Solidification Behavior and Hot Cracking Susceptibility of High Manganese Steel Weld Metals

THESIS

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By

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Abstract

Recent attention has been given to developing austenitic high-Mn steels for cryogenic service conditions. Specifically, the austenite stabilizing capacities of Mn and C are being exploited to create lower cost alternatives to other cryogenic materials (9Ni steel, Invar, 304 SS, etc.) which are commonly used during the construction of liquefied natural gas (LNG) tanks. The proposed steel alloys contain Mn levels in the range of 20 to 28 wt% and C additions on the order of 0.4 wt%. Although austenite stability is beneficial from a low temperature mechanical property standpoint, the presence of such high concentrations of austenite stabilizing elements causes concern with regard to hot cracking during welding.

The solidification cracking susceptibility of a wide range of high-Mn steel weld metal compositions was assessed through cast pin tear (CPT) testing, a small-scale laboratory test which has previously been used to assess solidification cracking in other austenitic materials. A new generation of the CPT test recently developed at The Ohio State University was employed which utilizes electromagnetic levitation casting. The tested composition ranges fell within the following ranges (wt%): Mn (14-34), C (0-0.7), and Al (0-3). Impurity elements were also present in the following ranges (wt%): S (0.005-0.011) and P (0.003-0.026). A total of 12 compositions were tested. It was found that C and P controlled the solidification cracking susceptibility of these alloys.
In addition to solidification cracking testing, solidification temperature range (STR) analysis was performed on the test matrix using single-sensor differential thermal analysis (SS-DTA) and modified Scheil solidification simulations. STR analysis has previously been related to the weld solidification cracking tendencies of austenitic alloy systems, with large STR values relating to an increased susceptibility to solidification cracking. The measured and calculated STR values in this investigation exhibited a similar relationship. Results indicate that the tested alloys all exhibit primary austenite solidification. It was determined that C and P segregation were primarily responsible for STR expansion.

Optical and scanning electron microscopy (OM and SEM) were used to characterize specimens from both CPT testing and SS-DTA analysis. It was found that fractured CPT specimens exhibited dendritic fracture surface morphologies typically associated with solidification cracking. Weld metal samples demonstrated microstructures of martensite (α’ or ε) and austenite in varying proportions. Increasing Mn and C contents tended to stabilize austenite, as expected. Solute segregation resulting from weld solidification tended to stabilize austenite along interdendritic regions of alloys containing martensite. Energy-dispersive X-ray spectroscopy (EDS) analysis was utilized to analyze Mn, S, and P segregation in various weld metal samples. It was found that S impurities tended to form MnS inclusions prior to terminal solidification, indicating that the presence of S is less detrimental to solidification cracking in high-Mn steels than other austenitic materials. Evidence of a P-rich eutectic constituent was found along interdendritic regions in the alloy which demonstrated the highest susceptibility to...
solidification cracking. The same alloy showed apparent interdendritic liquation cracking within the heat affected zone (HAZ) immediately adjacent to the fusion boundary (FB) in a welded sample having an as-solidified microstructure prior to welding.

In general, it was determined that the solidification cracking susceptibility of the high-Mn steel weld metal compositions explored in this investigation was relatively low. This conclusion was reached based on findings from CPT results that were obtained at the upper threshold of restraint conditions of the test.
Dedication

To my loving parents, James and Rosanne Sutton, who have unquestionably supported me and provided encouragement throughout my life.
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CHAPTER 1: INTRODUCTION AND MOTIVATION

As the global energy landscape is progressively changing due to increases in population, increased environmental awareness, continual economic development, and technological advancements, natural gas presents itself as an abundant and promising fuel source. A recently published report from ExxonMobil has projected that the global natural gas demand will increase by nearly 65% between now and the year 2040 [1]. This increase is attributed to the relative cleanliness of natural gas combustion compared to traditional fossil fuel sources, as well as new and improved drilling technologies that make natural gas more accessible than ever. Natural gas is expected to overtake coal as the second most used fuel source by the year 2040.

Reflecting the estimated increase in natural gas demand, there has been a recent interest in the development of cost-effective materials to be used for the transportation and storage of liquefied natural gas (LNG) [2]. The liquefaction of natural gas is achieved by decreasing its temperature to roughly -160 °C at atmospheric pressure, resulting in a 600-fold reduction in volume and greatly simplifying transportation and storage options [3]. Commonly used materials for the construction of primary components in low pressure storage tanks for liquefied hydrocarbon gases include, but are not limited to, ASTM A353 (9% Ni steel), ASTM A645 (5% Ni steel), ASTM A240 type 304 (304 stainless steel), ASTM A240 type 304L (low-C 304 stainless steel), and
various aluminum alloys [4]. An example of a land based LNG storage tank design is provided in Figure 1.1. The design uses a 9% Ni steel inner tank which is 84 m in diameter and is capable of containing 200,000 m$^3$ of LNG [5]. As can be seen, the amount of material required to construct such a tank is quite large.

