past two years. A special thanks to my fellow graduate research students whom have helped guide me in my research endeavors and provided great friendship during my graduate career.
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CHAPTER 1: INTRODUCTION AND MOTIVATION

The need for cleaner, more efficient and more versatile energy has generated increased interest in natural gas as an energy source. The global demand for natural gas is projected to rise by 65 percent from 2010 to 2040, the largest volume growth of any energy source [1]. The use of natural gas is expected to increase due to its cleaner-burning properties, versatility, efficiency and availability. This increased demand has generated a revival of interest in the transport and storage of liquefied natural gas (LNG) [2]. An example of the typical design of an above-ground LNG storage tank is shown in Figure 1. The storage tank shown below has a gross storage capacity of 200,000 m$^3$ with a diameter of 84 m [3].

![Figure 1: Example of a full containment LNG storage tank](image-url)
The increased demand for fabrication of LNG storage and transportation tanks will be required as well as development of new cost-effective materials. When natural gas is liquefied at cryogenic temperature (-163°C), the volume is decreased by about 1/600, which drastically simplifies the storage and transportation but results in increased fabrication costs due to the need to store the LNG at very low temperatures [5]. Conventionally, LNG tanks have been fabricated using Invar and high-Ni steels (i.e. 9%Ni steel, Type 304L, etc.), but these materials are undesirable due to high material and fabrication costs, low design strength, and welding difficulties [5]. As a result, high-Mn steels have become strong candidates due to their desirable low temperature properties and cost benefit from alloying with manganese. Choi et al. showed the price ratio of Ni to Mn from 2004 to 2011 and illustrated that the price of manganese is significantly lower than nickel. An adapted version of his chart is shown in Figure 2 to reflect the current price ratio of Ni to Mn over recent years. The figure demonstrates that the cost of manganese ranges from about 1/4 to 1/8 the price of nickel. The basic alloy design concept behind high-Mn steels for cryogenic service is to utilize the austenite stabilizing capability of manganese, as opposed to nickel, to achieve desirable low temperature properties [6]. High-Mn alloys closely mimic Ni alloys and are stable in the austenite phase field. With appropriate strengthening mechanisms, cost-effective high-Mn alloys can combine high strength with excellent toughness at cryogenic temperatures [5].
With further advancements in the development of high-Mn steels, attention has been drawn to the development of welding consumables. If efficient, low cost welding consumables are developed for these steels, the total construction costs of LNG tanks may be significantly reduced [5]. When fabricating LNG tanks, welding is a critical procedure and thus the weldability of these high-Mn steels and welding consumables must be evaluated. Little research has been done in regards to the weldability of high-Mn steels and one main concern for these alloys is the potential for solidification cracking. Alloys that solidify with fully austenitic microstructures, such as high-Mn steels, tend to be the most susceptible to solidification cracking [7]. The presence of a susceptible
microstructure and high weld restraint during fabrication of LNG storage tanks gives rise to the concern for solidification cracking.

The main purpose of this study is to examine the effect of the alloying additions tungsten and boron on the solidification behavior, microstructure and solidification cracking susceptibility of Fe-Mn-C filler metals. The Cast Pin Tear Test (CPTT) was used to examine the relative solidification cracking susceptibility of Fe-Mn-C alloys with the additions of tungsten and boron. In conjunction with the CPTT, the use of SS DTA, non-equilibrium Scheil solidification simulations, and LOM/SEM techniques were used to determine the susceptibility to solidification cracking in these high-Mn filler metals.
CHAPTER 2: BACKGROUND

2.1 HIGH-MN STEELS FOR CRYOGENIC APPLICATIONS

Over the years, high manganese steels have been extensively studied for cryogenic applications [5, 8-10]. The results from research showed that excellent cryogenic mechanical properties, specifically high strength and toughness, can be obtained. The use of structural materials for LNG applications requires high strength but also excellent low temperature toughness to prevent catastrophic failure during service. Liquefaction of natural gas requires a reduction in volume by 1/600, making storage and transportation easier. However, this liquefaction results in cooling to cryogenic temperatures as low as -163°C, which increases fabrication costs. Since conventional structural materials are unsuitable for cryogenic applications, as they have a BCC (Body-Centered-Cubic) structure and exhibit a ductile to brittle transition temperature, special alloys are required. These special alloys must exhibit an FCC (Face-Centered-Cubic) structure that does not normally undergo a ductile to brittle transition. These alloys include 9% Ni steels, austenitic stainless steels, maraging steels, titanium alloys, aluminum alloys, and nickel alloys [11]. The properties and cryogenic characteristics of commonly used base materials and welding consumables are shown in Figure 3.
With the majority of the conventionally used alloys containing high amounts of nickel, construction with these alloys will incur a high cost. Thus, there is a strong motivation to replace nickel with less expensive alloying elements, such as manganese. With manganese being significantly cheaper, it is a strong candidate to replace nickel as the Fe-Mn phase diagram is almost identical to the Fe-Ni diagram on the iron rich side, as illustrated in Figure 4 [2]. Manganese is readily available, inexpensive, and has an intriguing metallurgical similarity to nickel in its effect on the microstructures and phase relationships of iron-base alloys [12]. From what has just been explained, it can be seen that an understanding of the basic metallurgy, including the phase stability and low temperature behavior, of high-Mn steels must be examined.

Figure 3: Conventionally used base metals and welding consumables for LNG tank construction [5]
2.2 Metallurgy of High-Mn Steels

This section serves to give some background on the basic metallurgy of high-Mn steel alloys including the phase stability and low temperature behavior that is pertinent to the alloys used in this investigation. In addition to the metallurgy, a brief overview of the history and common applications for austenitic, high-Mn steels will be discussed.
2.2.1 Phase Stability

The term “high-Mn” steels can be somewhat vague in terms of exactly how much Mn is being added, and thus it is important to distinguish the various classes of high-Mn steels. Currently, there are different classes of binary Fe-Mn steels that exhibit significant differences in their metallurgy and properties [2]. Morris, separated them into four main classes:

1) Conventional ferritic (α) or martensitic (α’) alloys – [Mn < 8 wt%]
2) Mixed ferrite-ε martensite alloys (α’+ ε) - [Mn between 8-16 wt%]
3) Mixed austenite-ε martensite alloys (γ + ε) – [Mn between 17-30 wt%]
4) Austenitic Fe-Mn alloys (γ) – [Mn > 30 wt%]

It should be noted that these classes are just a basis for the binary system of Fe-Mn alloys and that the compositional ranges shown can be altered by alloying with elements that change the phase stability and/or martensitic transformation temperatures.

For this investigation, relatively high amounts of Mn are added and a good starting point to understand the phase stability of these alloys is the Fe-Mn binary system, shown in Figure 5. The basis of high-Mn steels is heavily alloying manganese (≥12 wt%) with iron to expand the austenite (γ) phase field and promote austenitic solidification. When analyzing the Fe-Mn phase diagram, suppression of the high temperature ferrite (δ) phase occurs when approximately 12 wt% Mn is alloyed with Fe. Another interesting feature of this phase diagram is the narrow two phase region separating the liquid (L) and the austenite (γ) phase fields. This narrow region suggests that very little segregation in
this binary system will occur during solidification in regards to manganese. When evaluating the high-Mn steel filler metals used in this investigation, due to the high alloying of austenite stabilizing elements, the formation of any low temperature ferrite (αFe) during solidification would not be expected.

Figure 5: Fe-Mn equilibrium phase diagram [13]

Another primary alloying addition to high-Mn steels is the addition of carbon. Carbon acts as both an austenite stabilizer and solution hardening element, which can combine high strength and toughness at cryogenic temperatures in carbon-containing high-Mn steels [5]. The Fe-Mn-C alloy system has been studied for some time and a more detailed thermodynamic assessment can be found here [14]. A more practical review of this system, in regards to the alloy compositions examined in this investigation,
will be discussed here. To start, it is useful to examine the pseudo-binary phase diagram of the Fe-Mn-C system at 20 wt% Mn, illustrated in Figure 6. As the figure illustrates, no high temperature ferrite is present, due to the high Mn additions (20 wt%). Another important feature to point out in this isopleth is the formation of high temperature, $M_3C$ carbides at elevated levels of carbon, where “$M$” represents either Fe and/or Mn. Other carbides, not shown in Figure 6, exist in this system including $M_{23}C_6$, $M_5C_2$, and $M_7C_3$ [15]. In addition to this carbide formation, a eutectic reaction ($L \to \gamma + M_3C$) is present in this system just below 1130°C and exhibits a composition of approximately Fe-20Mn-4.2C. The addition of carbon to the Fe-Mn system also appears to widen the two phase ($L+\gamma$) region, as compared to Figure 5, suggesting carbon readily segregates to the liquid during solidification.

Figure 6: High temperature isopleth of the Fe-Mn-C system at 20 wt% Mn [6]
Another important feature of high manganese steels, in contrast to Fe-Ni steels, is the intrusion of $\varepsilon$-martensite in between $\alpha'$-martensite and austenite regions [5]. These martensitic phases form as a result of non-equilibrium solidification conditions. A Fe-Mn-C stability diagram (Figure 7), that was developed by Schumann, illustrates these martensitic phases. The presence of the $\varepsilon$-phase is mechanically unstable with respect to deformation at low temperature and transforms to $\alpha$-martensite. This $\varepsilon$-phase appears to deteriorate the cryogenic toughness of austenitic alloys; both strength and toughness increase as the austenite is stabilized by increased Mn content [9]. Referring to the figure, when enough carbon and manganese are added, the austenite phase is stable, even at cryogenic temperatures.

Figure 7: Fe-Mn-C phase stability diagram [16]
When examining the binary Fe-Mn phase diagram, it can be seen that very high Mn contents are required to achieve stable austenitic microstructures, which is needed for use in cryogenic applications. In order to reduce the required amount of Mn needed to obtain stable austenite and inhibit the intrusion of ε-martensite, alloying with elements such as C, Al, and Si help permit the manufacture of austenitic alloys at 20-28 wt% Mn [2]. These elements, in addition to small amounts of Ni, enhance the overall strength of these alloys making them suitable for cryogenic applications. As can be seen, a variety of elemental additions and alloying combinations can be done that have an effect on the overall phase stability of these high-Mn alloys.

2.2.2 LOW TEMPERATURE BEHAVIOR

For alloys to be used in LNG fabrication at cryogenic temperatures, they must exhibit good low temperature toughness as well as meet strength requirements. A big factor in maintaining low temperature properties is exhibiting an FCC structure that will have a low ductile-brittle transition temperature. Research, dating back to the 1960’s, evaluating the Fe-Mn system for cryogenic applications has provided insight regarding the low temperature behavior of high-Mn steels at cryogenic temperatures. A primary factor for exhibiting good low temperature properties in these alloys is the suppression of any martensitic phases, more importantly ε-martensite, which can be controlled by chemical composition. Therefore, it is important to examine the low temperature behavior of high-Mn steels for LNG applications.
When examining the low temperature behavior, two important material properties should be looked at: low temperature toughness and low temperature fatigue behavior. To get an idea of material property requirements of high-Mn steels for LNG tank construction, Choi et al. listed target tensile strengths and charpy impact data at cryogenic temperatures. The initial material property requirements, according to IGC code, are shown in Table 1. The target tensile strengths (≥ 400 MPa) at room temperature and charpy impact energy at cryogenic temperature (-196°C) are shown for both the base material and welding consumables.

Table 1: Target properties of high-Mn steels for LNG tank [17]

<table>
<thead>
<tr>
<th>Chemical Composition (wt %)</th>
<th>High Mn</th>
<th>Welding Consumable (FCAW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Strength (0.2%, MPa)</td>
<td>≥ 400</td>
<td>≥ 400</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>≥ 560</td>
<td>≥ 560</td>
</tr>
<tr>
<td>Charpy impact energy (J, -196°C)</td>
<td>≥ 54 (transverse)</td>
<td>≥ 54</td>
</tr>
</tbody>
</table>

Charpy V-notch (CVN) tests determine the amount energy absorbed by a material during fracture that determine toughness properties and the temperature dependent ductile-brittle transition. In regards to high-Mn steels, two primary researches, Schanfein [9] and Tomota [18], have provided CVN impact data for various Fe-Mn steel compositions. The results from their investigations are shown in Figure 8, with variations in Mn from 4-36 wt%. The CVN data showed that as the Mn additions increased, the
ductile-brittle transition was decreased, or shifted to lower temperatures. This decrease in DBTT could be attributed to a decrease in the volume percent of α present [9].

Figure 8: CVN impact data for various Fe-Mn alloys: (Top) 4-20 wt% Mn [9] and (Bottom) 16-36 wt% Mn [18]
To further examine the properties of these alloys, Tomota et al. developed a strength-toughness relationship by plotting the CVN data versus strength at -196°C. This plot, Figure 9, shows that toughness decreases monotonically with strength and that a balance is required to achieve desirable properties.

![Graph showing strength-toughness characteristics of high-Mn alloys](image)

Figure 9: Strength-toughness characteristics of high-Mn alloys [18]

In addition to toughness properties of Fe-Mn alloys, the low temperature fatigue properties have been evaluated. In 2013, Choi et al. published fatigue crack growth data from an unspecified Fe-Mn alloy and compared it to fatigue data from conventionally used materials. The fatigue crack growth rates for this Fe-Mn alloy were measured at room temperature and -163°C. The results from the test, shown in Figure 10, demonstrated that growth rate in the Paris range was independent of test temperature and that at -163°C, the threshold stress intensity was higher, indicating a higher cyclic stress
is needed to initiate a fatigue crack [5]. When comparing the test results from the Fe-Mn alloy to other cryogenic materials (i.e. 9%Ni steel, AISI 304, etc.), the fatigue crack growth rate characteristics were similar.

![Figure 10: Effect of test temperature on the fatigue crack growth rate of high-Mn steel [5]](image)

2.2.3 HIGH-MN STEEL APPLICATIONS

The development of high-Mn steels originated from British metallurgist Robert Abbot Hadfield in 1868. The original austenitic manganese steel, named Hadfield steel, contained about 1.2% carbon and 12% manganese and was unique in that it combined high toughness and ductility [19]. Hadfield steels exhibited good wear resistance and were primarily used in earthmoving equipment, mining, railroading, and steelmaking products. Since their original discovery, a variety of applications, other than cryogenic applications, for these steels have been explored with the most notable one being the automotive industry. For the automotive industry, improved safety standards, reduced
automotive body-in-white weight, and manufacturing processes requiring a superior formability, have led to a strong interest in AHSS and high toughness, high Mn steel characterized by Twinning-Induced Plasticity (TWIP) [20]. As illustrated in a Figure 11, high-Mn alloys can exhibit superior ductility and strength, unlike other commonly used alloys in the automotive industry. The high strength and ductility results from two different modes of deformation: twinning induced plasticity (TWIP) and transformation induced plasticity (TRIP). In TWIP steels, the deformation is achieved by dislocation motion and twinning and believed to be due to a dynamic Hall-Petch effect [21]. Formation of mechanical twins create new crystallographic orientations that increases the flow stress by inhibiting dislocation motion that results in high strain hardening rates. TRIP steels obtain their high strength and ductility from a martensitic transformation that occurs during deformation. The ability of high-Mn steels to exhibit both high strength and ductility is extremely beneficial for use in the automotive industry.

Figure 11: Ductility-strength relationship of and high strength steels [22]
2.3 Weld Solidification Cracking

Weld solidification cracking is a phenomenon that has been the subject of considerable study, in a wide variety of engineering alloys, over the past 40 years [23]. Weld solidification cracking occurs during the final stages of solidification where liquid films persist along solidification grain boundaries (SGBs), and occasionally solidification subgrain boundaries (SSGBs), in the fusion zone. Though solidification crack formation is fairly well understood, the precise micromechanisms responsible for cracking is not fully known. What is known, is that the simultaneous presence of (1) thermally or mechanically imposed restraint and (2) a crack-susceptible microstructure will result in solidification cracking. The imposed weld restraint can be both intrinsic and extrinsic causes. The crack-susceptible microstructure comes from the presence of liquid films along solidification grain boundaries.

A schematic of the boundaries found in single-phase, austenitic materials weld metals is illustrated in Figure 12 [24]. In the fusion zone, various types of boundaries or interfaces can exist and it is important to understand the nature of boundaries since many of the defects associated with the fusion zone occur along these boundaries [23]. Three different boundaries can be observed in single-phase weld metals: (1) Solidification subgrain boundaries (SSGBs), (2) Solidification grain boundaries (SGBs), and (3) Migrated grain boundaries (MGBs). SSGBs are formed as a result of cells or dendrites during solidification process and carry a low angle misorientation. SGBs form when groups, or packets, of solidification subgrain boundaries intersect and create a crystallographic misorientation across the boundary. Solute redistribution and impurity
segregation occurs during solidification to SGBs and can lead to the formation of low-melting liquid films that can promote weld solidification cracking.