Figure 1.1: Typical above ground LNG storage tank [5]

The common factor among many of the alloys which are suitable for low-temperature service is that they are fully (or nearly fully) austenitic. This is often obtained in steels through alloying additions of Ni. Moreover, welding consumables that are commonly used to join these steels are either Ni-based (such as Inconel 625) or contain large amounts of Ni as an alloying addition (such as 308L stainless steel). Since Ni is quite expensive, replacing it with another austenite stabilizer such as Mn could potentially result in substantial cost savings. Figure 1.2 presents the market price ratio of
Ni to Mn from the years 2004 to 2011, and provides evidence of the monetary benefit that could be realized by replacing Ni with Mn. Choi et al. successfully demonstrated that Mn could be used in high concentration (between 20~28 wt%) as an alloying addition to create an austenitic steel with mechanical properties similar to traditional LNG tank materials [2]. Specifically, high strength and excellent toughness at room and cryogenic temperatures were observed.

![Figure 1.2: Price ratio of Ni to Mn over recent years, adapted from [2]](image)

Welding and post-weld inspections are essential parts of the construction process for LNG tanks [6]. As such, the weldability of high-Mn steels needs to be considered during their development for LNG applications. This would include both the weldability
of high-Mn base materials as well as developing compatible and weldable filler materials. One immediate concern that arises when considering the weldability of austenitic steels is the potential for solidification cracking during fabrication [7]. Very little research has been published specifically relating to the solidification behavior and cracking susceptibility of high-Mn steels.

It is the purpose of this investigation to identify the solidification behavior and solidification cracking susceptibility of a range of high-Mn steel compositions that are relevant for LNG applications. Specifically, various alloying additions (Mn, C, Al) and impurity elements (S and P) will be assessed for their influence on high-Mn weld metal behavior. This will be achieved through the use of both computational and experimental techniques.
CHAPTER 2: BACKGROUND

2.1 LNG TANK SERVICE REQUIREMENTS

The design and construction of both land-based and maritime transport LNG tanks are directed by various national and international codes [4, 8-10]. Contained within these codes are a variety of tank designs including single-wall, double-wall, and full containment for land-based tanks, as well as B-type and membrane tanks for LNG carriers. The commonality across all codes and tank designs is that the containment structure which is in contact with the liquefied gas must exhibit satisfactory fracture toughness at cryogenic temperatures. For example, American Petroleum Institute code 620 outlines the design and construction of large, welded, low-pressure storage tanks for liquefied hydrocarbon gases [4]. This code requires that primary components made of 5% Ni or 9% Ni steel meet a minimum transverse Charpy V-notch (CVN) impact value of 20 ft-lbs (~27 J) for a 10 mm x 10 mm sample at -320 °F (-196 °C). Designs must also account for the hydrostatic stresses associated with containing the liquid. A typical full containment LNG tank design would require hydrostatic testing at 125 % of the maximum product load [11].

In addition to designing for hydrostatic loads at low temperature, dynamic loads also need to be accounted for. In the case of land-based LNG storage tanks, seismic
events may introduce dynamic stresses [12]. In the case for LNG tanks on transportation ships, sloshing of the product within the tank can introduce tremendous impact loads on the containment structure [13]. This is especially true when considering the continued push by the LNG shipping industry to create vessels with larger load capacity and increased transportation efficiency. An example of this trend was recently observed when ExxonMobil and Qatar Petroleum created a new class of LNG vessels, referred to as “Q-max”, which are capable of transporting up to 266,000 m$^3$ of LNG [14].

2.2 HIGH-MN STEEL METALLURGY

2.2.1 Phase Stability

As the name suggests, high-Mn steels are based on alloying Fe with a large amount of Mn (≥12 wt%). This makes the Fe-Mn equilibrium phase diagram an excellent starting point to understand their behavior. Figure 2.1 presents the equilibrium phase diagram of the Fe-Mn system. As can be seen, increasing Mn content significantly expands the austenite (γ) phase field. High temperature ferrite (δ) formation is suppressed by an addition of approximately 12-13 wt% Mn, indicating that alloys with this amount of manganese or more will exhibit fully austenitic solidification from high temperature. Another feature of interest in the Fe-Mn system is that the two phase region separating liquid (L) and austenite (γ) is quite narrow, suggesting that Mn does not segregate strongly during solidification. Estimating the partition ratio from the diagram itself gives a value of approximately 0.75. Although slightly outside of the data presented in Figure 2.1, a eutectoid reaction exists in the system at 255 °C and 43 wt% Mn; γ→αFe+αMn [15]. From a practical standpoint, the high-Mn alloys which are
discussed here would not demonstrate any low temperature ferrite ($\alpha$Fe) formation during typical cooling conditions because of limited diffusion rates.

**Figure 2.1:** Fe-Mn equilibrium phase diagram [16]

In addition to Mn, C is often used to stabilize austenite and provide interstitial strengthening in high-Mn steels. Figure 2.2 represents a high temperature portion of a pseudo-binary phase diagram of the Fe-Mn-C system at 20 wt% Mn. No high temperature ferrite is present in the diagram, owing to the austenite stabilizing effect of Mn. As can be seen, sufficiently high C levels may result in the formation of $M_3C$ carbides at high temperature. Although not indicated in Figure 2.2, other carbides which
exist in the Fe-Mn-C system include $M_23C_6$, $M_5C_2$, and $M_7C_3$ [17]. The letter “M” in these carbides represents Fe and/or Mn as they often substitute for one another.

Referring back to Figure 2.2, the two phase region separating liquid and austenite ($\gamma$) is relatively wide, suggesting that C readily partitions to the liquid during solidification.

The system also has a eutectic reaction, Liquid$\rightarrow$$\gamma$+$M_3C$, which occurs just below 1130 °C. The eutectic composition in the 20 wt% Mn system is approximately Fe-20Mn-4.2C. The eutectic reaction reaches a minimum temperature of 1112 °C in the Fe-Mn-C system at 51 wt% Mn and approximately 4 wt% C [18].