Figure 12: Schematic of boundaries in single-phase weld metal [24]

With the primary application for these high-Mn steel alloys used in this investigation being LNG fabrication, there is concern for solidification cracking. These alloys exhibit a fully austenitic microstructure upon solidification and will be fabricated under high restraint conditions. This section will give an overview of weld solidification and weld solidification cracking theories. It will go over basic welding metallurgy concepts and proposed solidification cracking theories that have been developed since the 1940s.
2.3.1 Solidification of Welds

The integrity and performance of a weld is, to a large extent, controlled by the solidification behavior of the weld metal or fusion zone [25]. The solidification behavior in the fusion zone dictates the size and shape of grains, segregation effects, and weld metal microstructure. Thus, the properties and integrity of the weld greatly depend on the solidification behavior making it essential to understand. In solidification mechanics, there are various solidification parameters that influence the microstructure and solute redistribution during solidification [23]:

- Partition coefficient: \( k = \frac{C_S}{C_L} \)
- Liquid temperature gradient: \( G_L = \frac{dT_L}{dx} \)
- Solidification rate: \( R = \frac{dx}{dt} \)
- Cooling rate: \( G_L \times R = \frac{dT}{dt} \)

These solidification parameters can cause instabilities of the solid-liquid interface during non-equilibrium solidification and directly influence the chemical inhomogeneity of a solidifying weld pool, and as a result strongly influence solidification cracking behavior [6].

For weld solidification to begin, solid nucleation in the liquid phase must occur. Solid nucleation can occur in two ways: homogeneously or heterogeneously. In the case of fusion welding, heterogeneous nucleation, and often of the epitaxial nucleation type, occurs from an existing substrate or foreign particle, requiring little or no undercooling. Epitaxial nucleation results when the crystallographic orientation of the parent grain is maintained across the fusion boundary along \(<100>\) growth directions, or “easy growth” directions. As solidification continues, the misorientation of the solidifying grains will
cause an intersection of grains that will compete, referred to as competitive growth, and more favorably orientated grains will continue to grow. An illustration of epitaxial nucleation and the “easy growth” directions is shown in Figure 13.

![Figure 13: Schematic illustration of epitaxial nucleation](image)

During the solidification process, various modes of solidification can occur at the solid-liquid interface (S-L) that are primarily controlled by the temperature gradient (G_L), solidification rate (R), and composition. The morphologies that are possible are: planar, cellular, cellular dendritic, columnar dendritic, and equiaxed dendritic. The two most common solidification modes found in fusion welds and castings are cellular and cellular dendritic modes [23]. In weld metals, the two parameters that influence the solidification mode the most are the combination of solidification growth rate (R) and temperature gradient (G_L), as illustrated in Figure 14. As can be seen, planar growth is only favorable
when the gradient is high and/or the solidification rate is high. As the solidification rate is increased, cellular and dendritic modes of solidification are more favorable. It should be mentioned that composition also has an effect on the solidification mode and that most alloys will solidify as cellular or dendritic, or a combination of the two.

Figure 14: Effect of temperature gradient in the liquid and solidification growth rate on solidification mode [23]

Solidification occurring under nonequilibrium conditions, such as welding, can be examined from a macroscopic and microscopic standpoint. The macroscopic solidification viewpoint describes the solidification at the trailing edge of the weld pool and at solidification grain boundaries. This primarily considers the influence of welding parameters such as heat input and travel speed as well as the weld pool shape and size. For example, the weld pool can have either an elliptical or teardrop shape depending on the welding conditions. An elliptical weld pool is usually a result of high heat input and
low travel speeds while a teardrop weld pool results from fast travel speeds. Teardrop-shaped weld pools should be avoided, especially in high-restraint conditions as centerline cracking can be an issue. Other macroscopic aspects such as fluid flow and surface tension can have an effect on weld solidification [23]. Microscopic solidification describes the formation and solute redistribution of subgrains such as dendrites and cells as well as examine effect of solidification parameters.

Another important aspect of weld solidification is solute redistribution between the liquid and solid. The extent of solute redistribution that takes place within an alloy system is defined by the partition coefficient (k). If the partition coefficient is less than one, the liquid and solid become increasingly enriched in solute as the temperature decreases within the solidification temperature range, and the liquid phase is more highly enriched in solute than the solid phase [23]. It is important to examine the effects of solute redistribution as the formation of low-melting liquid films along boundaries can potentially result in solidification cracking.

2.3.2 Solidification Cracking Theory

As mentioned earlier, solidification cracking has been extensively studied over the past 40 years but the precise micromechanisms responsible for the cracking is not completely understood. Various theories of welding solidification cracking have been proposed and will be discussed here. The various theories are effectively identical and embody the concept of formation of a coherent interlocking solid network that is
separated by continuous liquid films and ruptured by the tensile stresses [26]. The most notable theories that will be discussed, from oldest to newest, include:

1) Shrinkage-Brittleness Theory
2) Strain Theory
3) Generalized Theory
4) Modified Generalized Theory
5) Technological Strength Theory

The Shrinkage-Brittleness Theory was developed in the 1940’s by Russian researcher Bochvar [27] as a result from his work done on aluminum castings. In addition to the work from Bochvar, the theory was further developed by Pumphrey [28] to describe the cracking behavior during castings and welding of aluminum alloys. The basis for this theory is the existence of a “coherency” temperature and “effective interval” during solidification. At the “coherency” temperature, solid begins to interact and a coherent dendritic structure is formed. These solid-solid bridges, or dendrites, then begin to accumulate strain due to shrinkage and is termed the “effective interval” during solidification. A schematic illustration of the Shrinkage-Brittleness Theory is shown in Figure 15. Above the “coherency” temperature, solidification cracking will not occur as a high ratio of liquid to solid is present allowing liquid to move freely between cells or dendrites. Solidification cracking can only occur during the “effective interval” or when some strain has accumulated due to solid-solid bridging. The susceptibility to solidification cracking increases as the “effective interval” size increases, illustrated in
Figure 15. The “effective interval” size is influenced primarily by the alloy’s composition and amount of eutectic liquid present. If some alloy system exhibits a eutectic reaction at the end of solidification, it is possible that crack “healing” could result from sufficient liquid present to backfill the crack.

![Figure 15: Shrinkage-Brittleness Theory based on a eutectic phase diagram [23]](image)

The Strain Theory, proposed by Pellini in the early 1950’s, was developed to explain the observations of hot tearing exhibited in castings and, later on, solidification cracking in welds [29]. In this theory, Pellini introduces two stages of solidification, a “mushy” stage and a “film” stage, as shown in Figure 16. The mushy stage during solidification is a mixture of solid and liquid, mainly liquid, that occurs at temperatures above the film stage. Weld solidification cracking, based on the strain theory, is not possible during the mushy stage due to the uniform distribution of strain in the solid-
During the film stage, continuous liquid films persist along grain boundaries that can be easily separated due to high strain accumulations during solidification. This differs from the Shrinkage-Brittleness Theory in that cracking is a liquid-solid separation as opposed to solid-solid separation.

The film stage is divided into two different stages: (1) normal film stage (equilibrium) and (2) segregate film stage (nonequilibrium). The normal film stage refers to the end of solidification where only liquid films remain in the structure. The segregate film stage refers to nonequilibrium weld solidification conditions where segregation extends the temperature range. As illustrated by Figure 16, the normal film stage only occurs over a short temperature range while the segregate film stage occurs over a larger temperature range. The depression of the solidus allows for increased strain accumulation during the film stage resulting in an increased susceptibility to solidification cracking. When strain accumulation exceeds the ductility of the boundary, resulting is separation of the liquid-solid boundary, cracking will occur.
In 1960, J.C. Borland of the British Welding Research Association proposed the Generalized Theory, a modification of the Shrinkage-Brittleness Theory and the Strain Theory [30]. Borland’s theory adopted the idea of the “coherency” temperature from the Shrinkage-Brittleness Theory and added an additional stage during solidification called the “critical solidification range”, or CSR. The CSR corresponds to the lower part of the “effective interval” and is illustrated in Figure 17. The Generalized Theory proposed by Borland can be broken down into four stages:

- **Stage 1:** “Mushy” stage – Widely dispersed dendrites surrounded by liquid capable of relative motion
- **Stage 2:** “Coherency” range – Dendrite interlocking and continuous liquid films move freely between interlocked dendrites where crack healing is possible
- **Stage 3:** “Critical” range – Semi-continuous network of solid dendrites – crack healing not possible
- **Stage 4:** Solidification has completed

Borland explained that above the “critical” range but below the “coherency” temperature, crack healing was possible with sufficient liquid present. In the “critical” range, no crack healing can occur due to more complex solid-solid networks and an insufficient amount of liquid present to backfill cracks. Borland also suggested that the wetting characteristics of the liquid films present at the end of solidification could be an important contributing factor.

Figure 17: Generalized Theory according to Borland [23]
In the early 1980’s, the Modified Generalized Theory was proposed by Matsuda and coworkers from the Japanese Welding Research Institute (JWRI) based on in-situ observations of welding solidification cracking [31]. This theory further modified the Shrinkage-Brittleness and Generalized Theories by making changes to Stages 1-3, illustrated in Figure 18. Through observation, it was found that solid networks form rapidly upon cooling and that Stage 1 occurred over a smaller temperature range than originally proposed. This resulted in more narrow temperature ranges for Stages 1 and 2. The next modification that was made was further division of the “film” stage. Matsuda divided Stage 3 into a “film stage”, or 3H, and a “droplet stage”, or 3L. The “film stage” (3H) is the region where crack initiation and propagation can occur. The “droplet stage” (3L) is the region where only crack propagation can occur. Crack initiation cannot occur in the 3L stage because of the extensive solid-solid network contact.

Figure 18: Modified Generalized Theory according to Matsuda [23]
In addition to the modifications of the Shrinkage-Brittleness and Generalized Theories, Matsuda took into account the fractographic features of weld solidification cracking. Metallography and fractography examination suggested that the dendritic characteristic of solidification cracks represents the initiation and propagation during Stage 3H while flat fracture surface features were representative of crack propagation occurring in Stage 3L. Matsuda proposed three different types of fracture behavior (Figure 19) based on metallographic and fractographic examination of solidification cracks:

- **Type D**: Dendritic fracture surface
- **Type D-F**: Transition region from dendritic to flat fracture
- **Type F**: Flat fracture surface

Figure 19: Modified Generalized Theory according to Matsuda [32]

In 1962, a Russian researcher named Prokhorov proposed the Technological Strength Theory that was based on the mechanical behavior of material during weld
solidification [33]. This theory is based off a material’s ductility signature, where a material will exhibit a drop in ductility within the brittle temperature range (BTR). When outside the BTR, it is assumed that a material has sufficient ductility to accommodate the induced strain from welding. An example of a ductility curve that illustrates this theory is shown in Figure 20. The occurrence of cracking is the result between the competition of ductility recovery and strain accumulation during weld solidification. According to this theory, cracking will occur only when the ductility of the material is exhausted by the induced strain in the system. It is important to note that this theory does not incorporate any aspects of weld microstructure. The characteristics of the BTR curve are influenced by the nature of liquid films present along grain boundaries and the solidification temperature range.

Referring to Figure 20, the various plotted lines represent the following:

- **Line A-B:** Represents the thermal contraction of the material
- **Line A-C:** Represents the contraction and mechanical deformation to cause cracking in the system
- **Line A-D:** Represents the critical amount of deformation to cause cracking

If a deformation line crossed through the ductility curve (i.e. a steeper line than A-D representing more accumulated strain), the ductility of the system is exhausted and cracking will occur.
2.4 Development in Welding of High-Mn Steels

Though there has been a limited amount of published research relating to the weldability of high-Mn steels and welding consumables for cryogenic applications, there has been work published investigating these steels for other applications. Even though the research was not specifically for cryogenic applications, the addition of Mn in high concentrations was to achieve a fully austenitic structure and it will help give insight to the weldability of high-Mn steels for cryogenic applications. This section serves to summarize the previous research done and the progression in development of high-Mn steel welding consumables.

A previous research associate at The Ohio State University, Benjamin J. Sutton, published research on the evaluation of the solidification behavior and hot cracking susceptibility of high manganese steel welds [6]. During his investigation, a literature
review of previously published research regarding the weldability of high-Mn steels for applications other than cryogenics. The investigations reviewed focused on evaluating the hot cracking susceptibility of various Fe-Mn alloys using weldability tests such as the Varestraint test, Programmable Deformation Rate Test, Gleeble simulations, and others. After reviewing various publications, Sutton made a table that summarized the key influences that various elements have on the weldability of high-Mn steel weld metals. This summary is shown in Table 2 below. As can be seen, alloying with carbon as well as impurities such as sulfur and phosphorus can play a major role on hot cracking susceptibility. More in depth information regarding his literature review can be found here [6]. The rest of this section will focus on recent developments of high-Mn steel weldability and welding consumables for cryogenic applications.

Table 2: Reported effect of alloying elements on high-Mn steel weld metals [6]

<table>
<thead>
<tr>
<th>Element</th>
<th>Effect of Addition</th>
</tr>
</thead>
</table>
| Mn      | Stabilizes austenite  
|         | Segregates to dendrite boundaries  
|         | Can promote β-Mn formation  
|         | Readily evaporates from weld pool |
| C       | Stabilizes austenite  
|         | Segregates to dendrite boundaries  
|         | Promotes solidification cracking  
|         | Promotes HAZ liquation cracking |
| Al      | Stabilizes ferrite  
|         | Reduces solidification cracking |
| P       | Segregates to dendrite boundaries  
|         | Promotes solidification cracking  
|         | Promotes HAZ liquation cracking |
| S       | Little influence on solidification cracking |
A majority of the current research in regards to the weldability and development of high-Mn steel consumables was published and presented at the International Society of Offshore and Polar Engineers (ISOPE) conference. Over the past few years, several papers have been published and will be reviewed here.

In 2012, Choi et al. presented a paper discussing the development of high-Mn steel for use in LNG tanks that included mechanical properties of welded joints [5]. Due to proprietary reasons, the chemical compositions of the base metal and welding consumable were given as a range and were as follows: Mn (20-28), C (0.2-0.6), P (<0.1), S (0.01), N (<0.1), with Ni, Cr, Mo, Cu, Al, Si, Ti, Nb, and B as necessary. The mechanical properties at ambient and cryogenic temperatures that were tested for included tensile properties, Charpy impact energy, crack tip opening displacement (CTOD), fatigue, and corrosion resistance for the base and weld metal. In regards to the welded joints, the yield and ultimate tensile strengths exceeded the target values for mechanical properties. The failure occurred in the weld metal, but was expected as the welding metal strength matched the base metal strength. The Charpy impact energy (left) and CTOD (right) results are shown in Figure 21. The Charpy measurements were taken at various locations with the lowest values being exhibited at -196°C. All impact energy data was above the target design criteria of 54 J. The CTOD results, shown on the right in Figure 21, were measured at -163°C from the weld metal, across the fusion line, and to the base metal. All the CTOD results were comparable and were only slightly dependent on sample position.
Figure 21: Charpy impact energy results (Left) and CTOD results (right) for welded samples [5]

In another experiment, Lee et al. examined the hot cracking susceptibility of Fe-Mn-Al-C alloys using a longitudinal/transverse Varestraint technique as a function of Al content [34]. Three different material classifications were used with a base composition of roughly Fe-18Mn-0.6C: (1) No Al (Al-free alloy), (2) Low-Al (<3.0 wt %), and (3) High-Al (>3.0 wt %). The results from the Varestraint tests showed that the cracking susceptibilities of these alloys in the fusion zone (FZ), weld metal heat-affected zone (WMHAZ), and base metal heat-affected zone (BMHAZ) all decreased with increasing Al content, except for the WMHAZ. This is illustrated in Figure 22 below. The addition of Al led to the significant reduction in total crack length (TCL) and max crack length (MCL) in all regions.
The addition of Al also changed the solidification mode from austenite (A) to ferrite-austenite (FA), dramatically reducing grain size and decreasing the solidification cracking susceptibility. In addition to the increased resistance to solidification cracking, liquation cracking sensitivity of the BMHAZ was reduced with Al additions by suppression of the low melting $\gamma^+ (\text{Fe, Mn})_3\text{C}$ eutectic during solidification.

In a similar study to the previous one, the Varestraint test was used to evaluate the effect of silicon additions on the solidification cracking susceptibility of Fe-18Mn-0.6C [35]. The results from the testing, shown in Figure 23, demonstrated that the addition of 1.5 wt% Si increased the sensitivity of solidification cracking. It was found that additions
of silicon suppressed the formation of (Fe, Mn)$_3$C eutectic carbide during solidification. Furthermore, extensive silicon segregation caused the formation of low melting liquid films at the grain boundaries and was a contributing factor to the increased susceptibility to solidification cracking.

![Figure 23](image1.png)

Figure 23: Varestraint results of fusion zone cracking as a function of augmented strain (a) total crack length (TCL), (b) max crack length (MCL)

In another study, the microstructure and mechanical properties for high manganese weld metals, produced by flux cored arc welding consumables, were examined for cryogenic applications [17]. The investigation focused on examining the effects of varying C and Ni contents on the microstructure and mechanical properties of welds. The welding consumables had a constant Mn composition of 20 wt% with C three different carbon contents: (1) 0.2 wt%, (2) 0.4 wt%, and (3) 0.6 wt%. For evaluating the effects of Ni, the same compositions were used only with the addition of 8 wt% Ni. For the Mn-C alloys, it was found that as the C increased, the deformed phases, generated by
external stresses, were not observed. It was found that increasing additions of C suppressed the martensitic transformations by increasing the stacking fault energy (S.F.E.), which as a result, increased the tensile properties and impact toughness in the weld metal. The effects of Ni alloying to the Mn-C welding consumables was also examined, due to the mechanical properties being lower than target values. The addition of Ni suppressed all ε-martensite from forming in the weld metal and lead to high elongation and impact toughness values. The weldability of these alloys was not mentioned.

Lastly, in 2013, researcher Benjamin J. Sutton at The Ohio State University evaluated the influence of alloying additions in high-Mn steels on the solidification behavior and cracking susceptibility [6]. Sutton used the Cast Pin Tear Test to evaluate the effect of various alloying elements on cracking susceptibility. The compositions tested ranged from 14-35 wt% Mn, 0.01-0.65 wt% C, and a few compositions with Al additions from 1.5-3 wt%. Results from his investigations showed that Mn, S, and Al had little effect on the solidification cracking susceptibility while C, and P had detrimental effects on hot cracking susceptibility. C additions increased the solidification cracking susceptibility as a result of C segregation and STR expansion. P segregation caused the formation of a phosphide eutectic which resulted in an increase in hot cracking susceptibility (both liquation and solidification). In general, it was found that these high-Mn alloys had a relatively low solidification cracking susceptibility through the various test techniques used in this investigation.
2.5 Effect of Tungsten and Boron Alloying Additions

With the primary focus of this study being on the evaluation of tungsten and boron additions on the solidification cracking susceptibility of high-Mn steel filler metals, it is important to understand the fundamental role of alloying with these elements. Research regarding additions of tungsten and boron to high-Mn steels is extremely limited but the general effects and weldability of boron and tungsten in austenitic steels has been investigated and will be discussed in this section. Though the research might not be directly related to use in high-Mn steels, it can provide insight on how elemental additions of W and B may affect the solidification cracking susceptibility.

In regards to alloying with boron, it is typically added as a hardenability agent. It has a strong influence on the hardenability even with small additions (0.003 wt %). Boron strongly segregates to the grain boundaries and act as a melting point depressant in steel that can increase solidification cracking susceptibility. In regards to the weldability, the deleterious effects of boron on weld solidification cracking susceptibility in stainless steels, nickel-based alloys, and one Fe-Mn alloy have been reported [36-43]. A brief summary of these investigations are below.

A study done by the University of Alabama at Birmingham was performed to determine the effect of boron on intergranular hot cracking in Ni-Cr-Fe superalloys. The results showed that boron both increased the solidification temperature range as well as promote a Lavas phase formation [43]. It was found that this combination is detrimental to welding as it increases the possibility of liquid existing along the grain boundaries.
during solidification that could result in solidification cracking. It was suggested that additions of boron should be avoided.

In 2003, Shankar et al. [42] examined solidification cracking in austenitic stainless steel welds and found that segregation plays an overwhelming role in determining cracking susceptibility. It was found that sulfur, phosphorus, and boron were the most harmful as they partitioned to the liquid and form low melting eutectics expanding the solidification range. This is consistent with what Hull mentions in 1960 where he found that impurity elements such as sulfur and phosphorus, and minor alloy elements such as boron, silicon, titanium and niobium promote hot cracking, particularly in fully austenitic steels [36].

Kelly [38] investigated the elemental effects on cast 718 weldability and determined that boron had the most detrimental effect on weldability, far greater than S, Si, Ph, Hf, Zr, and C. Kelly stated that mechanical properties of the alloy should be evaluated for elemental effects to determine if elements detrimental to weldability, such as boron, are required.

Another study, performed by J.C. Lippold [40], examined the solidification cracking susceptibility of pulsed laser welds in austenitic stainless steels. During this investigation, it was found that boron added as an impurity element acted to embrittle welds. The precise mechanism by which the impurities act to embrittle welds in the solidification range is still unclear, but a preponderance of evidence suggests that segregation of elements such as phosphorus, sulfur and boron to solidification grain and subgrain boundaries aids in depressing the local solidification temperature and promoting
the formation of liquid films [40]. Boron also aids in the wetting ability of liquid films, could be potentially damaging in regards to solidification cracking.

Lastly, an investigation on the use of boron additions to prevent intergranular embrittlement in Fe-12Mn steels was performed by Hwang et al. [37]. Though this article doesn’t provide any weldability information, it does give information on the benefit of adding boron to high-Mn steels for cryogenic applications. It was found that the addition of 0.002 to 0.01 wt% boron successfully prevented intergranular fracture leading to spectacular improvement in low temperature impact toughness [37]. They did indicate that boron segregates to the austenite grain boundaries during annealing, and from previous research mentioned above, could pose a problem during welding operations.

The next elemental addition to these high-Mn steel filler metals, tungsten, is known to be a carbide former and provide excellent hardness for tool steels. Little research regarding the effects of adding tungsten to high-manganese steel, or for that matter austenitic stainless steels has been published. The original intentions for adding tungsten to the filler metals used in this investigation was not disclosed, but research done by Y. Hosoi et al. may be able to provide insight on the influence of alloying with tungsten.

In 1992, Y. Hosoi et al. [44] investigated the influence of tungsten, carbon and nitrogen on toughness and weldability of low activation austenitic high manganese stainless steels. The alloy system evaluated was the Fe-Cr-Mn with about 12 wt% Cr and 15 wt% Mn. The toughness of the material was evaluated by charpy impact tests at various temperatures and the weldability was determined using the Varestraint test.
Through charpy impact tests, it was found that the addition of 2-3 wt% tungsten resulted in an increase in high temperature strength and creep strength without affecting the ductility of the material. It was found that the hot cracking susceptibility of the weld metal was reduced by lower sulfur content and that tungsten containing welds did not result in an increase in susceptibility to hot cracking.

Even though little research has been done regarding the effects of elemental additions of W and B relating directly to high-Mn steels, previous research provides insight to why these elements were added and how they may affect the weldability of these filler metals investigated. Boron appears to provide strength and increase the hardenability of these alloys, but in terms of weldability, boron additions have been shown to be detrimental to hot cracking susceptibility. Though only a single reference relating to tungsten additions in high-Mn steels, it is possible that the intentions of alloying with tungsten in these filler metals was to help increase the low temperature properties and possibly counteract the potentially deleterious effects of adding boron to these filler metals for strength.

2.6 Weldability and Material Testing

Weldability testing is widely used to assess the fabricability of materials by various welding processes and to determine the service performance of welded construction [23]. When evaluating a material’s susceptibility to solidification cracking, there are various test methods that can be performed. These test methods generate strain conditions in two different ways: (1) self-restraint (intrinsic) or (2) external-restraint
Self-restraint tests cause cracking from the inherent restraint of the test assembly. With self-restraint tests, the inherent restraint of the test assembly causes strain accumulation during solidification in the material specimen that can result in cracking. The drawback of these tests is that there is usually little quantification of cracking susceptibility – the specimen either cracks or it does not [7]. An example of a self-restraint test is the Cast Pin Tear Test, which was the primary test used for this study. External-restraint tests simulate restraint conditions seen in welds by mechanically applying restraint through tension or bending. Examples of externally-restrained tests for solidification cracking are the Transvarestraint test, Hot Tensile Test, and Programmable Deformation Rate Test (PVR) [23, 45].

The weldability and materials testing pertaining to this research includes the third generation CPTT and Single-Sensor Differential Thermal Analysis (SS DTA). The original CPT Test was developed in the 1950’s to evaluate a material’s susceptibility to solidification cracking and has since been further developed at OSU in the Welding and Joining Metallurgy Group. SS DTA testing is a way of analyzing phase transformations and structural changes in materials that can be used as a predictive tool for determining an alloy’s susceptibility to solidification cracking. These test methods will be discussed in detail below.

2.6.1 THE ORIGINAL CAST PIN TEAR TEST

The cast pin tear test (CPTT) was originally developed by F.C. Hull in the 1950’s to evaluate the susceptibility of alloys to hot cracking [46]. Before the CPT test, all tests
for evaluating hot cracking were slow and expensive and thus a simpler test for hot cracking was needed. The CPT test was designed to be a quick and inexpensive way to evaluate the effects of alloying additions and impurities on hot cracking, or solidification cracking. The concept for the test was created from an observation that rapid cooling and high-tensile stresses from groove welding led to hot cracking during welding. These conditions leading to hot cracking in welds were very similar to conditions during castings which led to hot tearing in cast specimens. Thus, the idea of casting pins under conditions of restraint led to the creation of the cast pin tear test.

The original CPT test uses samples weighing 19 grams that are levitation-melted and cast into a series tapered copper pin molds contained within an inert environment. The use of levitation melting was chosen because it simplified the testing process in comparison to conventionally used crucible melting, which requires costly crucibles and risks the possibility of melt contamination. Another advantage of using levitation melting is that the coil acts like a magnetic funnel with an adjustable pouring rate, simplifying the pouring process. When casting samples, restraint at the ends of the tapered pin molds impose tensile stresses on the sample as the mold expands and the sample contracts upon solidification. The extent of hot cracking that is produced during testing provides a way of ranking or classifying an alloy’s susceptibility to hot cracking.

The original CPT test apparatus is shown in Figure 24. The CPTT apparatus consists of a vacuum-tight glass chamber that contains the induction coil, up to 18 pin molds, and a rotating specimen rack. The water-cooled induction coil is powered by a high frequency power source capable of levitating the 19 gram samples. When the
samples are ready to be cast into the mold, the power is lowered and the molten charge pours into the molds in a repeatable and controlled manner. The rotating specimen rack allows for up to 18 melts, or pins, to be made in succession. During casting, the CPTT chamber is purged to one atmosphere of pressure with either helium or argon for melting to ensure an inert environment is maintained.

Figure 24: Schematic of the original levitation melter [46]

Hull observed during testing that cracking in the molds decreased if the pin length was shortened or if the mold diameter was increased. Consequently, a series of diameters and sizes of molds were tested until a series of molds produced comparable changes at
each pin length interval. The mold design is shown in Figure 25 below. The original mold design consisted of split mold, split retaining lock, and a bottom plate. All the molds maintained a volume of 2.4 cm$^3$, meaning either the length and/or mold diameter was varied. Table 3 below shows the various molds that were used to generate a “cracking index” based on changes in pin length and mold diameter.

Figure 25: CPTT mold design [46]
To evaluate the cracking response between cast pins, Hull developed a “cracking index”. The “cracking index” was a way of measuring an alloy’s susceptibility to solidification cracking. The “cracking index” was measured by examining the circumferential cracking exhibited on a pin’s surface. To examine the surface of the pin for cracks, a binocular microscope at 30X magnification and a light source was used. As the pin was rotated in a fixture, the angular measurement of the crack size was recorded. The sum of the angular measurement of all cracks present on the surface, up to 100%, was termed the “cracking index”. The “cracking index” was then plotted versus the mold number as a way for ranking an alloy’s susceptibility to solidification cracking. An example of this for 3 different stainless steel alloys is shown in Figure 26.

Table 3: Dimensions for the CPTT molds [46]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>7/32</td>
<td>4</td>
<td>1 11/32</td>
<td>2 3/4</td>
<td>3/4</td>
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<td>7/32</td>
<td>4</td>
<td>1 17/64</td>
<td>2 9/16</td>
<td>3/4</td>
<td>19/32</td>
</tr>
<tr>
<td>6</td>
<td>10/64</td>
<td>5</td>
<td>5/32</td>
<td>2 9/16</td>
<td>3/4</td>
<td>21/32</td>
</tr>
<tr>
<td>7</td>
<td>11/64</td>
<td>6</td>
<td>13/32</td>
<td>1 13/16</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>8</td>
<td>9/32</td>
<td>6</td>
<td>10/32</td>
<td>1 15/16</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>9</td>
<td>19/64</td>
<td>6</td>
<td>+29/32</td>
<td>1 1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>10</td>
<td>19/64</td>
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<td>+29/32</td>
<td>1 1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>11</td>
<td>5/32</td>
<td>7</td>
<td>+29/32</td>
<td>1 1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>12</td>
<td>11/32</td>
<td>7</td>
<td>+1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>13</td>
<td>11/32</td>
<td>7</td>
<td>+1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>14</td>
<td>11/32</td>
<td>7</td>
<td>+1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>15</td>
<td>11/32</td>
<td>7</td>
<td>+1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
<tr>
<td>16</td>
<td>11/32</td>
<td>7</td>
<td>+1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>2 1/4</td>
</tr>
</tbody>
</table>
The CPT test was primarily used to examine the weldability of various stainless steels. Hull developed crack-susceptibility ratings on over 100 different stainless steels as well as evaluated the effects of composition of the Fe-Ni-Cr system on solidification cracking susceptibility. Hull also studied the effect of impurities on solidification cracking to better understand the fundamental cause of cracking in alloy systems. The CPT test became a useful tool for evaluating an alloy’s susceptibility to solidification cracking.
2.6.2 The Cast Pin Tear Test (OSU)

The concept of the original CPT Test has since been modified by researchers in The Welding and Joining Metallurgy Group at The Ohio State University. To date, OSU has designed and implemented three different iterations of the CPT test. A brief overview of the first two iterations will be covered but more detailed information can be found elsewhere [47-49].

The first-generation CPTT apparatus developed by OSU utilized a standard GTAW torch and power supply that melted charges of material on a water-cooled copper hearth contained within an inert environment. The levitation melting system, which was originally used by Hull, was not used due to complexity and high cost. The copper hearth was equipped with a retractable gate that allowed the molten material to flow into a copper mold placed below the hearth. Although a successful system was initially developed using this approach, problems with complete mold filling and reproducibility of the cracking results were encountered [48].

The issues with reproducibility and mold filling led to the development of a second-generation CPTT apparatus. An optimized testing procedure was developed that provided improved test sensitivity and reproducibility in alloys that are highly susceptible to solidification cracking. The second-generation CPTT apparatus and a pin mold are shown in Figure 27 below. The CPTT operating parameters are listed in Table 4.
Figure 27: Second-generation CPTT [49]

Table 4: CPTT operating parameters [49]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mold material</td>
<td>Cu; Cu-Be</td>
</tr>
<tr>
<td>Shielding gas</td>
<td>Ar</td>
</tr>
<tr>
<td>Gas flow rate, ml/s</td>
<td>70–80 (9–10 ft³/h)</td>
</tr>
<tr>
<td>Arc current, A</td>
<td>250</td>
</tr>
<tr>
<td>Arc length, mm</td>
<td>15 (0.6 in.)</td>
</tr>
<tr>
<td>Arc time, s</td>
<td>5–7</td>
</tr>
<tr>
<td>Over-pressure, MPa</td>
<td>0.007–0.014 (1–2 psi)</td>
</tr>
<tr>
<td>Cast pin diameter, mm</td>
<td>9.525 (0.375 in.)</td>
</tr>
<tr>
<td>Cast pin length, mm</td>
<td>12.7–50.8 (0.5–2 in.)</td>
</tr>
<tr>
<td>Length increments, mm</td>
<td>3.175 (0.125 in.)</td>
</tr>
</tbody>
</table>

The molds used in with this version of the CPTT differed from Hull’s design in that the mold diameter and head/foot geometry remained constant. The stress level applied to the sample is controlled by the mold material and pin length [49-51]. This allowed replacing the arbitrary mold numbering in the Hull’s solidification susceptibility ranking with the actual mold/pin length [49]. The enlarged head and foot of the pin impose restraint on the sample during solidification allowing stress to accumulate in the
last liquid to solidify, longer pin lengths and fast cooling rates typically result in the accumulation of more stress [52]. The range of mold (pin) lengths varied from 0.5 in. to 2.0 in. and were made from a copper-beryllium alloys with a measured cooling rate of 245°C/s [51]. For each pin length, a corresponding pin/charge mass was assigned (Table 5).

Table 5: Range of mold lengths and corresponding pin/charge volume and mass [49]

<table>
<thead>
<tr>
<th>Mold length, mm (in.)</th>
<th>Volume, mm³</th>
<th>Mass, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.700 (0.500)</td>
<td>1,122.6</td>
<td>10.0</td>
</tr>
<tr>
<td>15.875 (0.625)</td>
<td>1,178.7</td>
<td>10.5</td>
</tr>
<tr>
<td>19.050 (0.750)</td>
<td>1,234.8</td>
<td>11.0</td>
</tr>
<tr>
<td>22.225 (0.875)</td>
<td>1,291.0</td>
<td>11.5</td>
</tr>
<tr>
<td>25.400 (1.000)</td>
<td>1,347.1</td>
<td>12.0</td>
</tr>
<tr>
<td>28.575 (1.125)</td>
<td>1,403.2</td>
<td>12.5</td>
</tr>
<tr>
<td>31.750 (1.250)</td>
<td>1,459.4</td>
<td>13.0</td>
</tr>
<tr>
<td>34.925 (1.375)</td>
<td>1,515.5</td>
<td>13.5</td>
</tr>
<tr>
<td>38.100 (1.500)</td>
<td>1,571.6</td>
<td>14.0</td>
</tr>
<tr>
<td>44.450 (1.750)</td>
<td>1,683.9</td>
<td>15.0</td>
</tr>
<tr>
<td>50.800 (2.000)</td>
<td>2,806.5</td>
<td>16.0</td>
</tr>
</tbody>
</table>

To examine the cast pins for cracks, a binocular microscope was used at magnifications between 10X and 70X. The circumferential cracking was measured in degrees (0-360 degrees) and converted to a percentage of circumferential cracking (0-100%). Based on the cracking response of an alloy, a response curve of Maximum Circumferential Cracking (MCC) is plotted versus pin length. To rank an alloy’s susceptibility to solidification cracking, the maximum pin length with 0% cracking and the minimum pin length with 100% cracking are used (Figure 28).
The newest (3rd) generation of the CPTT was developed by T. Luskin at The Ohio State University. A combination of the original design by Hull and the previous iterations of the CPTT developed at OSU were utilized. The newest generation of the test incorporates induction levitation melting of the sample in a specially designed copper coil [53]. Samples, or “buttons”, are prepared using a GTA button melting apparatus an inert environment. The “buttons” are then induction levitation melted and cast into a series of molds ranging in pin lengths from 0.5 in. to 2.5 in. in increments of 0.125 in. The setup and for the 3rd generation CPTT is shown in Figure 29 below.
The 3rd generation CPTT apparatus was used in this study to evaluate the solidification cracking behavior of high-Mn steel filler metals and thus the process and procedure are discussed in further detail in the Materials and Procedure section of this document.