![Image](image.png)

**Figure 2.2:** High temperature isopleth of the Fe-Mn-C system at 20 wt% Mn, adapted from [18]
An interesting feature in the Fe-Mn-C system is that there are actually two martensitic products which may form as a result of non-equilibrium cooling conditions from a fully austenitic state. These metastable products are known as $\alpha'$-martensite, which is body centered cubic (BCC) or body centered tetragonal (BCT) based on C content, and $\varepsilon$-martensite, which is hexagonal close packed (HCP). Schumann created a metastable phase diagram for the Fe-Mn-C system for samples that were fully austenitized and quenched to room temperature [19]. Figure 2.3 presents the metastable phase diagram which contains both martensitic phases ($\alpha'$ and $\varepsilon$) and austenite ($\gamma$). Figure 2.3 also presents the approximate martensite start ($M_s$) temperatures for both $\alpha'$-martensite and $\varepsilon$-martensite in the Fe-Mn-C system as indicated by Schumann.

Figure 2.3: Metastable phase diagram of the Fe-Mn-C system (left) and corresponding $M_s$ temperatures (right), adapted from [19]
2.2.2 Low Temperature Behavior

The idea of using High-Mn steel alloys at LNG temperatures is by no means a new one. Researchers have been exploring the use of Mn steels for cryogenic applications since the late 1960’s [20]. The primary factor controlling the low temperature mechanical properties of high-Mn steels is the stability of austenite, which relates back to the chemical composition.

The CVN impact data for a variety of binary Fe-Mn alloys as determined by Schanfein is presented in Figure 2.4 [21]. As can be seen, increasing Mn content tends to shift the ductile-brittle transition temperature (DBTT) to lower values. This behavior is attributed to increased suppression of α’-martensite and ε-martensite transformations. Figure 2.5 is also provided which shows the CVN impact data which was obtained by Tomota [22], and represents higher Mn concentrations than those explored by Schanfein [21]. Note that the scales are slightly different.
Figure 2.4: CVN impact data for various binary Fe-Mn alloys (4-20 wt% Mn) [21]

Figure 2.5: CVN impact data for various binary Fe-Mn alloys (16-36 wt% Mn) [22]
Low temperature fatigue behavior for high-Mn steels can also be found in the literature. For example, Choi et al. recently published fatigue crack growth data for an experimental fully austenitic high-Mn steel at room and LNG temperatures [2]. The experimental alloy fell within the following composition constraints of primary alloying elements (wt%): Mn (20-28) and C (0.2-0.6). Other elements were indicated as potentially being present, but no quantities were given. Figure 2.6 presents the experimentally determined data from Choi et al. as well as a comparison between the fatigue behavior of the experimental alloy and alloys which have been traditionally used for LNG tank construction at room temperature (left) and -163 °C (right). Interestingly, the fatigue threshold stress intensity of the experimental high-Mn alloy is higher at cryogenic temperature than it is at room temperature. The fatigue crack growth behavior in the Paris law regime is similar to other cryogenic alloys.

![Fatigue crack growth behavior comparison](image)

Figure 2.6: Fatigue crack growth behavior of an experimental high-Mn steel compared to traditionally used LNG tank materials at 25 °C (left) and -163 °C (right) [2]
Choi et al. also presented the tensile properties of the experimental high-Mn alloy at various temperatures. Table 2.1 summarizes the measured yield strength (YS), ultimate tensile strength (UTS), and elongation (El.) from tensile specimens at three test temperatures. As can be seen, decreasing tensile testing temperature shifts the engineering stress-strain behavior to higher stresses, lower strains, and lower elongations at failure.

Table 2.1: Tensile properties of an experimental high-Mn steel, adapted from [2]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>El. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>470</td>
<td>901</td>
<td>54</td>
</tr>
<tr>
<td>-100</td>
<td>569</td>
<td>1038</td>
<td>49</td>
</tr>
<tr>
<td>-163</td>
<td>691</td>
<td>1125</td>
<td>45</td>
</tr>
</tbody>
</table>

2.2.3 Other High-Mn Steel Applications

High-Mn austenitic steels have been used for a variety of applications ever since their discovery in the late 19th century by Sir Robert Hadfield and his associates were searching for an alloy which exhibited both high hardness and toughness [23]. Hadfield found that an alloy with approximately 1.2 wt% C and 12 wt% Mn could achieve high hardness without becoming brittle, puzzling researchers at the time. Most of the steels which were used prior to the discovery by Hadfield were of much lower alloy content, showing an inverse relationship between hardness and toughness. This was likely due to the presence or absence of untempered α'-martensite. Alloys of the Hadfield composition are commonly referred to simply as Hadfield steel, and have since been
successfully used by a number of industries for wear resistant castings. Example industrial applications include rock crushers, dredge buckets, fragmentizer hammers, railway frogs, and railway switches [24]. Providing some indication of their widespread use, a standard specification has been developed by ASTM International outlining Hadfield austenitic manganese steel castings [25]. In addition to chemical limits, the Hadfield steel specification describes typical heat treatment requirements to achieve both toughness and ductility. The heat treatment procedure consists of heating to a minimum of 1000 °C, holding until a uniform temperature distribution is reached, and quenching. This heat treatment would fully austenitize the microstructure at high temperature and prevent carbide precipitation during cooling.