2.6.3 SS DTA TESTING

SS DTA testing, or Single Sensor Differential Thermal Analysis, is a novel technique for studying the phase transformations and structural changes in materials that was developed at The Ohio State University in the Welding and Joining Metallurgy Group [54]. SS DTA is based on the principle of the Differential Thermal Analysis
(DTA) and is a technique used for detecting phase transformations and structural changes in materials. This technique utilizes a single temperature sensor that records the temperature at a particular point of interest in the tested material, which makes it applicable to actual or simulated thermal processing of materials in liquid or solid state and an unlimited range of temperatures and heating and cooling rates [54]. Traditional DTA compares thermal histories from the tested alloy to a reference sample that are subject to similar heating and cooling. SS DTA differs in that the reference sample is not needed to determine phase transformations but instead uses mathematical functions to generate a reference curve from the thermal data obtained from a single sensor. SS DTA has been applied in a range of applications including the construction of continuous cooling transformation (CCT) diagrams, weldability studies, development of welding consumables and new alloys, and development and testing of processing procedures. The detailed description of this technique and the welding-related applications can be found elsewhere [54-56].

Though there are many applications for using SS DTA, the primary use of this technique for this study was to measure the solidification temperature range (STR). Experimentally measuring the STR with SS DTA in austenitic alloys during solidification has been shown to relate well in regards to an alloy’s susceptibility to solidification cracking [56]. STR data can be a good indication of susceptibility to solidification cracking because weld solidification cracking occurs during the final stages of solidification when tensile shrinkage stress accumulates and liquid films still persist along solidification grain boundaries in the structure [57]. Therefore, as the STR range
expands, there is more time for liquid films to persist along solidification grain boundaries and, in general, results in an increased susceptibility to solidification cracking.

At OSU, multiple variations of SS DTA testing have been performed to obtain thermal histories. Some of the variations include the original method of melting a 20 gram button with a thermocouple placed in the center of the button, a thermocouple plunging technique, and a newly developed method utilizing the induction melting capabilities of the CPT test. The original method, shown in Figure 30, involved melting material using a GTAW torch onto a thermocouple. The test required two buttons to be prepared, a 20 gram button with a hole drilled through the middle to house the thermocouple and a 1 gram button configured as shown in Figure 30. Once the setup was completed, the thermal histories were recorded by melting the 1 gram button on top of the thermocouple. Three runs (melts) were performed with data only being recorded on the final two melts. The thermal data is then processed using an SS DTA™ software (discussed later).
The thermocouple plunging technique varies slightly from the original method in that the thermocouple is plunged into the molten weld pool. A schematic of the process is shown in Figure 31. The process, like the original, uses a GTAW torch that melts a 16 g button that is resting on a copper cooling block. When the button reaches the molten state, the thermocouple is plunged into the weld pool immediately after the arc is extinguished. The thermal data is then recorded and analyzed in the same fashion as the original SS DTA method.

Figure 30: Experimental setup for the original SS DTA method
Figure 31: Schematic of thermocouple plunging technique prior to (a) and immediately following welding (b) [6]

The newest method for SS DTA utilizes the induction melting capabilities of the CPT Test to record the thermal data. Greater detail regarding this method will be in the Materials and Experimental Procedures section of this document.
CHAPTER 3: OBJECTIVES

With advancements in the development of high-Mn steels, attention has been drawn to the development of welding consumables for joining these steels. When fabricating LNG tanks, welding is a critical procedure and thus the weldability of high-Mn steels and welding consumables must be evaluated. Very little research of high-Mn steels has been published in regards to solidification behavior and cracking susceptibility and thus the weldability of these materials needs to be examined. The main objective of this study is to examine the effect of alloying additions of tungsten and boron on the solidification behavior, microstructure, and solidification cracking susceptibility of Fe-Mn-C filler metals. The primary objectives of this research are as follows:

1) Evaluate the effect of tungsten and boron additions on the weldability of high-Mn steel filler metals intended for use in cryogenic applications through the use of both computational and weldability testing techniques.

2) Assess the solidification cracking susceptibility of five high-Mn steel filler metals using the Cast Pin Tear Test. A baseline solidification cracking susceptibility of the five compositions will be established.
3) Evaluate the solidification and segregation behavior both computationally and experimentally using Thermo-Calc™ and SS DTA™ test techniques. The solidification temperature ranges for each composition will also be examined to aid in ranking these filler metals according to their solidification cracking susceptibility.

4) Metallographically characterize the five filler metal compositions using Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) to quantify partitioning during solidification, identify secondary phases, and evaluate the fracture surface morphologies.

5) Determine the range of tungsten and boron additions that provides adequate resistance to weld solidification cracking. A solidification cracking susceptibility ranking will be generated for these filler metals as well as a discussion on the development of an optimum composition.
CHAPTER 4: MATERIALS AND EXPERIMENTAL PROCEDURES

This chapter contains information on the materials used as well as the weldability and material testing techniques used in this study.

4.1 MATERIALS

The materials used in this study were high-Mn steel filler metals developed and created by POSCO laboratories. There were five different filler metal compositions tested during this investigation with the following designations: Base, Low W/Low B, Low W/High B, High W/Low B, and High W/High B. The welding consumables were rutile (TiO$_2$) flux cored arc welding (FCAW) wires with a constant base composition of Fe, Mn, Ni, and C. The Ni-equivalent of this base composition was $\text{Ni}_{\text{eq}} = 22$, as determined using the Schaeffler equivalency. Due to proprietary restrictions, the actual Fe, Mn, Ni, and C compositional information cannot be provided. Filler metals using this base composition contained additions of boron up to 27 ppm and tungsten up to 4.7 wt%, as shown in Table 6. It should be noted that not all the elements listed in Table 6 were provided by POSCO and therefore samples of each composition were sent out to independent laboratories for chemical analysis.
Table 6: Chemical composition of FCAW filler metals

<table>
<thead>
<tr>
<th>Designation</th>
<th>Composition (wt %)</th>
<th>Ni_{eq}</th>
<th>W</th>
<th>Si</th>
<th>Ti</th>
<th>S</th>
<th>P</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>22</td>
<td>0.5</td>
<td>0.09</td>
<td>0.005</td>
<td>0.010</td>
<td>0.010</td>
<td>0.005</td>
<td>0.010</td>
</tr>
<tr>
<td>Low W/Low B</td>
<td>22</td>
<td>1.12</td>
<td>0.5</td>
<td>0.10</td>
<td>0.005</td>
<td>0.010</td>
<td>0.009</td>
<td>0.0019</td>
</tr>
<tr>
<td>Low W/High B</td>
<td>22</td>
<td>1.26</td>
<td>0.5</td>
<td>0.09</td>
<td>0.004</td>
<td>0.009</td>
<td>0.008</td>
<td>0.0012</td>
</tr>
<tr>
<td>High W/Low B</td>
<td>22</td>
<td>4.7</td>
<td>0.5</td>
<td>0.07</td>
<td>0.004</td>
<td>0.008</td>
<td>0.008</td>
<td>0.0012</td>
</tr>
<tr>
<td>High W/High B</td>
<td>22</td>
<td>4.4</td>
<td>0.5</td>
<td>0.08</td>
<td>0.005</td>
<td>0.008</td>
<td>0.008</td>
<td>0.0027</td>
</tr>
</tbody>
</table>

Note: Ni_{eq} = Ni + 0.5Mn + 30C

4.2 Weldability Test Procedure

This section describes the testing procedures used in this study. The testing can be broken down into the following seven phases:

1) Material Preparation
2) Button Melting
3) Cast Pin Tear Testing
4) Analysis of Cracking Response
5) Metallurgical Characterization
6) Thermal Analysis (SS DTA)
7) Computational Modeling

4.2.1 Material Preparation

The material to be tested must go through three steps before converting the material into small charges, or “buttons”, in the button melter apparatus. The material must be (1) cut, (2) cleaned, (3) and weighed. The following three steps are performed before button melting begins:
1) Depending on how the material of interest is formed, (i.e. plate or spooled wire) different approaches are taken to cut the material into small enough pieces to properly fit within the hearth of the button melter.

a) If the material is in plate form, small, plate length strips of material are sectioned on a metal working bandsaw and then subsequently cut into the smaller pieces using a Techcut 5 precision sectioning saw equipped with a carbide blade. To aid in the weighing process (Step 3), material shavings from the base plate were obtained using an end mill equipped with a 5 flute, high performance carbide bit. Shavings make it such that the sectioned material does not have to weigh exactly the desired amount.

b) If the material is in wire form, the material is cut using a rotating blade in conjunction with a Miller automatic wire-feed system (Figure 32). The cutting apparatus continuously feeds the spooled wire through the rotating blade creating 1 inch pieces that fit in the hearth of the button melter.

Figure 32: Cutting apparatus for material in wire form
2) After cutting, the material is ultrasonically cleaned in an ethanol bath for a minimum of 30 minutes. If the material is in wire form and contains a flux, the material is cleaned during the cutting process as the wire is fed through the cutting apparatus using ethanol soaked wipes. At this stage in the material preparation, nitrile gloves are worn while handling materials to avoid contamination.

3) After cleaning, the material is then weighed out using a scale capable of measuring to a mass (g) that corresponds to a given pin length (in.), shown in Table 7. Typically, six buttons for each pin length are initially made in order to generate a complete cracking response curve using the CPTT.

<table>
<thead>
<tr>
<th>Sample Mass (g)</th>
<th>10.3</th>
<th>10.5</th>
<th>11.0</th>
<th>11.5</th>
<th>12.0</th>
<th>12.5</th>
<th>13.0</th>
<th>13.5</th>
<th>14.0</th>
<th>14.5</th>
<th>15.0</th>
<th>15.5</th>
<th>16.0</th>
<th>16.5</th>
<th>17.0</th>
<th>17.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pin Length (in.)</td>
<td>0.5</td>
<td>0.625</td>
<td>0.75</td>
<td>0.875</td>
<td>1.0</td>
<td>1.125</td>
<td>1.25</td>
<td>1.375</td>
<td>1.5</td>
<td>1.625</td>
<td>1.75</td>
<td>1.875</td>
<td>2.0</td>
<td>2.125</td>
<td>2.25</td>
<td>2.375</td>
</tr>
</tbody>
</table>

4.2.2 BUTTON MELTING

The button melting system consists of a gas tungsten arc welding (GTAW) torch that is positioned over a copper hearth. The copper hearth and GTAW torch are both contained within a sealed, glass chamber to create an inert environment in order to prevent atmospheric contamination. The GTAW torch uses a high frequency arc start that is powered by a Lincoln Electric Aspect 375 constant current power supply. The button melter system setup (Top) is pictured in Figure 33 in addition to a schematic of the button melting apparatus (Bottom).
Figure 33: Button melting apparatus setup (Top) and Schematic (Bottom)
Prior to placing the cut and cleaned material onto the copper hearth for melting, the hearth must be thoroughly cleaned. The surface of the hearth is polished using 800-grit sandpaper to remove any material or oxidation leftover from a previous melt. Once removed, the surface is wiped clean using a Kimtech wipe and ethanol to ensure cleanliness before melting. Material is then placed within the copper hearth and the chamber is secured using 3 spring clamps at the bottom of the apparatus. Once the chamber is sealed properly, the chamber is purged with high purity argon prior to melting. The button melting chamber is purged with argon using the following procedure:

1) Open inlet valve opens to allow argon to flow into button melting chamber
2) Adjust argon flow rate to 20 CFH
3) Close upper exhaust valve to build chamber pressure that exceeds 10 psi
4) Open upper exhaust valve to reduce chamber pressure to below 5 psi
5) Repeat steps 3 and 4 five times

Once the chamber is purged, argon continues to flow through the button melter for the entirety of the melting process. At this point, the material is ready to be melted into buttons.

The melting process begins by initiating the arc using a GTAW torch and a variable current foot pedal. The maximum current is set to 170 amps on the power supply. During melting, slowly rotate the torch around the copper hearth until the material is shaped into a “button”. Table 8 below shows the typical parameters that are used when operating the button melting system. The melting times for each sample vary
between 5 and 20 seconds to obtain adequate mixing in the molten state. After the melting is completed, the sample is cooled within the inert chamber until the button is completely solidified. Once the alloy has solidified and cooled (between 2-3 min.), the button is removed and the chamber is cleaned for the next charge of material to be melted. Typically, a charge of material, or button, only needs to be melted once prior to the CPTT, but if additional mixing is needed, a second melt can be done. When more thorough melting is required, the melted button is flipped over and the procedure mentioned above is repeated.

Table 8: Parameters for button melting

<table>
<thead>
<tr>
<th>Arc Melting System Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge Mass (g)</td>
<td>10.3 – 17.5</td>
</tr>
<tr>
<td>Shielding Gas</td>
<td>Argon (99.998%)</td>
</tr>
<tr>
<td>Gas Flow Rate (CFH)</td>
<td>20</td>
</tr>
<tr>
<td>Build Pressure (psi)</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Release Pressure (psi)</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Purge Cycles (#)</td>
<td>5</td>
</tr>
<tr>
<td>Current (A)</td>
<td>170</td>
</tr>
<tr>
<td>Melt Time (sec)</td>
<td>5-20</td>
</tr>
<tr>
<td>Cool Time (min)</td>
<td>2-3</td>
</tr>
</tbody>
</table>

4.2.3 CAST PIN TEAR TESTING

A newly developed, third generation, CPTT apparatus was used to assess the susceptibility to solidification cracking. This apparatus consists of a water cooled induction coil within a cylindrical, quartz chamber. The coil is powered by a 10kW industrial power supply and work head that operates at 224 kHz. The quartz chamber is purged with argon to ensure an inert environment is created during testing. Once purged,
an argon flow rate of 2.5 CFH and a pressure of 0.3 psi is maintained during testing. The CPTT setup is illustrated in Figure 34 along with an example of a pin mold used during the casting process. The Al-Bronze molds vary in pin length ranging from 0.5 - 2.5 inches in increments of 0.125 inches. As the pin length increases, the inherent restraint level during solidification increases.

The CPTT apparatus communicates with a configurable program using LabVIEW software. The purging and casting processes are automated by using LabVIEW software that communicates with the multiple valves, an optical pyrometer and a proportional-integral-derivative controller (PID). To begin the casting process, the sample, or button,
is placed inside the quartz chamber within the induction coil. A funnel-shaped, quartz insert is placed within the coil to electrically isolate the charge of material and the coil before levitation occurs. Two different size funnels are used to isolate the button from the coil; a small funnel for charges 13g or less and a large funnel for charges 13.5g and higher. Once the charge of material is placed, the chamber is closed and the mold retainer can now be assembled. The appropriate pin mold length is then selected for a given mass of material (Table 7) and the CPTT operating parameters are set (Table 9). The mold retainer is then assembled by placing the mold halves, copper disk, spring, and spacer into the position. The internal stack up inside mold retainer is shown in Figure 35. The proper spring/spacer combination is needed to ensure adequate pressure is applied to the bottom of the copper disk to limit flashing at the foot of the pin. The copper disk is used to keep the molten charge within the mold. A specific sample mass for a given pin length is required to ensure that the mold does not under/overfill with molten material.

Table 9: CPTT operating parameters

<table>
<thead>
<tr>
<th>Set Temp (°C)</th>
<th>Casting Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1550</td>
<td>385-400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ramp Down (A)</th>
<th>Ramp Down (Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>0.85</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow Rate (CFH)</th>
<th>Pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Once the mold retainer was assembled and locked into position, the casting parameters can be set (Table 9). The set temperature is typically 50-100°C above the liquidus temperature. In this study, the set temperature was higher than 50-100°C due to excessive manganese evaporation during melting that prevents the optical pyrometer from reading accurate temperatures. This limitation results in the pins having to be manually cast once the molten charge has undergone sufficient superheating. Once the parameters are set, the purge cycle begins by running the program. A flow chart of the purge cycle is shown in Figure 36. The initial purge begins with the hi-flow valve and top release valves open for a designated time (typically 80 seconds). Once the initial purge is complete, the top release valve closes building pressure for a designated time (typically 4 seconds) and then opens, releasing pressure for a designated time (typically 4 seconds). After the pressurization and release cycles are completed, the high-flow valve closes and allows argon to flow into the chamber through the 0.5 psi regulator and low-flow valve. The variable flow valve is then set such that a flow rate of 2.5 CFH and a chamber pressure of 0.3 psi is achieved.
After the chamber is purged, the casting process begins by ramping up the coil current (set casting current) causing the charge of material to levitate within the induction coil. Once the set temperature is reached, the current is reduced from the casting current to the ramp down current which allows the molten charge to descend into the mold. The coil current is then shut off and the material begins to solidify.