In addition to alloys which have been established for wear resistance, high-Mn steel concepts have been explored for applications which require exceptional strength and ductility during plastic deformation [26], low magnetic permeability [27], and shape memory effects [28]. Of these examples, the most attention has been given to high-Mn steels which demonstrate high strength and ductility for automotive applications [26, 29]. Figure 2.7 compares the strength and elongation during tensile testing of experimental high-Mn steel compositions to materials which are currently used during automotive construction. It can be seen that high-Mn steels show both higher strength and ductility compared to conventional automotive alloys, making them appealing for potential weight reduction, anti-intrusion reinforcement, and parts requiring deep or stretch forming [30].
Figure 2.7: Tensile properties of high-Mn steel compositions (hashed region) compared to currently used automotive alloys [30]

The ability for high-Mn austenitic steels to achieve both high strength and elongation stems from their mode of plastic deformation [31]. Strain accommodation in these steels can take place through dislocation glide, displacive microstructural transformation, or mechanical twinning. Those which accommodate strain through a mixture of dislocation glide and martensitic transformation are known as transformation induced plasticity (TRIP) steels, while those which exhibit dislocation glide and mechanical twinning are referred to as twinning induced plasticity (TWIP) steels. The formation of martensite and/or mechanical twins during plastic deformation progressively refines the austenitic matrix by introducing dislocation barriers and reducing the effective glide distance of dislocations. This behavior has been referred to as a “dynamical Hall-
Petch effect” [32]. The tendency for high-Mn steels to display either TRIP or TWIP behavior has been associated with their low stacking fault energy (SFE) [33]. In general, SFE values below roughly 20 mJ/m² favor martensitic transformation, and energies between roughly 20 mJ/m² and 30 mJ/m² favor twinning [34]. The low fault energies of TRIP and TWIP steels are a direct result of their chemical composition, being most notably influenced by their unconventionally high Mn content.

**2.3 SOLIDIFICATION CRACKING**

The area of solidification crack formation during fusion welding processes has been studied for quite some time and is fairly well understood [35]. Solidification cracking occurs as a result of the simultaneous presence of: 1) depressed solidification temperature liquid films along solidification sub-grain boundaries (SSGBs), or more commonly, solidification grain boundaries (SGBs) in the fusion zone (FZ); and 2) weld restraint resulting from both intrinsic and extrinsic sources. Figure 2.8 schematically indicates the boundary types which can exist in the FZ of fully austenitic materials during solidification as described by Lippold et al. [36]. SSGBs represent the boundaries between adjacent cells or dendrites with similar orientation, while SGBs are those boundaries which are formed when packets of subgrains intersect. A solidification crack is formed when liquid films along SSGBs and/or SGBs rupture during solidification.
Continued research involving solidification cracking focuses mainly on identifying the relative susceptibility of various engineering alloy systems, as well as developing new ways to economically evaluate cracking susceptibility. These methodologies fall under the general term “weldability testing”, and can be conducted in a laboratory setting to aid in material selection and development for real world applications [37].

This section will serve to introduce weld solidification and various solidification cracking theories, describe testing techniques that have been developed to assess solidification cracking susceptibility, and review the relevant available literature related to welding and solidification of High-Mn steels.

Figure 2.8: Schematic representation of interfaces which may exist in a single phase weld metal following solidification [36]
2.3.1 Weld Solidification

The evolution of microstructures in the FZ during weld solidification is dependent on various parameters including crystal growth rate (R), liquid temperature gradient (G), undercooling, and alloy constitution [38]. These parameters dictate the non-equilibrium solidification conditions that cause solid-liquid interface instabilities as crystallization occurs. Interfacial instabilities directly influence the chemical inhomogeneity of a solidifying weld pool, and as a result strongly influence solidification cracking behavior.

A natural starting point for considering weld solidification is to look at initial crystal nucleation and growth. Crystal nucleation in the FZ of weldments is a highly heterogeneous process and is commonly described as being epitaxial in nature [39]. An abundance of nucleation sites for crystallization exist along the fusion boundary where the molten weld pool is in contact with surrounding grains. Nucleation from these sites is quite easy from a thermodynamic standpoint, i.e. little undercooling is necessary when compared to homogenous nucleation. It should be mentioned that it is possible to have nucleation in the weld metal away from the fusion boundary when inoculants such as detached grains or dendrite fragments are present [35], however only nucleation from the fusion boundary is considered here. Grains which nucleate from the fusion boundary maintain the crystallographic orientation of the parent grains from which they form. Eventually, solidifying grains with dissimilar orientations will impinge on one another in a process referred to as competitive growth. In BCC and FCC materials crystal growth takes place along <100> preferred (also referred to as “easy”) growth directions. As
indicated previously, these general growth characteristics give rise to the formation of SSGBs and SGBs.

Once nucleation has occurred and a crystal begins to solidify, solute redistribution takes place between the liquid metal and crystal being formed [40]. The degree in which particular elements will tend to preferentially segregate to the liquid or solid is defined by the partition coefficient, \( k \). The partition coefficient of an element in a solidifying system represents the ratio of solute in the solid to solute in the liquid at a particular temperature. A partition coefficient less than one indicates that an element will segregate to the liquid during solidification, while a partition coefficient more than one indicates segregation to the solid. Partition coefficients closer to a value of one will tend to segregate less than those which are much higher (or lower) than one.

Solidification growth morphologies can generally be described as being planar, cellular, or dendritic [38]. The occurrence of these morphologies can be understood by considering mass and heat transfer that takes place locally at a theoretical planar solidification front. The liquid immediately adjacent to the solidification front will have a freezing point which deviates from that of the bulk composition as a result of solute segregation. Liquid which is far removed from the solidification front will still have a freezing point equal to that of the bulk composition since it has not yet experienced segregation effects. As a result, the freezing point of the liquid varies as a function of distance into the liquid, being bounded by the bulk liquidus temperature and the temperature at the liquid-solid interface. In addition to the liquidus temperature changing with distance, a positive thermal gradient exists from the liquid-solid interface extending
into the weld pool. Two conditions can then be considered for a given solute profile in
front of the solidifying planar front. The first condition is where the temperature gradient
in the liquid is sufficiently steep so that the liquidus is exceeded at all locations in the
weld pool with the exception of the liquid-solid interface. In this situation, planar growth
will be maintained as any naturally occurring crystal extensions past the interface will
immediately melt. On the other hand, a shallow temperature gradient can result in liquid
temperatures which are below the local liquidus temperature. In this situation, any
protrusions from the planar interface will continue to grow as the liquid is in a
supercooled condition. The second situation, where planar growth is not stable is
referred to as constitutional supercooling [41].

Figure 2.9 presents a schematic representation of the solute profile surrounding a
planar solidification front, as well as the liquidus and temperature profiles which describe
growth stability and instability. Figure 2.10 presents the general relationship between
solidification growth morphology, solute concentration (C), temperature gradient in the
liquid (G), and solidification rate (R). Increasing levels of constitutional supercooling
result in transitions from planar growth to cellular, columnar dendritic, and eventually
equiaxed dendritic growth. For a typical arc weld traverse each of the morphologies may
be present in the fusion zone [35]. Along the fusion boundary where the temperature
gradient is high but the solidification rate is low a planar front is possible, while at the
weld centerline where the temperature gradient is low but the solidification rate is high an
equiaxed structure is possible. The regions between the fusion boundary and weld
centerline may then exhibit a range of other morphologies. Although not indicated in
Figure 2.10, the product of G•R (cooling rate) has an effect on solidification feature size. Faster cooling rates lead to a more refined solidification structure.

Figure 2.9: (a) Solute profile around a planar solidification front; (b) condition resulting in planar solidification stability; (c) condition resulting in constitutional supercooling [38]
Various models exist to describe the solute redistribution that occurs during solidification [38]. The most significant deviations between these models come from how they account for diffusion in the immediate vicinity of the solidification front and what solidification morphology is assumed. For the discussion here, three simple cases with a planar solidification front, varying levels of diffusion, and solute partition...
coefficients less than one will be considered for a fixed volume element. The solid and liquid at the interface are at equilibrium throughout the solidification process in each case; however the solute profiles surrounding the interface differ.

Case I assumes that there is complete diffusion of all elements in both the liquid and solid. In this situation, solidification will occur in a state of equilibrium and no composition gradients will exist in the final solid structure. On the other extreme, case II accounts for no diffusion in the solid and complete diffusion in the liquid. These assumptions provide the most severe condition of solute partitioning. The solid which forms in case II solidification will behave according to the maximum solid solute solubility at a particular temperature. Once formed, the solid remains at that composition and any remaining solute is rejected into the liquid, causing a composition gradient to form in the solid. As a consequence of these considerations, both the solid and liquid compositions are continuously being enriched in solute until maximum solubility in the system is reached, such as when a eutectic reaction occurs. This behavior has been described mathematically by the well-known Scheil equation [43], which solves for the solute concentration in the solid \((C_S)\) as a function of fraction solidified \((f_S)\) for a given partition coefficient \((k)\) and initial solute composition \((C_0)\). The Scheil equation is given in Equation 2.1 below. As mentioned by Nastac and Stefanescu [44], an intermediate level of solute segregation between case I and case II assumptions is expected for most solidification processes.

\[
C_S = kC_0(1 - f_S)^{k-1}
\]

Equation 2.1: Scheil equation for calculating solute concentration during solidification
The final case, case III, assumes no solid diffusion and limited diffusion in the liquid. Deviating from case II solidification, the solute which is rejected from the solidification front is contained within a solute-rich boundary layer that advances in front of the solid [45, 46]. In this case, three distinct regions of solidification have been described. These are the initial transient, steady-state, and final transient regions. The initial transient condition is marked by rapid solute segregation to the liquid which forms a solute rich boundary layer. A steady state condition is then reached where the solid being formed is of the nominal composition and the solute exchange across the liquid-solid interface remains constant. The final transient region occurs at the end of solidification where both the solid and liquid are rapidly enriched in solute due to the presence of the boundary layer.

The models which have been described thus far have been relatively simple in nature, and their usefulness in describing solute redistribution during welding depends heavily on alloy constitution, processing conditions, and the interfaces which are being described. Advances in computing power and model development have made it possible to better describe more complex systems during solidification [47]. For example, Thermo-Calc and DICTRA are commercially available computational thermodynamic and kinetic modeling packages, respectively [48], that can be used to simulate various aspects of multi-component alloy systems.