Between casts, the molds are cleaned with 9 µm diamond paste and a felt cord until the oxidation or contaminants are removed. The molds are then wiped with a kimwipe soaked with ethanol and allowed to dry. In addition to the molds, the optical pyrometer is cleaned with ethanol to ensure the accuracy of the measured charge temperature during casting. After the casting procedure is completed and the pin fully solidified, it is removed from the mold and ready for crack analysis. This casting process was repeated until four to six acceptable pins were produced at each pin length tested. Acceptable cast pins are defined as those that are free of casting defects and filled the mold completely.

Figure 36: Flow chart of CPTT purge procedure
4.2.4 Analysis of Cracking Response in CPTT Samples

The intrinsic restraint that accumulates in the pin molds is controlled by the pin length. As mentioned earlier, as the pin length increases, the inherent restraint increases. Cracking is typically observed in the top half of the pin near the head where the strain level is the highest. To evaluate the cracking response after casting is completed, the cast pins are examined at up to 70X magnification using a binocular microscope equipped with a rotating fixture capable of measuring radial lengths (0-360 degrees). The crack length is measured circumferentially on the pin surface in degrees and then converted to percent cracking using Equation 1.

Equation 1: Circumferential cracking equation for evaluation of CPTT samples

\[
\% \text{Cracking} = \frac{L_T \circ}{360} \times 100
\]

\(L_T\): Total length (in degrees) of all cracks measured on pin surface

The equipment used to evaluate circumferential cracking (top) and an example of how the cracks are counted (bottom) are shown in Figure 37. The equipment consists of a binocular microscope equipped with a rotating fixture and light source. The bottom image is an example of a CPTT sample exhibiting 41% circumferential cracking. The circumferential cracking counter converts the rotation (in degrees) to percent cracking using the equation seen earlier. In this example, the cracking occurred over 148 degrees, representing 41% of the circumference.
Figure 37: Crack evaluation equipment (Top) and example of circumferential cracking measurement on pin surface (Bottom)
The susceptibility to solidification cracking for an alloy can be ranked using three different criteria:

1) Maximum pin length with an average of 0% circumferential cracking
   [Lower Cracking Threshold (LCT)]

2) Minimum pin length with an average of 100% circumferential cracking
   [Upper Cracking Threshold (UCT)]

3) The 0% to 100% cracking pin length range

The first criterion, LCT, is primarily used to characterize an alloy’s susceptibility to solidification cracking. The UCT can be hard to determine as longer pin lengths can be more difficult to obtain defect free cast pins. In this particular study, the high Mn levels made longer pin lengths (> 1.25 in.) even more difficult to cast due to the significant manganese evaporation that occurs during melting. This evaporation can be attributed to the high vapor pressure of manganese. The Mn vapor prevents the optical pyrometer from reading an accurate temperature and requires the pins to be manually cast. This can result in inconsistent casts and led to cast defects. Therefore, the LCT was the main criterion used to rank these alloy compositions.

Using the LCT criterion, the susceptibility to solidification cracking can be visualized by generating a cracking response curve that plots the average circumferential cracking versus pin length. An example of this is shown in Figure 38. The average circumferential cracking is an average of all measured circumferential cracking values for a given pin length. The alloys can then be compared and ranked according to the LCT criterion.
4.2.5 Metallurgical Characterization

Metallography of button and cast pin samples were prepared using the following procedure. Sectioning of samples was done using a Techcut 5 precision sectioning saw equipped with a silicon carbide blade and high speed cutting fluid. Cast pins were sectioned in both the longitudinal (along the pin length) and transverse directions to evaluate the microstructure and solidification cracks. After sectioning, the samples were mounted in conductive resin using a LECO PR-36 mounting press. Once the samples were mounted, they were ground using 240, 400, 600, and 800 grit silicon carbide paper disks on rotating polishing wheels with continuous water flow. Once the samples were ground, polishing was performed using 9, 6, 3, and 1 µm diamond paste. Final polishing
was conducted using 0.05 µm colloidal silica. Between each polishing step, the samples
were ultrasonically cleaned in an ethanol bath to prevent contamination between
polishing steps.

After polishing, the samples were etched with a 2% nital solution (98 ml ethanol
and 2 ml HNO₃). The etchant was applied to the polished surface by submerging the
sample into a glass dish containing the nital solution. Etching times ranged from 2-10
seconds. After the etchant was applied, the samples were removed from the glass dish of
etchant, rinsed with ethanol and air dried. If a sample was over etched or did not etch
properly, samples were taken back to the 1 µm step and polished again.

Light optical microscopy (LOM) and scanning electron microscopy (SEM) were
both used to evaluate button and cast pin samples. For optical microscopy, an Olympus
GX-51 inverted microscope equipped with a differential interference contrast (DIC) filter
was used to characterize etched button samples and cast pins. There were two scanning
electron microscopes used for characterization: a XL-30 field emission ESEM, and a
Sirion field emission SEM. For both SEMs, the secondary electron (SE), backscatter
electron (BSE), and energy dispersive spectrometer (EDS) detectors were used to
evaluate the fracture surface morphologies, quantify partitioning during solidification,
and identify secondary phases.

4.2.6 THERMAL ANALYSIS (SS DTA)

The solidification temperature ranges were calculated from thermal histories
obtained using Single Sensor Differential Thermal Analysis (SS DTA). Conventionally, a
thermocouple plunging technique is used to obtain thermal data but a new procedure has
been developed that has improved the reliability and repeatability of the test procedure. The new method utilizes the induction melting capabilities of the CPTT to conduct SS DTA testing. Since the new method for SS DTA utilizes the CPTT apparatus, the setup and procedures were similar. In addition to the CPTT equipment mentioned earlier, a data acquisition system, type-C thermocouples, and new molds are used to record thermal histories during testing.

The test uses six gram buttons of a desired composition that are cast onto a type-C (W-W/Re) thermocouple within a mold. Once the material is cast, the data acquisition system records the thermal history from above the liquidus to nearly room temperature.

The new mold, shown in Figure 39, was made from a copper-nickel-silicon-chromium (Mold Max V) alloy. There are two holes drilled on the sides of the mold to allow gas to flow through the mold assembly during the purge process. Another hole in the center is drilled through the bottom of the mold to position the thermocouple where the button will be cast.

Figure 39: Mold design for SS DTA
Due to the new mold geometry, a new mold assembly is required. The new setup and mold assembly are shown in Figure 40. Once the setup is complete, a six gram button is placed onto the glass insert within the CPTT coil. The chamber is then sealed and the purge process begins. Once the chamber is purged, the button is inductively heated, melted, and then cast on top of the thermocouple. The data acquisition software then records the thermal data from the thermocouple as the cast button solidifies. The thermal data is then processed using the SS DTA™ software.

Figure 40: Setup for SS DTA testing (left) and mold assembly (right)
In this study, three 6 gram buttons were cast for each alloy composition (15 total tests) to obtain experimentally determined solidification temperature ranges (STRs). In order to calculate the STR, the liquidus \( T_L \) and the solidus \( T_S \) temperatures must be determined by processing the recorded thermal data with the SS DTA™ software. This software mathematically generates a reference curve based upon the thermal history that is then overlaid onto the actual acquired thermal data. The mathematical models used to process the data in this study was either a 5-term Rosenthal or a 3-term, 2\textsuperscript{nd} order Polynomial model to generate the reference curves. The software is then able to determine transformation temperatures by locating deviations between the thermal data and the reference curve. The deviations occur due to latent heat of fusion being released or absorbed during solidification. More details regarding the methodology for using the SS DTA™ software can be found elsewhere [54]. After obtaining the liquidus and solidus temperatures, the STR was calculated by subtracting the \( T_S \) from \( T_L \). The STR data measured from thermal histories was used to aid in ranking these alloys in terms of solidification cracking susceptibility. In addition to the STR data, the solidification sequence of these alloys was also analyzed.

4.2.7 Computational Modeling

Thermodynamic simulations of the solidification process were conducted using the Scheil-Gulliver module within Thermo-Calc™. The Scheil-Gulliver module, which accounts for solute redistribution, was used to predict solidification temperature ranges, elemental partition coefficients, and the formation of interdendritic second phases and eutectic reactions. The thermodynamic database for steel and Fe-alloys, TCFE8, was used
to run the simulations. All simulations were executed under the following conditions. All phases were permitted and there was no miscibility gap check. Both carbon and boron were selected as fast-diffusing elements to account for back diffusion. The transition of BCC to FCC was allowed. The starting temperature was 2000°C with a temperature step of 1°C. All simulations were stopped once solid phase fraction ($f_S$) reached 0.98.
CHAPTER 5: RESULTS AND DISCUSSION

5.1 SOLIDIFICATION ANALYSIS

This section contains the results and discussion regarding the solidification behavior for the welding consumable compositions tested in this study. The solidification behavior is useful to examine when performing weldability testing as it can help evaluate or explain solidification cracking susceptibility rankings that will be developed in later sections. Both computational and experimental techniques were used to examine the solidification behavior.

5.1.1 COMPUTATIONAL MODELING

Computational modeling software, such as Thermo-Calc™, can be used to provide information on the solidification and segregation behavior for a given alloy system. This study utilized the Scheil-Gulliver module to predict the solidification sequence, solidification temperature ranges, and partition coefficients, as well as the formation of any interdendritic second phases. The use of this predictive software can help identify compositions of interest for optimizing the resistance to solidification cracking of these filler metals.

Each of the weld metals evaluated in this study exhibited primary austenite solidification that was predicted by Scheil solidification simulations and verified later
through experimental thermal analysis and metallographic characterization. The solidification sequence for the Base composition is shown below in Figure 41. The black line represents solidification under equilibrium cooling conditions while the colored lines represent solidification using the Scheil-Gulliver method. The Base composition exhibited primary austenite solidification along with the formation of a Ti₄C₂S₂ secondary phase upon further solidification. The Ti₄C₂S₂ phase begins to form at 1383°C and continues until the solidus temperature is reached.

Figure 41: Solidification sequence for Base composition – Simulations to fraction solidified (fₚ) =0.99
Figure 42 is the solidification sequence for the Low W/High B composition and is representative of all the compositions with W and B additions. The compositions with W and B additions exhibited primary austenite solidification in addition to the formation of $\text{Ti}_4\text{C}_2\text{S}_2$ and $\text{MB}_2$ secondary phases upon further solidification. The $\text{Ti}_4\text{C}_2\text{S}_2$ phase forms at around 1380°C but varies slightly depending on the composition. The “M” in the $\text{MB}_2$ phase can represent any of the following elements in this compound: $(\text{AL,TI,ZR,Y})(\text{B})_2$. ZR, Al and Y are not in the chemical make-up of these alloys, making the only likely boride compound to form being $\text{TiB}_2$. Though aluminum is not present in the composition given from POSCO, it has been used as an alloying addition to reduce the solidification cracking susceptibility in high-Mn steels (Table 2) [6]. The $\text{MB}_2$ phase begins to form at approximately 1270°C but varies depending on the composition. It should be noted that this phase forms at approximately 0.98 fraction solidified during the simulations and typically this is when simulations are stopped. Therefore, the final temperature recorded for the $\text{MB}_2$ phase was at 0.99 fraction solidified. The $\text{MB}_2$ phase was predicted to form in each of the compositions with W and B additions.
A summary of the solidification simulation results are shown in Table 10. For each composition, the temperature at which the phase for a given composition starts and ends is provided. It should be noted that the temperature range for the “FCC” phase is the equivalent to the STR. The solidification temperature range will be discussed later but it is important to note that the Ti₄C₂S₂ forms over a large portion of the predicted STR, illustrated in Figure 43. When performing the simulations, if the Ti₄C₂S₂ phase was rejected, MnS would form in place of the Ti₄C₂S₂. It appears that the Ti₄C₂S₂ phase preferentially forms over MnS, even though manganese is known to act as a scavenging element and tie up sulfur during solidification.
Table 10: Scheil-Gulliver solidification results for each phase of a given composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Phase</th>
<th>Start (°C)</th>
<th>Solidus (°C)</th>
<th>Temp Range [Start - Solidus] (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>FCC (STR)</td>
<td>1421</td>
<td>1288</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>Ti₄C₂S₂</td>
<td>1383</td>
<td>1288</td>
<td>95</td>
</tr>
<tr>
<td>Low W/ Low B</td>
<td>FCC (STR)</td>
<td>1418</td>
<td>1283</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>Ti₄C₂S₂</td>
<td>1383</td>
<td>1283</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>B₂M*</td>
<td>1262</td>
<td>1254</td>
<td>8</td>
</tr>
<tr>
<td>Low W/ High B</td>
<td>FCC (STR)</td>
<td>1418</td>
<td>1281</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>Ti₄C₂S₂</td>
<td>1378</td>
<td>1281</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>B₂M*</td>
<td>1277</td>
<td>1260</td>
<td>17</td>
</tr>
<tr>
<td>High W/ Low B</td>
<td>FCC (STR)</td>
<td>1413</td>
<td>1288</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>Ti₄C₂S₂</td>
<td>1369</td>
<td>1288</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>B₂M*</td>
<td>1269</td>
<td>1265</td>
<td>4</td>
</tr>
<tr>
<td>High W/ High B</td>
<td>FCC (STR)</td>
<td>1413</td>
<td>1283</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>Ti₄C₂S₂</td>
<td>1374</td>
<td>1283</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>B₂M*</td>
<td>1284</td>
<td>1268</td>
<td>16</td>
</tr>
</tbody>
</table>

* To 0.99 fraction solidified

Figure 43: Scheil-Gulliver solidification simulation results. Temperature range for each phase predicted during solidification. STR (Liquidus – Solidus) shown in blue.
When examining the effect of alloying additions, especially tungsten and boron, on the solidification behavior of these alloys, it is useful to know the segregation behavior of each element during solidification. This can be done by using the Scheil-Gulliver module within Thermo-Calc™ to calculate the partition coefficient, $k$, for each element. The partition coefficients were calculated using the compositions provided in Table 6. The partition coefficient ($k$) for each element is calculated by using the composition of the first solid to form divided by the nominal composition for a given element. A partition coefficient less than one indicates that the element will segregate to the liquid during solidification and greater than one that it will segregate to the solid. The partition coefficients for each element in these alloys are shown in Figure 44. All the compositions exhibited similar partition coefficients and therefore the figure below shows the average partition coefficient for each element from the five compositions tested.

![Partition Coefficients Graph](image)

Figure 44: Average partition coefficient ($k$) for each element
It can be seen that tungsten, manganese, nickel, and iron, have k-values close to one indicating that little partitioning of these elements should occur during solidification. Carbon, boron, phosphorus, sulfur, and titanium have much lower k-values and will partition to the liquid during solidification. These elements (carbon, titanium, sulfur, phosphorus, and boron) all partition strongly to the liquid during solidification and have the potential to form liquid films along solidification grain boundaries that can promote solidification cracking. Elements with low partitioning coefficients also have the effect of expanding the solidification temperature range.

In addition to the partition coefficients, the solidification temperature ranges were also predicted by using the Scheil-Gulliver module within Thermo-Calc™. The liquidus and solidus temperatures were calculated to approximate the STR for these alloys. The results from the simulations are shown in Table 11. Note that the simulations were stopped once the solid phase fraction ($f_S$) reached 0.98, which is common practice. In this investigation, borides started to form at around 0.98 $f_S$, which means these results may not fully reflect the effects of boron during solidification but it is not common practice to collect data past 0.98 $f_S$. Results from the simulations indicated only slight variation in STR among the five compositions. The STR only varied by 12°C with the Low W/High B exhibiting the highest STR while the High W/Low B had the lowest STR. W appeared to lower the liquidus temperature and subsequently the STR while B expanded the STR. The expansion of the STR is attributed to the strong partitioning effect of B. More detailed information regarding the solidification temperature range will be discussed in the Solidification Temperature Range Analysis section.
Table 11: Scheil-Gulliver simulated solidification results

<table>
<thead>
<tr>
<th>Designation</th>
<th>Scheil STR</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquidus (°C)</td>
<td>Solidus (°C)</td>
<td>STR (°C)</td>
</tr>
<tr>
<td>Base</td>
<td>1421</td>
<td>1288</td>
<td>133</td>
</tr>
<tr>
<td>Low W / Low B</td>
<td>1418</td>
<td>1283</td>
<td>135</td>
</tr>
<tr>
<td>Low W / High B</td>
<td>1418</td>
<td>1281</td>
<td>137</td>
</tr>
<tr>
<td>High W / Low B</td>
<td>1413</td>
<td>1288</td>
<td>125</td>
</tr>
<tr>
<td>High W / High B</td>
<td>1413</td>
<td>1283</td>
<td>130</td>
</tr>
</tbody>
</table>

*Simulation to 0.98 fraction solidified

One of the overall goals of this study was to examine the interactive effect of W and B. To illustrate this interaction, a 3D contour plot of simulated solidification temperature ranges was generated by running Scheil simulations with varying W and B concentrations. All other elements were held constant while W was varied up to 6 wt% and B up to 30 ppm. The effect that W and B have on the solidification temperature ranges is illustrated in Figure 45. It shows that as W is increased, the STR is reduced, for a fixed B concentration. For a fixed W concentration, increasing B expanded the STR. The overall trend is that higher W and lower B reduce the STR. There appears to be no interactive effect of tungsten and boron on the STR.

It should also be noted that over the entire range of W and B evaluated, the difference in STR is less than 20°C and that the STR varies in the range from 120°C to 140°C. These represent relatively small changes in STR and the predicted range of STR suggests only moderate susceptibility to weld solidification cracking [23].
Figure 45: Effect of varying tungsten and boron on the STR

5.1.2 Solidification Temperature Range Analysis (SS DTA)

STR values can be a good indication of susceptibility to solidification cracking. Weld solidification cracking occurs during the final stages of solidification when tensile shrinkage stress accumulates and liquid films still persist along solidification grain boundaries in the structure [57]. Therefore, as the STR range expands, there is more time for liquid films to persist along solidification grain boundaries and, in general, results in an increased susceptibility to solidification cracking. SS DTA has been shown to be a useful tool for determining the non-equilibrium solidification behavior associated with welding to solidification cracking susceptibility [56]. In this study, the STR for each alloy composition was determined using computational (Thermo-Calc™ simulations) and
experimental techniques. It should be noted that the SS DTA results in this section were obtained using FCAW wire and not the weld metal samples. SS DTA testing with the welded samples was not possible due to insufficient amount of material to perform both CPTT and SS DTA testing. The use of both computational and experimental techniques provides a way to predict the behavior of these alloys, in regards to their solidification cracking susceptibility, when examining the effect of alloying additions.

In order to determine the STR experimentally, the liquidus and solidus temperatures were measured by processing the thermal data using SS DTA™ software. This software mathematically generates a reference curve based upon the thermal history that is then overlaid onto the actual acquired thermal data. The software is then able to determine transformation temperatures by locating deviations between the thermal data and the reference curve. The deviations occur due to latent heat of fusion being released or absorbed during solidification. The liquidus temperature can be difficult to determine depending on how many data points were recorded at high temperatures. Due to the high solidification rates at the start of solidification, there may not be enough data at high temperature for the SS DTA™ software to determine the $T_L$. The $T_S$ measurements are relatively easy to identify as more data points are recorded during solidification at lower temperatures.

Figure 46 illustrates a processed SS-DTA curve with the liquidus, solidus, and subsequent STR shown for the Base alloy composition. For each composition, the liquidus and solidus temperatures were extracted by processing the thermal data in the SS DTA™ software. When processing the thermal data, it can be somewhat subjective when
identifying phase transformations and therefore an average of the three trials per composition was used to determine the transformation temperatures. Identifying the presence of a transformation from the thermal data is simple, but determining the exact transformation temperatures can be difficult and subjective since the analysis depends on correctly identifying model parameters that generate the reference curve.

Figure 46: Processed SS DTA curve illustrating the STR for the Base alloy showing the $T_L (1422^\circ C)$ and $T_S (1268^\circ C)$

The measured SS DTA solidification results are summarized in Table 12. The SS DTA measurements exhibited more variation than the Scheil simulations. Among the five
compositions, the STR varied by 24°C with the Low W/High B exhibiting the highest STR and the Base exhibiting the lowest STR. In addition to a larger variation in STR between alloy compositions, the solidification temperature ranges measured were, on average, 30°C higher than the Scheil simulated STRs. This can be attributed to the differences in the solidus temperatures. The measured $T_S$ values from SS DTA testing were consistently lower than the simulated $T_S$ values. Differences in $T_S$ could be attributed to the simulations being terminated at 0.98 fraction solid. Higher fraction solid values will lead to lower $T_S$ values and higher STRs, but the use of values above 0.98 is not common [23]. The $T_L$ measurements, that could be reliably determined, correlated well with the Scheil simulated values. The measured $T_L$ slightly decreased as W increased, demonstrating a trend similar to the Scheil simulated data. Tungsten appeared to lower the liquidus temperature and subsequently the STR while B expanded the STR, demonstrating the same trend as the Scheil simulated STRs.

Table 12: Summary of solidification behavior determined by SS DTA for FCAW wire

<table>
<thead>
<tr>
<th>Value [°C]</th>
<th>Base</th>
<th>Low W/ Low B</th>
<th>Low W/ High B</th>
<th>High W/ Low B</th>
<th>High W/ High B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquidus ($T_L$)</td>
<td>1422</td>
<td>1419</td>
<td>1419</td>
<td>1411</td>
<td>1412</td>
</tr>
<tr>
<td>Solidus ($T_S$)</td>
<td>1268</td>
<td>1255</td>
<td>1241</td>
<td>1240</td>
<td>1256</td>
</tr>
<tr>
<td>Measured STR</td>
<td>154</td>
<td>164</td>
<td>178</td>
<td>171</td>
<td>157</td>
</tr>
</tbody>
</table>

Note: $T_L$ and $T_S$ values are an average of at least three trials

To compare both the computational and experimental analysis results, a chart comparing the STRs from each technique is shown in Figure 47. A common trend
between the two techniques is that the Low W/ High B composition exhibited the highest STR. This would suggest that this particular composition would have the highest susceptibility to solidification cracking, based on the STR. The composition predicted to have the lowest susceptibility to solidification cracking differs based on which technique was used. Scheil simulation predicted the High W/ Low B to be the least susceptible while the SS DTA technique predicted the Base composition.

In general, alloys with a STR greater than 150°C tend to be susceptible to solidification cracking, while alloys with a STR less than 100°C are considered resistant to solidification cracking. Based on the data in Table 12, these weld metals would be expected to have moderate susceptibility, with increasing susceptibility under high restraint conditions.

![Comparison between Scheil and SS DTA STR](image)

Figure 47: Comparison between Scheil and SS DTA STR
5.1.3 **Solidification Analysis Summary and Conclusions**

To this point, only computational and material testing has been performed and discussed. These first two techniques provided insight on how alloying additions, such as W and B, can have an effect on the solidification behavior. These two techniques are used in conjunction with weldability tests, such as the CPTT, to generate an overall ranking of these alloy’s susceptibility to solidification cracking.

The analysis performed regarding the solidification behavior of these high-Mn steel filler metals revealed the following:

1) Scheil-Gulliver solidification simulations demonstrated that these filler metals exhibit primarily austenite solidification in addition to the formation of a Ti₄C₂S₂ phase upon further solidification. The compositions with W and B additions had an additional phase form, MB₂, at lower temperature.

2) Carbon, phosphorus, titanium, boron, and sulfur exhibited low partition coefficients indicating that they will partition strongly during solidification and have the potential to form low melting liquid films that promote solidification cracking.

3) Scheil-Gulliver solidification simulations predicted only slight variations in the STR among the alloys. W additions reduced the solidification temperature range while B additions expanded the STR. Boron’s low partition coefficient (k) suggests it will strongly partition to the liquid during solidification.

4) There appears to be no interactive effect of tungsten and boron on the solidification temperature range.
5) STRs measured with SS DTA were larger than the Scheil-Gulliver simulations with the Low W/ High B demonstrating the largest STR and the Base demonstrating the lowest STR.

6) The Low W/ High B composition had the highest STR using both techniques and thus it is predicted to have the highest susceptibility to solidification cracking. Boron appears to have the most influential effect on expanding the STR of these alloys due to segregation.

### 5.2 Cast Pin Tear Test Results

This section contains the results and discussion for the Cast Pin Tear Test. Two rounds of the CPT Test were performed to examine and verify the lower cracking thresholds of the five filler metal compositions tested. To evaluate and rank the filler metal’s susceptibility to solidification cracking, the lower cracking threshold (LCT) was the main criterion used. As a reminder, there are three different CPTT ranking criteria that can be used to evaluate an alloy’s susceptibility to solidification cracking:

1) Maximum pin length with an average of 0% circumferential cracking
   
   [Lower Cracking Threshold (LCT)]

2) Minimum pin length with an average of 100% circumferential cracking
   
   [Upper Cracking Threshold (UCT)]

3) The 0% to 100% cracking pin length range
The LCT was chosen as the best method for comparison among alloy compositions. It was found that using the LCT criterion produced the most reproducible and consistent data that can be compared among compositions. Large amounts of scatter in the data at longer pin lengths makes ranking alloys according to their UCT more difficult.

5.2.1 1st Round CPTT Results

The first round of CPTT was performed using FCAW consumables that were melted into buttons prior to casting. The results from the first round CPTT for each of the compositions tested will be presented and discussed here. Only the average circumferential cracking plots for each composition are shown in this section but more detailed data for each alloy tested can be found in the Appendix.

Individual cracking response curves for the Base, Low W/ Low B, Low W/ High B, High W/ Low B, and High W/ High B compositions are shown in Figures 48-52, respectively. The error bars on each plot represent the standard deviation between all casts for a given pin length. The deviation between cracking percentage was typically the highest at longer pin lengths. The Base composition exhibited an LCT of 0.75 inches and an UCT of 1.5 inches. The Low W/ Low B composition exhibited an LCT of 0.625 inches and an UCT of 1.75 inches. The Low W/ High B composition exhibited a LCT of less than 0.5 inches and an UCT of 1.625 inches. The actual LCT for the Low W/ High B composition cannot be measured since the 0.5 inch mold is the smallest pin length that can be tested in the CPTT apparatus and cracking was present at this pin length. The
High W/ Low B composition exhibited a LCT of 0.5 inches and an UCT of 1.625 inches. Lastly, the High W/ High B composition exhibited a LCT of 0.625 inches and an UCT of 1.5 inches. The last plot, Figure 53, is the same plot of the average circumferential cracking verses pin length, but with all of the compositions present for comparison purposes.

Figure 48: 1st Round CPTT average circumferential cracking percentage versus pin length for the Base composition
Figure 49: 1\textsuperscript{st} Round CPTT average circumferential cracking percentage versus pin length for the Low W/ Low B composition

Figure 50: 1\textsuperscript{st} Round CPTT average circumferential cracking percentage versus pin length for the Low W/ High B composition
Figure 51: 1st Round CPTT average circumferential cracking percentage versus pin length for the High W/ Low B composition

Figure 52: 1st Round CPTT average circumferential cracking percentage versus pin length for the High W/ High B composition
To summarize the results, Table 13 shows CPTT results based on the three ranking criteria: lower cracking threshold (LCT), upper cracking threshold (UCT), and 0 to 100% cracking pin length range. Since the LCT is the main criterion used for ranking, alloys are listed from the highest to lowest LCT. The Base composition exhibited the highest LCT with a pin length of 0.75 inches while the Low W/High B composition displayed the lowest LCT with a pin length of less than 0.5 inches.

Figure 53: 1st Round CPTT average cracking response curves for each alloy tested
Table 13: Summary of 1st Round CPTT cracking response data

<table>
<thead>
<tr>
<th>Composition</th>
<th>LCT (in)</th>
<th>UCT (in)</th>
<th>0% to 100% Pin Length Range (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.75</td>
<td>1.5</td>
<td>0.75</td>
</tr>
<tr>
<td>Low W/Low B</td>
<td>0.625</td>
<td>1.75</td>
<td>1.125</td>
</tr>
<tr>
<td>High W/High B</td>
<td>0.625</td>
<td>1.5</td>
<td>0.875</td>
</tr>
<tr>
<td>High W/Low B</td>
<td>0.5</td>
<td>1.625</td>
<td>1.125</td>
</tr>
<tr>
<td>Low W/High B</td>
<td>&lt;0.5</td>
<td>1.625</td>
<td>&gt; 1.125</td>
</tr>
</tbody>
</table>

All the compositions tested in the 1st round of CPTT had LCT values that varied between <0.5-0.75 inches, which indicates that all five filler metals tested have a relatively poor resistance to solidification cracking, based on previous CPTT results [48]. Typically, LCT values below 1.0 inch indicate that a material would be susceptible to solidification cracking depending on the restraint level present during fabrication. To generate a ranking between alloy compositions in terms of cracking susceptibility, a larger separation in pin length is desired. If these alloys were retested (2nd Round CPTT), it is not uncommon for the LCT to deviate up or down by one pin length. Based on the LCT criterion, the CPTT ranked the susceptibility to solidification cracking from least to most susceptible as follows: Base, Low W/Low B = High W/High B, High W/Low B, and Low W/High B. From these results, additions of W and B resulted in an increase in cracking susceptibility compared to the Base composition. There is no discernable difference between the compositions with W and B additions for the 1st round of CPTT testing as the pin length deviation is so small. Figure 54 below illustrates the increasing solidification cracking susceptibility based on the LCT criterion for the filler metals testing in the 1st round of CPTT.
The second round of CPPT testing was performed to verify the lower cracking thresholds obtained from the first round of testing. The first round of testing used button melt samples that were made from cut up pieces of flux-cored welding wire provided by POSCO. The second round of testing used actual welded samples provided by POSCO that were sectioned from plate welds. The concern from the first round of testing was that the flux was becoming contaminated during the melting process used to make buttons. The following results are from the second round of testing. It should be noted that a welded sample for the Base composition was not provided and instead of a welded sample, the Base composition was retested using the same procedure as the first round.

**5.2.2 2nd ROUND CPPT RESULTS**

The second round of CPPT testing was performed to verify the lower cracking thresholds obtained from the first round of testing. The first round of testing used button melt samples that were made from cut up pieces of flux-cored welding wire provided by POSCO. The second round of testing used actual welded samples provided by POSCO that were sectioned from plate welds. The concern from the first round of testing was that the flux was becoming contaminated during the melting process used to make buttons. The following results are from the second round of testing. It should be noted that a welded sample for the Base composition was not provided and instead of a welded sample, the Base composition was retested using the same procedure as the first round.
Due to a limited amount of material provided by POSCO, only pin lengths located around the LCT from the first round of testing were cast.

The 2nd round CPTT focused on identifying LCT and therefore fewer pins needed to be cast. The cracking response characteristics and LCT values for each composition is shown in Table 14 and a plot of average circumferential cracking versus pin length for each compositions is shown in Figure 55. For more detailed plots and cracking characteristics from the 2nd round of CPTT, please see the Appendix. Following the same trend from the 1st round of CPTT, the Base composition exhibited the highest LCT of 0.875 inches while the Low W/ High B had the lowest LCT of less than 0.5 inches. The LCT pin varied between <0.5-0.875 inches among the five alloy compositions tested.

Table 14: 2nd Round CPTT cracking response data and LCT for each alloy composition tested

<table>
<thead>
<tr>
<th>Pin Length (in)</th>
<th>Base Count</th>
<th>Avg. Cracking</th>
<th>Low W / Low B Count</th>
<th>Avg. Cracking</th>
<th>Low W / High B Count</th>
<th>Avg. Cracking</th>
<th>High W / Low B Count</th>
<th>Avg. Cracking</th>
<th>High W/High B Count</th>
<th>Avg. Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>3 0%</td>
<td>4 9%</td>
<td>3 0%</td>
<td>2 0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td>-</td>
<td>-</td>
<td>5 5%</td>
<td>2 8%</td>
<td>3 0%</td>
<td>4 5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>2 0%</td>
<td>3 39%</td>
<td>4 13%</td>
<td>3 31%</td>
<td>3 34%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.875</td>
<td>4 0%</td>
<td>3 21%</td>
<td>2 25%</td>
<td>4 31%</td>
<td>3 40%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4 27%</td>
<td>3 66%</td>
<td>- -</td>
<td>- -</td>
<td>- -</td>
<td>3 34%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.125</td>
<td>2 22%</td>
<td>- -</td>
<td>- -</td>
<td>- -</td>
<td>- -</td>
<td>- -</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lower Cracking Thresholds (LCT)

<table>
<thead>
<tr>
<th>Pin Length (in)</th>
<th>0.875</th>
<th>0.5</th>
<th>&lt;0.5</th>
<th>0.625</th>
<th>0.5</th>
</tr>
</thead>
</table>
As with the 1\textsuperscript{st} round of CPTT, a larger separation in pin length is desired to generate a ranking among alloy compositions in terms of solidification cracking susceptibility. Based on the LCT criterion, the CPTT ranked the susceptibility to solidification cracking from least to most susceptible as follows: Base, High W/Low B, High W/High B = Low W/Low B, and Low W/High B. From these results, additions of W and B resulted in a slight increase in cracking susceptibility compared to the Base composition. Different from the 1\textsuperscript{st} round of CPTT, there appears to be a trend with the varying W and B additions. When examining the low B compositions, increased W additions resulted in an increase to cracking resistance (i.e. Low W/Low B vs. High W/Low B). The same trend appears to be true for the high B compositions, increased W
additions resulted in a slight increase to cracking resistance (i.e. Low W/High B vs. High W/High B). A possible explanation for this trend is that tungsten slightly reduces the solidification temperature range which results in a slight increase in resistance to solidification cracking. This is illustrated in Figure 56, which shows the increasing solidification cracking susceptibility based on the LCT criterion for the filler metals tested in the 2nd round of CPTT.