2.3.2 Solidification Cracking Theory

There have been a number of theories proposed over the years to describe the evolution of solidification cracks during welding [49-54]. As mentioned previously, the
common factor among these theories is that low temperature liquid films exist at the end of solidification and may be pulled apart due to the stresses experienced during cooling. The liquid films which exist during weld solidification are a direct result of solute segregation stemming from non-equilibrium cooling conditions. The commonly recognized theories for describing solidification cracking behavior include (in chronological order): Shrinkage-Brittleness Theory [49, 50], Strain Theory [51], Generalized Theory [52], Technological Strength Theory [53], and Modified Generalized Theory [54].

The Shrinkage-Brittleness Theory originated in the late 1940’s when Bochvar developed a concept to describe the formation of cracks in aluminum castings above the solidus temperature [49]. Similar to Bochvar’s work with aluminum castings, Pumphrey extended a theory to describe the cracking behavior of aluminum alloy weldments during solidification [50]. The basis of the Shrinkage-Brittleness Theory is that a solidifying alloy exhibits a temperature of coherence, representing a condition on cooling where dendritic interlocking occurs. The proportion of liquid to solid above the temperature of coherence is large and cracking will not occur. Once below the temperature of coherence, solid-solid interactions begin to take place between adjacent dendrites and the remaining liquid films may rupture due to strain accumulation. Given that a sufficient amount of liquid is present (such as in alloys with a large amount of eutectic formation) in close proximity to a forming solidification crack, “healing” may occur where liquid will flow into a freshly formed void.
In the early 1950’s Pellini, of the United States Naval Research Laboratory, developed a theory to explain the observation of hot tears in castings [51]. This explanation, known as the Strain Theory, was then applied to describe the occurrence of solidification cracking in weld metals. In his explanation Pellini indicated that solidifying metal undergoes a “mushy condition” which is then followed by a “film stage” where solidification cracking may occur. The mushy condition is marked by the simultaneous presence of both liquid and solid in the solidifying weld pool, but a uniform distribution of strain prevents cracking. During the film stage a thin and essentially continuous molten film exists along interdendritic regions and can be separated as a result of strain accumulation due to temperature gradients in the solid. A schematic representation of this phenomenon, taken from a report on hot cracking in types 347 and 304 stainless steels from Pellini and his associates [55], is provided in Figure 2.11. The Strain Theory also offers reasoning for the formation of hot cracks in the base metal adjacent to the fusion boundary as a result of impurity segregation and liquation, now commonly referred to as HAZ liquation cracking.
In 1960 Borland introduced the Generalized Theory to describe solidification cracking and overcome the apparent shortcomings of both the Shrinkage-Brittleness Theory and Pellini’s Strain Theory [52]. In this theory, Borland breaks the solidification process into 4 distinct stages based on the relative quantity and distribution of liquid present. During the earliest stage of solidification (stage 1), dendrites are widely dispersed and are surrounded by large amounts of liquid. Similar to the Shrinkage Brittleness Theory, Borland defined a coherent temperature during solidification that once crossed dendrite interlocking occurs and solidification cracks may form. Any cracks which form just below the coherent temperature may experience crack healing (stage 2). Upon further cooling, a critical temperature is reached in which dendrite formation has progressed to the point that interdendritic liquid networks become isolated and crack healing is not possible (stage 3). Borland referred to this region as the critical solidification range (CSR). It is in this region, below the critical temperature and before complete solidification takes place, that solidification cracking occurs. Non-equilibrium
solidification conditions result in depression of the solidus temperature due to limited diffusion, effectively extending the CSR and increasing the tendency for solidification cracking. During the final stage of solidification no liquid is present and cracking cannot occur (stage 4). An additional concept was proposed by Borland that had not appeared in either the Shrinkage-Brittleness Theory or the Strain Theory. The new concept was that grain boundary energies and interphase (liquid/solid) energies play a role in solidification cracking behavior by controlling boundary wetting characteristics.

In 1962 a Russian researcher by the name of Prokhorov introduced a solidification cracking theory which was based on mechanical considerations [53]. Known as the Technological Strength Theory, Prokhorov described the occurrence of solidification cracks in weldments as a result of decreased ductility through a temperature regime known as the brittle temperature range (BTR). The BTR for a particular alloy is unique and provides insight into its solidification cracking susceptibility relative to other materials. Strain accumulation takes place in the solidifying weld pool as a result of thermal contraction within the material as well as any externally applied loads. If a critical level of strain is reached within a solidifying weld pool within the BTR, solidification cracking will occur.

In the early 1980’s Matsuda and his associates at the Japanese Welding Research Institute proposed a modification to the Generalized Theory following in-situ microscopic observations of weld solidification cracking [54]. This proposal simply became known as the Modified Generalized Theory. The modifications to the Generalized Theory were as follows. The coherent temperature was higher than
originally proposed by Borland, which was indicated by extensive solid network formation early in the solidification process. Secondly, the CSR of a solidifying alloy can be broken into two regions, differing from the single region proposed by Borland. In Borland’s theory the CSR was referred to as stage 3 of solidification, therefore Matsuda divided the region into stage 3(h) and stage 3(l). During stage 3(h) the solidifying melt is susceptible to solidification crack initiation due to the presence of liquid films along grain boundaries. During stage 3(l) the solidifying melt is not susceptible to crack initiation, but to crack propagation due to the presence of liquid droplets along grain boundaries. The various stages of solidification as described by Matsuda using a binary alloy system with a eutectic reaction are provided schematically in Figure 2.12. The in-situ observations of solidification cracking by Matsuda were further developed and later used as a quantitative tool, known as the MISO technique, to assess cracking behavior in carbon steels, stainless steels, and aluminum alloys [56].
Figure 2.12: Weld solidification for a binary system as described by Matsuda’s Modification to the Generalized Theory [54]

2.3.3 Weldability Tests for Solidification Cracking

Many weldability tests have been created over the years to assess the solidification cracking susceptibility of engineering alloy systems. These tests, although in different forms, try to identify the influence of metallurgical aspects that are unique to the alloy system being tested. This is typically accomplished by providing some type of restraint on a solidifying melt to amplify the tendency for liquid films along grain boundaries to rupture. The restraint in tests can either be intrinsic or extrinsic in nature. Material systems are assessed using these weldability testing techniques and then compared against one another using various metrics to determine relative cracking
tendencies. Although many tests have been developed, some of the more common techniques will be reviewed below.