Figure 56: Summary of 2nd Round CPTT cracking response – Solidification Cracking Susceptibility Ranking (LCT)
5.2.3 CPTT Summary and Conclusions

All the compositions tested using the CPTT from both rounds had LCT values that varied between < 0.5-0.875 inches. As mentioned earlier, LCT values below 1.0 in generally indicate that a material would be susceptible to solidification cracking depending on the restraint level present during fabrication. The bar chart shown in Figure 57 illustrates the similarities and differences between the two different rounds of CPTT. The LCT values for each composition only deviated by one pin length between the two different rounds. This slight deviation in LCT was deemed acceptable as small changes in test variables can cause slight changes in results or even slight changes in chemical composition. It can also be concluded that the material form (FCAW wire vs weld metal) did not have an effect on the outcome of the test results.

The overall conclusions that can be made from the CPTT is that the Base composition (No W or B) proved to perform the best among the five filler metals tested and the Low W/ High B composition performed the worst in regards to solidification cracking susceptibility. Though a trend from the 1st round of CPTT could not be established when evaluating the effects of W and B additions, the 2nd round of CPTT did. The 2nd round of testing showed that higher W additions to both low and high B compositions resulted in a slight increase in resistance to solidification cracking susceptibility.
To illustrate that these filler metals would be expected to perform poorly in regards to solidification cracking susceptibility, it is useful to compare the LCT values from this study to other austenitic alloys tested using the CPTT. Figure 58 compares the alloys tested in this study to a number of Ni-base alloys that have been previously tested using the CPTT. It should be noted that this CPTT data was not collected using the current generation CPTT and procedures. The Renè alloys (Renè 125 and 142) are known to be extremely susceptible to solidification cracking, while Alloy 600 is known to be resistant [50]. Since all the alloy compositions in this study exhibited LCT values less than 1.0 inch, prior CPTT data coupled with actual fabrication experience predicts that these Fe-Mn-C filler metals would be susceptible to solidification cracking.

Figure 57: Comparison of LCT between 1st and 2nd Rounds of CPTT
Figure 58: Comparative ranking of the Fe-Mn-C filler metals (2nd Round CPTT) to Ni-base alloys using the LCT criterion

5.3 Metallurgical Analysis

Metallurgical characterization was performed on button samples and cast pins for each of the filler metal compositions. Metallography, microscopy, and fractography techniques were performed to fully characterize the microstructure and evaluate the precipitation behavior in these filler metals. Metallography was performed using an Olympus GX-51 inverted microscope at the Ohio State University while microscopy and fractography were performed using two different scanning electron microscopes available at the Center for Electron Microscopy and Analysis (CEMAS): (1) XL-30 field emission ESEM (2) Sirion field emission SEM. The use of energy dispersive spectroscopy (EDS)
was used to quantify partitioning during solidification and evaluate secondary phase formation occurring along solidification cracks/crack tips and on fracture surfaces.

5.3.1 General Microstructure of Fe-Mn-C Filler Metals

The microstructure of these Fe-Mn-C welding consumables was characterized by examining the cross-section of button samples made from the FCAW wire of each composition. Each composition exhibited the same solidification structure and a similar precipitation behavior. A representative microstructure (Base composition) for all the compositions evaluated is shown in Figure 59. All the button samples were etched with 2% nital. The microstructure exhibits primary austenite (FCC) solidification with precipitates present in the interdendritic regions. The austenite (FCC) solidification mode is in agreement with Thermo-Calc™ predictions and SS DTA data. The rectangular, golden precipitates present have been identified using EDS as titanium nitrides. The spherical phases (dark) may be TiO₂, which is a component of the flux-cored welding consumable [17]. There was no evidence of a ferrite transformation or any martensitic products (α’ and ε) in any of the weld metals examined. The high Mn and C content, in addition to Ni, stabilizes the austenite phase to room temperature and below, suppressing the martensite transformation. The addition of Ni also increases the stacking fault energy preventing strain-induced ε-martensite formation [17].
To further analyze the microstructure of these filler metals, the button samples were examined using the Sirion equipped with an EDS detector to obtain compositional information on any secondary phase formation. An SEM image of the Base composition is shown in Figure 60. It is evident that there is a large amount of both intergranular and intragranular secondary phase precipitation occurring in these alloys. Compositional information of these precipitates was obtained by performing EDS spot scans and elemental maps.
Figure 60: SEM image of secondary phase precipitation in Base composition

Figure 61 and Figure 62 are SEM micrographs that illustrate the types of secondary phase formation found in the microstructure. Figure 61 exhibits two different precipitates present with two different precipitation morphologies. The large, rectangular precipitate was identified as a titanium nitride (TiN) from both an EDS spot scan and elemental map. A large amount of titanium nitrides were present along interdendritic regions and appeared in all of the compositions tested in this investigation. These are believed to be high temperature titanium nitrides that form above the liquidus. The smaller, oval-shaped precipitate was rich in titanium and sulfur and is presumed to be either a titanium sulfide or titanium carbosulfide. Referring back to the solidification
analysis results, Scheil solidification simulations predicted the formation of a titanium carbosulfide during solidification in each of the alloys tested and could be the phase forming in these alloys. This precipitation reaction will be discussed in further detail when examining the fractography of CPTT pins.

The next micrograph, Figure 62, is an elemental map showing the precipitate is enriched in titanium and sulfur with trace amounts of nitrogen. It is possible that an agglomeration of titanium nitrides and titanium sulfides or carbosulfides are forming. In both figures, the presence of titanium and sulfur rich constituents were present and seen throughout the microstructure of the Base composition. The other compositions also exhibited the same precipitation behavior with a large amount of precipitates rich in titanium, sulfur, and nitrogen.
Figure 61: SEM micrograph and EDS analysis showing secondary phases rich in Titanium, Sulfur, and Nitrogen in the Base composition
Figure 62: SEM micrograph and elemental map of secondary phases rich in Titanium, Sulfur, and Nitrogen in the Base composition
5.3.2 Verification of Solidification Cracking in CPTT Samples

The fracture surface morphologies for each composition were analyzed to verify the presence of solidification cracking. The fracture surface morphology of cast pins that exhibited 100% (complete circumferential) cracking were analyzed using a combination of the ESEM and Sirion. The fracture morphologies for each alloy are shown in Figure 63. All of the alloys exhibited a dendritic, “egg-crate” fracture morphology that is characteristic of solidification cracking.

Figure 63: Fracture surface morphology of cast pins exhibiting 100% cracking

Continued
Figure 63 continued:

Low W/ High

High W/ Low

High W/ High
To further verify the presence of solidification cracking, optical metallography was done on CPTT samples to examine the cracks. All of the cracking initiated and propagated along solidification grain boundaries which is characteristic of solidification cracking. Evidence of this is shown in Figure 64 for each filler metal composition. It is important to note that no evidence of backfilling was present in any of the samples examined.

Figure 64: Evidence of solidification cracking occurring along SGBs in CPTT samples

Continued
Figure 64 continued:
5.3.3 Evaluation of Secondary Phase Formation

This section serves to further characterize these Fe-Mn-C filler metals through evaluation of the secondary phase formation on the fracture surfaces and crack openings of CPTT pins. There were three secondary phase precipitation reactions that were identified during this investigation: (1) Titanium nitride formation, (2) Manganese sulfide formation, and (3) Titanium sulfide/carbosulfide formation.

5.3.3.1 Titanium Nitride Formation

The fracture surfaces of cast pins in each of the alloys analyzed exhibited a relatively large amount of titanium nitride precipitation. The titanium is introduced into these alloys through the flux, which is made from a rutile (TiO2) type flux cored welding wire. The actual composition of the flux used in these filler metals are confidential and cannot be disclosed. The cuboidal shaped, titanium nitrides present along the fracture surfaces are shown in Figure 65. EDS analysis of spot and line scans showed elevated levels of titanium and nitrogen, verifying these precipitates were titanium nitrides. These titanium nitrides found in these samples form at high temperatures in the liquid and are most likely swept into the solidification grain boundaries and solidification subgrain boundaries during solidification. The titanium nitrides were found in both the 1st and 2nd rounds of CPTT samples and had the same precipitation morphology throughout each of the five filler metal compositions.
Figure 65: Titanium Nitride (TiN) formation along fracture surfaces of CPTT pins
5.3.3.2 Manganese Sulfide Formation

In addition to the formation of titanium nitrides, manganese sulfides (MnS) were present along the fracture surfaces. Examples of MnS formation in cast pins are shown in Figures 66 and 67. The elevated sulfur and manganese content is well above the nominal compositions, illustrated by the EDS spot and line scan data in the upper corners of the micrographs. In the case of these alloys, manganese is a primary alloying addition used in high concentrations to promote austenitic solidification, but historically, manganese has been added to prevent hot shortness during casting. Manganese more readily combines with sulfur, rather than iron, preventing the formation of iron-sulfides and eliminating hot shortness from occurring. The MnS examined in this investigation were found in each of the compositions analyzed but were in a much smaller quantity than the TiN.

![Figure 66: EDS spot scan of Manganese Sulfide (MnS) formation along the fracture surface of a CPTT pin – Low W/ High B composition](image)

120
Figure 67: EDS line scan of Manganese Sulfide (MnS) formation along the fracture surface of a CPTT pin – Low W/ High B composition

5.3.3.3 Titanium Sulfide/Carbosulfide Formation

The most prominent precipitation reaction that was observed in these filler metals was the formation of either titanium sulfides or titanium carbosulfides. This secondary phase was observed on every fracture surface analyzed in each of the compositions tested during this investigation, including the Base composition. The precipitation morphology and size varied slightly but was easily identified on the fracture surfaces of cast pins. Examples of the precipitation morphology can be seen in Figure 68.
Figure 68: Precipitation of secondary phases rich in titanium, sulfur, and carbon with trace amounts of nitrogen in 1st round CPTT samples for each alloy composition

Through SEM analysis, EDS spot scans and elemental maps were used to obtain compositional information on these precipitates. Elemental maps of these particles,
shown in Figure 69, demonstrated that they were rich in titanium and sulfur. Occasionally, small portions of the map would be enriched in nitrogen, suggesting the possible formation of titanium nitrides on or near these particles. These particles are not to be mistaken for manganese sulfides as elemental maps showed a depletion of Mn where the particles were located (See Figure 74). Spot scans showed that the particles were also carbon rich in addition to titanium, sulfur, and nitrogen.

Figure 69: EDS analysis of secondary phases present on the fracture surfaces in 1st round CPTT samples for each composition

Continued
Figure 69 continued:

Low W/ High B

<table>
<thead>
<tr>
<th>EDS Analysis</th>
<th>wt% Ti</th>
<th>wt% S</th>
<th>wt% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot Scan</td>
<td>3.11</td>
<td>9.78</td>
<td>11.66</td>
</tr>
</tbody>
</table>

High W/ Low B

<table>
<thead>
<tr>
<th>EDS Analysis</th>
<th>wt% Ti</th>
<th>wt% S</th>
<th>wt% C</th>
<th>wt% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot Scan</td>
<td>6.33</td>
<td>5.96</td>
<td>10.71</td>
<td>10</td>
</tr>
</tbody>
</table>

High W/ High B

<table>
<thead>
<tr>
<th>EDS Analysis</th>
<th>wt% Ti</th>
<th>wt% S</th>
<th>wt% C</th>
<th>wt% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot Scan</td>
<td>6.33</td>
<td>5.96</td>
<td>10.71</td>
<td>10</td>
</tr>
</tbody>
</table>
The elemental maps only picked up trace amounts of carbon on the particles while EDS spot scans performed directly on the particles showed that they had elevated levels of carbon and occasionally nitrogen, demonstrated in Figure 70.

<table>
<thead>
<tr>
<th>EDS Analysis</th>
<th>wt% Ti</th>
<th>wt% S</th>
<th>wt% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot Scan</td>
<td>7.36</td>
<td>8.57</td>
<td>9.73</td>
</tr>
</tbody>
</table>

Figure 70: EDS spot scan of secondary phase rich in Ti, S, and C – Low W/ High B composition

After analyzing the 1st round CPTT samples, it was hypothesized that these particles enriched with titanium, sulfur, and carbon may not be a product of the solidification process due to the irregular precipitation morphology. These particles could be undissolved particles from the flux and being swept into the last regions to solidify.
The 1st round samples were cast from buttons that were not as-welded samples which gave rise to the concern that the flux may be behaving differently when melting the filler wire into buttons. To evaluate this hypothesis, an analysis of the flux was done to examine if any sulfur rich particles were present. EDS analysis was performed on a small piece of FCAW wire to examine the surface for any particles rich in sulfur. As can be seen in Figure 71, EDS spot scans revealed that the flux did not have any sulfur rich particles and the composition was consistent with that of a rutile (TiO$_2$) type flux.

![EDS analysis of FCAW welding wire – Low W/ High B composition](image)

<table>
<thead>
<tr>
<th>Spot Scan ID</th>
<th>wt% Ti</th>
<th>wt% O</th>
<th>wt% Fe</th>
<th>wt% Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot Scan 1</td>
<td>-</td>
<td>-</td>
<td>1.98</td>
<td>98.02</td>
</tr>
<tr>
<td>Spot Scan 2</td>
<td>8.08</td>
<td>6.4</td>
<td>81.51</td>
<td>-</td>
</tr>
<tr>
<td>Spot Scan 3</td>
<td>13.88</td>
<td>36.86</td>
<td>3.79</td>
<td>45.47</td>
</tr>
</tbody>
</table>

Figure 71: EDS analysis of FCAW welding wire – Low W/ High B composition
In addition to the EDS analysis, X-Ray Diffraction (XRD) was performed to provide a more in-depth analysis on the flux. Flux powder was carefully removed from the welding consumables to examine if any particles in the flux were rich in sulfur. The equipment used was a Rigaku SmartLab X-Ray Diffractometer equipped with a monochromatic detector. Results from the XRD testing were consistence with a rutile type flux and did not show any indications of particles rich in sulfur or carbon ruling out any titanium sulfide/carbosulfide particles being introduced from the flux.

With EDS and XRD testing not showing any presence of the titanium sulfide/carbosulfide particles seen in the 1\textsuperscript{st} round CPTT samples, the hypothesis that these particles were not part of the solidification process was disproved. To further verify that these particles were part of the solidification process, sectioned CPTT samples and a 100\% cracked pin from the 2\textsuperscript{nd} round of testing (weld metal samples) were examined for secondary phase formation. The weld metal samples exhibited the same precipitation behavior that the 1\textsuperscript{st} round of cast pins exhibited. A large of amount of titanium, sulfur, carbon, and nitrogen rich constituents were present along the fracture surface of pins and near/along the solidification cracks of polished samples. Fractography performed on the 2\textsuperscript{nd} round CPTT sample from the High W/Low B composition is shown in Figure 72. The precipitation morphology of these particles was consistent with the precipitation morphologies from the 1\textsuperscript{st} round CPTT samples.
Figure 72: Precipitation of secondary phases rich in Ti and S with trace amounts of C and N in 2nd round CPTT sample – High W/ Low B composition

To verify that the particles from the 2nd round of testing were the same as the 1st round, compositional information was obtained through EDS analysis. EDS analysis, shown in Figure 73, was consistent with the 1st round showing that the particles were rich in titanium, sulfur, carbon, and occasionally trace amounts of nitrogen.
In addition to the fractographic analysis, solidification cracks in cross-sectioned CPTT samples were analyzed. As with the fracture surfaces, titanium, sulfur, and carbon rich constituents were present along solidification cracks or in close vicinity of the
cracks. Micrographs shown in Figure 74 show the formation of titanium nitrides (top image) and titanium sulfides/carbosulfides. As mentioned before, there is a depletion of manganese where the particles exist eliminating the possibility that these are manganese sulfides. The enrichment of titanium and sulfur in particles near/along solidification cracks is consistent with what was seen on fractures surfaces from both rounds of CPTT testing.

Figure 74: Secondary phase precipitation near/along solidification cracking rich in Ti, S, C, and N in 2nd round sectioned CPTT samples
5.3.4 Metallurgical Analysis Summary

Through characterization of these high-Mn steel filler metals, three main secondary phase precipitation reactions were identified: (1) Titanium nitrides (2) Manganese sulfides (3) Titanium sulfides/carbosulfides. The formation of titanium nitrides and manganese sulfides were not a surprise. Titanium nitride formation during solidification was expected to occur due to the use of a rutile type flux cored welding consumables that are comprised of titanium. Manganese sulfides are a common precipitation reaction that preferentially forms over iron-sulfides during solidification and with these alloys having high concentrations of manganese added, it was anticipated that they would form during solidification. The formation of titanium sulfides/carbosulfides, though predicted by Thermo-Calc™, was unexpected. The fracture surfaces were decorated with the formation of these particles in each of the alloy compositions tested during this investigation. The formation of these titanium sulfides/carbosulfides expands the solidification temperature range and is a contributing factor to the overall poor resistance to solidification cracking demonstrated through results from the solidification analysis and CPTT.