In the mid 1960’s researchers from the Rensselaer Polytechnic Institute developed a weldability test, known as the Varestraint (variable restraint) test, to assess hot cracking susceptibility during welding [57]. During this test, an autogenous weld traverse is made on a thin coupon of material fixtured over a removable radiused die block in a cantilever configuration. The weld direction is perpendicular to the radiused die block. At a particular time in the weld sequence a pneumatic system suddenly bends the test coupon over the block, introducing strain to the solidifying weld pool. Multiple coupons could be tested for a particular material while varying the radius of the die block for each test, and consequently varying the amount of imposed strain on the solidifying weld pool. Metrics for comparison between materials using the Varestraint test include: minimum strain required to cause cracking, maximum crack length (MCL), total-combined crack length (TCL), and number of cracks. Each of these cracking responses can be measured using optical metallographic techniques. By fixing weld parameters and external loading conditions the cracking response of alloys is dependent solely on metallurgical factors.

Shortly after the introduction of the Varestraint test by Savage [57], Sinda and his associates modified the test configuration to focus primarily on solidification cracking along the weld centerline [58]. The was achieved by rotating the weld geometry of the original Varestraint test by 90°, straining the solidifying weld pool in the transverse direction. This modification was therefore called the Trans-Varestraint test. A side view schematic of the Trans-Varestraint test is provided in Figure 2.13. In this orientation the
welding arc and trailing weld pool would be moving into (or out of) the page. With the exception of the weld and strain orientation, the Varestraint and Trans-Varestraint tests are nearly identical. In addition to measuring crack lengths and counting cracks as a function of strain like Savage proposed, Sinda utilized high temperature thermocouple measurements in the weld pool to directly relate cracking behavior, temperature, and strain rate. This gave the researchers the ability to generate a ductility signature curve and identify the BTR for a given alloy.

Figure 2.13: Schematic side view of the Trans-Varestraint test with weld travel in/out of the page [58]

To this point, the solidification cracking weldability tests which have been presented here have all induced cracking via extrinsic sources. Other weldability tests have been developed which are intrinsic in nature, in that solidification cracking is promoted through the natural thermal contraction associated with cooling as opposed to being loaded by external means. An example of such a test was originally proposed by
Hull in the late 1950’s to assess the solidification cracking susceptibility of stainless steel weld metals [59]. In his test, the Cast-Pin Tear (CPT) test, Hull used an induction heating levitation coil to melt small charges (19 g) of material and cast them into Cu molds with varying “pin” geometries. Mold geometries were axisymmetric in nature, and designed in such a way that the solidifying material would be restrained during solidification to promote liquid film rupture. Several molds were available to provide varying levels of restraint. Pins of a particular composition were cast into a range of molds under argon shielding. Following casting, pins were removed from their molds and analyzed under a stereo-binocular microscope. The angular lengths of cracks which formed on the surface of pins were then measured and recorded. The length of all cracks which formed on the surface of a particular pin were then added together, divided by 360°, and multiplied by 100 to give a value referred to as the cracking index. The cracking index for each pin was then plotted as a function of descending mold restraint. The cracking index curves for various materials could then be compared to one another as a qualitative indicator of cracking susceptibility.

Taking Hull’s original concept as a starting point, researchers at The Ohio State University have designed and implemented two iterations of the CPT test [60-63]. These systems were primarily used to assess the solidification cracking susceptibility of various Ni-base weld metals. The first system which was originally developed by Ryan in the early 2000’s utilized a gas tungsten arc welding (GTAW) torch to melt small charges (10 g – 16 g) of material in a water cooled Cu hearth under Ar shielding [60]. Once molten, an individual charge would be cast into an axisymmetric split Cu mold containing a
“head” and “foot” feature to provide restraint during solidification. Deviating from Hull’s approach, the molds used at Ohio State maintained fixed geometry with the exception of the length of a gauge section between the head and foot features. Mold lengths ranging from 0.5 in (12.7 mm) to 2.0 in (50.8 mm) were used to introduce varying levels of restraint during solidification. Charge masses were scaled to match the particular mold length being used. Cracks were measured in the same manner as the pins which Hull tested. Cracking response curves were then constructed by plotting the amount of cracking as a function of pin length, allowing for the comparison between various materials. The most recent CPT test design developed at Ohio State combines the levitation melting system of Hull with the mold geometries originally used by Ryan [63]. This system will be discussed in greater detail in the Materials and Experimental Procedures portion of this document.

2.4 WELDING OF HIGH-MN STEELS

As indicated previously, there is an insufficient amount of published research readily available related to the welding metallurgy of high-Mn steels for cryogenic service. There are, however, a small number of researchers which have investigated and published their work to provide insight to the weldability of high-Mn steels for other applications. In general, these investigations involve the welding of steels which utilize Mn in high concentration to achieve a fully austenitic structure. These investigations will be summarized below.