When comparing the metallography and fractography of CPTT samples, there was no discernable differences among the alloys tested. The amount and distribution of secondary phase precipitation was very similar among the five filler metal compositions tested with only the Base composition varying slightly. The Base composition had a slightly smaller amount of titanium sulfide/carbosulfide formation compared to the compositions with W and B additions. Though the Base composition did perform the best
in regards to the CPTT ranking, there is no way of correlating the precipitation behavior to the CPTT results, especially with the W and B added alloys.

    It should be noted that throughout the entire characterization process, no boron rich compounds or constituents were found. To determine the segregation behavior of boron during solidification, higher level characterization, such as Secondary Ion Mass Spectroscopy (SIMS) and/or TEM work, would be needed to quantify boron segregation and determine its effect on solidification cracking in these alloys. If the segregation behavior of boron could be determined, it may provide insight on the trends and rankings that were found during CPT testing.
CHAPTER 6: SUMMARY OF TESTING AND FINAL ALLOY RANKING

The overarching goal of this project was to test five filler metal’s susceptibility to solidification cracking and determine a range of W and B additions that would exhibit the adequate resistance to solidification cracking from a fundamental standpoint. To achieve this, computational modeling, CPTT, and advanced characterization techniques were used to examine the solidification characteristics and predict the susceptibility to solidification cracking in these Fe-Mn-C welding consumables. The solidification temperature range analysis paired with the CPTT provided insight into how these filler metals may perform and the role of alloying with W and B. Additionally, the analysis of secondary phase formation in these filler metals was used to determine the effect of alloying elements on the microstructure and cracking susceptibility. The following is a summary of the testing performed that led to the final ranking of these filler metals in terms of susceptibility to solidification cracking.

Referring to Table 15, when comparing the results from both rounds of CPTT to the solidification temperature range results (SS DTA and Scheil Simulations), there was one trend that each test technique demonstrated. Each test showed that the Low W/High B composition had the least resistance to solidification cracking based on it exhibiting the largest STR and the smallest LCT from both CPTT rounds. The Base composition
exhibited the highest resistance in both rounds of CPTT and SS DTA testing but not in the Scheil simulations.

Table 15: Ranking of Cracking Susceptibility by Test Technique

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Scheil Simulation (STR)</th>
<th>SS DTA (STR)</th>
<th>1st Round CPTT</th>
<th>2nd Round CPTT</th>
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<tr>
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<td>3</td>
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Note: 1 = Highest Susceptibility

The 1st round of CPTT and SS DTA rankings were almost identical with the Low W/High B having the highest susceptibility and the Base exhibiting the lowest susceptibility. A reminder that SS DTA was only performed with buttons made from the FCAW wire and not weld metal samples. Thus, comparing the SS DTA data to the 2nd round of CPTT may not yield the truest comparison as chemical composition variations from the 1st (flux-cored wire) to the 2nd (weld metal samples) round of samples could have changed the STR ranking. The correlation between SS DTA and the 1st round CPTT data is useful in that SS DTA testing uses a very small amount of material for testing and could help with future development of more resistant Fe-Mn-C filler metals. Provided more weld metal samples were available, a second SS DTA trial could have been done for further comparison.
The 2\textsuperscript{nd} round of CPTT demonstrated a trend that showed that higher W additions to both low and high B compositions resulted in a slight increase in resistance to solidification cracking susceptibility. Referring to the Scheil STR data, the same trend exists in that the STR was lower when W was increased to both low and high B compositions. It does appear that the effect of tungsten on the STR may be exaggerated when running Scheil-Gulliver simulations as the Base composition exhibited the lowest susceptibility in both rounds of CPT testing, differing from the prediction that both high W alloys would exhibit a higher resistance.

Advanced characterization of these filler metals demonstrated that they exhibit primary austenitic solidification that was consistent with Scheil solidification simulations. Three main precipitation reactions were identified through EDS analysis: titanium nitrides, manganese sulfides, and titanium sulfides/carbosulfides. The most prominent secondary phase being the formation of titanium sulfides/carbosulfides. Interestingly, the Scheil solidification simulations predicted the formation of a titanium carbosulfide, Ti$_4$C$_2$S$_2$, during solidification in each of the alloys tested and it is believed that the phases present in these alloys were indeed titanium carbosulfides. The Scheil simulations did predict the formation of a MB$_2$ phase but no boron rich compounds or constituents were found during this investigation. If the effects of boron segregation could have been determined, it could provide insight on the trends and rankings that were found during CPT testing. It appeared that boron had a deleterious effect on the solidification cracking susceptibility of these filler metals tested.
When comparing the microstructure and fracture surface of CPTT samples, there were no metallographic or fractographic differences among the alloy compositions tested. The size and distribution of the secondary phases, in particular the titanium sulfides/carbosulfides, were very similar. The Base composition did appear to exhibit slightly less precipitation of the titanium sulfide/carbosulfide secondary phase and could be a contributing factor, in addition to having no B, to why the Base composition performed the best in the CPTT. The formation of titanium sulfide/carbosulfide during solidification acts to expand the solidification temperature range and contributes to the overall poor resistance to solidification cracking exhibited in these alloys.

Combining all of the results and discussion from the testing techniques used in this investigation, a final ranking of these filler metals has been generated, shown in Figure 75. The Base composition had the highest resistance while the Low W/High B exhibited the lowest resistance to solidification cracking. Though the Base performed the best, results from testing performed during this investigation concluded that each composition would be expected to be susceptible to solidification cracking depending on the restraint level present during fabrication. Any combination of W and B additions to the Base composition resulted in an increased susceptibility to solidification cracking.

![Figure 75: Final alloy ranking according to solidification cracking susceptibility](image)
CHAPTER 7: CONCLUSIONS AND FINAL REMARKS

Based on the results and discussion from Chapter 5 and 6, the following conclusions can be made from this investigation in regards to the solidification behavior and cracking susceptibility of high-Mn steel filler metals:

SOLIDIFICATION ANALYSIS:

1) Carbon, sulfur, titanium, boron, and phosphorus strongly segregate to the liquid during solidification and had the strongest effect on expansion of the STR and on the solidification cracking susceptibility.

2) Additions of W appeared to lower the liquidus temperature and subsequently the STR while B expanded the STR due to the strong partitioning effect of boron.

3) The Low W/High B composition had the highest STR using both techniques and thus it is predicted to have the highest susceptibility to solidification cracking. Boron appears to have the most influential effect on the expansion of the STR in these alloys due to segregation.

CPTT TESTING:

1) Based on the LCT criterion, both rounds of CPTT ranked the Base composition the least susceptibility to solidification cracking while the Low W/High B compositions exhibited the highest susceptibility to solidification cracking.
2) All the compositions tested using the CPTT from both rounds had LCT values that varied between < 0.5-0.875 inches. LCT values below 1.0 in. generally indicate that a material would be susceptible to solidification cracking depending on the restraint level present during fabrication.

3) Though a trend from the 1st round of CPTT (melted filler wire) could not be established when evaluating the effects of W and B additions, the 2nd round of CPTT did. The 2nd round of testing (weld metal samples) showed that higher W additions to both low and high B compositions resulted in an increase in resistance to solidification cracking susceptibility.

4) Comparing the CPTT results for these high-Mn filler metals to previously tested Ni-base alloys suggested that these alloys would be susceptible to solidification cracking under moderate restraint conditions.

**METALLURGICAL ANALYSIS:**

1) Each filler metal composition tested exhibited primary austenite solidification with no evidence of martensite or other primary phases.

2) Through characterization of these high-Mn steel filler metals, three main secondary phase precipitation reactions were identified: (1) Titanium nitrides 
(2) Manganese sulfides (3) Titanium sulfides/carbosulfides.

3) The formation of titanium sulfide/carbosulfide at the end of solidification expands the solidification temperature range and contributes to the overall poor resistance to solidification cracking exhibited in these alloys.
4) No boron rich constituents were found during this investigation and more advanced characterization techniques would be needed to evaluate the segregation behavior of boron during solidification. Though it could not be quantified, it is believed that boron has a detrimental effect on the susceptibility to solidification cracking based on the results from the CPTT and solidification analysis.

5) No evidence of backfilling was observed in any of the cross-sectioned CPTT samples examined during this investigation.

**Final Remarks:**

The additions of W and B to the Base composition resulted in an increase in cracking susceptibility in these filler metals. Scheil simulations predicted that increased tungsten additions to boron added compositions would result in an increased resistance to solidification cracking. Though this trend held true during the 2nd round of CPTT, the benefit from adding W was not significant enough to overcome the deleterious effects of boron additions and yield a more resistant composition than the Base. Since the Base composition was ranked the least susceptible to solidification cracking, the additions of W and B to these filler metals is not recommended as no combination of W and B will provide adequate resistance to solidification cracking. The effects of W and B were not examined separately, but from this investigation it appears that B plays the more dominant role in regards to cracking susceptibility. In addition to the increased susceptibility to solidification cracking resulting from W and B additions, it was found that the formation of titanium sulfides/carbosulfides expanded the solidification temperature range and contributed to the overall poor resistance to solidification cracking.
in these alloys. Therefore, all of the compositions tested, including the Base composition (No W or B), would be expected to be susceptible to solidification cracking depending on the restraint level present during fabrication.

It is apparent from this investigation that the presence of boron and sulfur, even at relatively low levels (≤ 50ppm), in these Fe-Mn-C filler metals promotes an increase in solidification cracking susceptibility. Further research regarding the solidification cracking susceptibility of high-Mn steel filler metals is needed to develop a filler metal composition that provides adequate resistance to solidification cracking and reduce the overall cost of fabricating LNG storage tanks.
CHAPTER 8: FUTURE WORK

The following is a list of recommendations for future research in development of high-Mn steel filler metals:

1) Examine the effects of tungsten and boron separately. Develop compositions that only have one of the alloying elements, W or B, added to the Base composition and examine the cracking response using the CPTT. This would allow the effects of W or B to be studied independently rather than observing the interactive effect between the W and B.

2) The role of boron in this investigation was not fully understood. More advanced characterization techniques are needed to conclude if boron plays a detrimental role in these filler metal’s susceptibility to solidification cracking. The use of Secondary Ion Mass Spectroscopy (SIMS) and TEM work may be able to quantify boron segregation in these alloys. It may influence eutectic formation and liquid film wetting during solidification.

3) SEM analysis of the fracture surfaces and polished surfaces of CPTT samples revealed a large amount of secondary phase precipitation. Though EDS identified the titanium nitrides and manganese sulfides relatively easily, the constituents rich in titanium, sulfur, and carbon could not specifically be identified and were presumed to be titanium sulfides or titanium carbosulfides. It is proposed that
these precipitate phases could be analyzed further by an electrochemical extraction procedure. Once extracted, the precipitate phases could be analyzed by X-Ray Diffraction.

4) Further investigation with weldability testing on hot cracking susceptibility would be beneficial. In addition to the CPTT results already generated, it would be useful to perform Transvarestraint testing on weld metal samples to quantify weld solidification cracking. The cracking response for these alloys at varying strain levels could then be assessed and qualitatively be compared to the CPTT data already obtained.

5) In addition to performing Transvarestraint testing, it is proposed that the effects of multi-pass welding on the precipitation behavior in high-Mn steel filler metals should be examined. With relatively high concentrations of C and W present in these filler metals, carbide precipitation could be problematic when performing multi-pass welding and/or post-weld heat treatments. The Gleeble thermo-mechanical system available at OSU could be used to simulate multi-pass welding conditions on as-solidified weld metal tensile samples. Characterization techniques (LOM/SEM/TEM) could then be used to examine the precipitation behavior in these filler metals.

6) Though solidification cracking was the main focus of this research, evaluating the susceptibility of high-Mn steels to ductility-dip cracking (DDC) could be assessed. The fully austenitic microstructures that high-Mn steels exhibit are desirable for low-temperature properties but when welding is introduced, straight,
mobile grain boundaries can form and raise concern for DDC. To assess the susceptibility to DDC, the Strain-To-Fracture Test (STF) could be performed.
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APPENDIX: CAST PIN TEAR TEST DATA

All of the data collected from both rounds of CPTT are shown in the figures and tables below.

1ST ROUND CPTT DATA

Table 16: 1st Round CPTT cracking response data for the Base composition

<table>
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<th>Pin Length (in.)</th>
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Figure 76: 1st Round CPTT cracking response curve: Complete data set versus pin length for the Base composition

Table 17: 1st Round CPTT cracking response data for the Low W/ Low B composition

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Figure 77: 1st Round CPTT cracking response curve: Complete data set versus pin length for the Low W/ Low B composition

Table 18: 1st Round CPTT cracking response data for the Low W/ High B composition

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Figure 78: 1st Round CPTT cracking response curve: Complete data set versus pin length for the Low W/ High B composition

Table 19: 1st Round CPTT cracking response data for the High W/ Low B composition

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Figure 79: 1st Round CPTT cracking response curve: Complete data set versus pin length for the High W/ Low B composition

Table 20: 1st Round CPTT cracking response data for the High W/ High B composition

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<td>0.875</td>
<td>4</td>
<td>0%</td>
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<td>15%</td>
<td>12%</td>
</tr>
<tr>
<td>1.0</td>
<td>5</td>
<td>3%</td>
<td>43%</td>
<td>21%</td>
<td>16%</td>
</tr>
<tr>
<td>1.125</td>
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<td>17%</td>
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<td>25%</td>
</tr>
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<tr>
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<td>100%</td>
<td>85%</td>
<td>18%</td>
</tr>
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<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>1.625</td>
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<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>0%</td>
</tr>
</tbody>
</table>
Figure 80: 1\textsuperscript{st} Round CPTT cracking response curve: Complete data set versus pin length for the High W/ High B composition

\textbf{2\textsuperscript{nd} ROUND CPTT DATA}

Table 21: 2\textsuperscript{nd} Round CPTT cracking response data for the Base composition

<table>
<thead>
<tr>
<th>Pin Length (in.)</th>
<th>Sample Count</th>
<th>Min Cracking</th>
<th>Max Cracking</th>
<th>Avg. Cracking</th>
<th>Stand. Dev</th>
</tr>
</thead>
<tbody>
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<td>0%</td>
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<tr>
<td>0.875</td>
<td>4</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
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<td>4</td>
<td>11%</td>
<td>41%</td>
<td>27%</td>
<td>16%</td>
</tr>
<tr>
<td>1.125</td>
<td>2</td>
<td>19%</td>
<td>24%</td>
<td>22%</td>
<td>4%</td>
</tr>
</tbody>
</table>
Figure 81: 2nd Round CPTT cracking response curve: Complete data set versus pin length for the Base composition

Table 22: 2nd Round CPTT cracking response data for the Low W / Low B composition

<table>
<thead>
<tr>
<th>Pin Length (in.)</th>
<th>Sample Count</th>
<th>Min Cracking</th>
<th>Max Cracking</th>
<th>Avg. Cracking</th>
<th>Stand. Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
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<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>0.625</td>
<td>5</td>
<td>0%</td>
<td>16%</td>
<td>5%</td>
<td>7%</td>
</tr>
<tr>
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<td>7%</td>
<td>57%</td>
<td>39%</td>
<td>28%</td>
</tr>
<tr>
<td>0.875</td>
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<td>7%</td>
<td>34%</td>
<td>21%</td>
<td>14%</td>
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<tr>
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<td>38%</td>
<td>94%</td>
<td>66%</td>
<td>28%</td>
</tr>
</tbody>
</table>
Figure 82: 2\textsuperscript{nd} Round CPTT cracking response curve: Complete data set versus pin length for the Low W/ Low B composition

Table 23: 2\textsuperscript{nd} Round CPTT cracking response data for the Low W/ High B composition

<table>
<thead>
<tr>
<th>Pin Length (in.)</th>
<th>Sample Count</th>
<th>Min Cracking</th>
<th>Max Cracking</th>
<th>Avg. Cracking</th>
<th>Stand. Dev</th>
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</thead>
<tbody>
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</tr>
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</tr>
<tr>
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<td>13%</td>
<td>11%</td>
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<tr>
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<td>38%</td>
<td>25%</td>
<td>19%</td>
</tr>
</tbody>
</table>
Figure 83: 2nd Round CPTT cracking response curve: Complete data set versus pin length for the Low W/ High B composition

Table 24: 2nd Round CPTT cracking response data for the High W/ Low B composition

<table>
<thead>
<tr>
<th>Pin Length (in.)</th>
<th>Sample Count</th>
<th>Min Cracking</th>
<th>Max Cracking</th>
<th>Avg. Cracking</th>
<th>Stand. Dev</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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<td>0%</td>
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<td>31%</td>
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<td>10%</td>
</tr>
</tbody>
</table>
Figure 84: 2\textsuperscript{nd} Round CPTT cracking response curve: Complete data set versus pin length for the High W/ Low B composition

Table 25: 2\textsuperscript{nd} Round CPTT cracking response data for the High W/ High B composition

<table>
<thead>
<tr>
<th>Pin Length (in.)</th>
<th>Sample Count</th>
<th>Min Cracking</th>
<th>Max Cracking</th>
<th>Avg. Cracking</th>
<th>Stand. Dev</th>
</tr>
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<tbody>
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<tr>
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<td>5%</td>
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<tr>
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<tr>
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<td>8%</td>
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<td>34%</td>
<td>23%</td>
</tr>
</tbody>
</table>

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Figure 85: 2nd Round CPTT cracking response curve: Complete data set versus pin length for the High W/ High B composition