In the late 1970’s Japanese researchers from the Daido Steel Co. investigated various high-Mn steel compositions for nonmagnetic applications [64]. During this study
Kato et al. considered the elemental effects on magnetic permeability, mechanical properties, machinability, and weldability of austenitic Mn steels. The weldability results from this investigation will be discussed here. It was found that C and P levels were most influential in determining hot cracking (both HAZ liquation and solidification) behavior as determined through two separate tests. The first test involved taking a nominal base material composition of Fe-13Mn-0.025P (wt%) and gradually adding C to determine its effect on hot cracking in the HAZ. An I-groove weld geometry was used to provide restraint during testing and promote cracking. It was observed that if the base metal C content was kept below 0.8 wt% that no cracking occurred in the HAZ. Increasing C above 0.8 wt% resulted in crack formation, with increasing crack occurrences with increasing C content. The Trans-Varestraint test was then used to identify the influence of impurity elements on solidification cracking. A nominal composition of Fe-15Mn-0.7C-1Ni (wt%) was used with varying levels of P and S. The Trans-Varestraint results at an augmented strain level of 1.5% are presented in Figure 2.14. As can be seen, Kato found that increasing P was detrimental to solidification cracking behavior while S had little effect. Additionally, electron probe micro-analysis (EPMA) showed that P segregated strongly to austenitic weld metal grain boundaries in electron beam welded high-Mn steel specimens.
Figure 2.14: Trans-Varestraint cracking response of a Fe-15Mn-0.7C-1Ni (wt%) alloy with various impurity additions showing that P is more detrimental than S [64]

In the 1980’s attention was given to the Fe-Mn-Al system to develop a lower cost replacement to 300 series austenitic stainless steels [65]. The basic idea behind this system was to replace Ni with Mn (and sometimes C) for austenite stability, and to replace Cr with Al for oxidation resistance. The weldability of such alloys was also considered [66, 67]. Aidun investigated the influence of C on solidification morphology in two such steels. The investigated heat compositions were approximately (in wt%) Fe-21Mn-5.6Al-0.13C and Fe-23Mn-7.1Al-0.45C. GTAW spot welds were placed on each material and subjected to metallographic analysis. It was determined that increasing C from 0.13 wt% to 0.45 wt% resulted in a shift in ferrite morphology from acicular to vermicular. In another study conducted by Makhamreh and Aidun, the mechanical
properties of various Fe-Mn-Al-C flux-cored weld deposits were evaluated in conjunction with optical and electron microscopy [67]. A total of six Fe-Mn-Al compositions were tensile tested at room temperature and compared to types 310 and 316 stainless steels. The tested Fe-Mn-Al alloy compositions all fell within the following ranges (wt%): Mn (20-32), Al (5-11), C (0.1-1), Si (0.1-1.4). It was found that the tensile properties of the Fe-Mn-Al alloys were comparable to both 310 and 316 stainless steel. Microstructures of the welded specimens consisted of austenite and various ferrite morphologies with the exception of two alloys that showed fully austenitic solidification. The fully austenitic alloys were of the approximate compositions (wt%): Fe-20Mn-5Al-0.5C and Fe-20Mn-5Al-1C. It was noted that one alloy formed solidification cracks during welding. The peculiarity with the formation of solidification cracks in this sample was that it was not one of the fully austenitic samples, and had a ferrite number (FN) of 10. The formation of solidification cracks was attributed to an increased P content of 0.028 wt%, being nearly twice as high as any of the other materials. It was also suggested that β-Mn formation could be deleterious to mechanical properties for high-Mn weld metals.

Another source of information regarding the weldability and welding metallurgy of high-Mn steels comes from recent investigations involving TWIP and High-Mn TRIP steels for automotive applications [68-75]. The various investigations focused on a variety of welding processes and steel compositions.

Keil and his associates published two separate investigations related to welding high-Mn steels for automotive applications [68, 69]. The first of these investigations focused on the hot cracking susceptibility of four high-Mn steel compositions and
compared their behavior to other austenitic alloys [68]. The tested high-Mn compositions fell within the following ranges (wt%): Mn (15-25), C (0.08-0.7), Al (1.33-3.22), Si (0.22-2.95), P (<0.001-0.036), S (0.0008-0.01). Cracking susceptibility was assessed using the programmable deformation cracking (PVR) test and a developed self-restrained lap joint test. In addition to testing for cracking susceptibility, optical microscopy and scanning electron microscopy were performed to characterize samples. It was found that the high-Mn steels were more susceptible to hot cracking than materials X8CrMnNi19-6-3 and X5CrNi18-10 (304 stainless steel), while having similar cracking behavior to NiCr23Mo16Al (Ni-base alloy 59) and X15CrNiSi25-20 (314 stainless steel). Both solidification cracks and heat affected zone (HAZ) liquation cracks were identified in the tested high-Mn alloys. Each of the tested high-Mn alloys solidified as primary austenite. PVR test results showed that the high-Mn alloy with the highest level of C (0.68 wt%) had the highest solidification cracking susceptibility. Differential thermal analysis also determined this alloy to have the largest solidification temperature range of the tested high-Mn steels. Room temperature linear thermal expansion coefficients were also presented, indicating that the high-Mn steels had values close to $21 \times 10^{-6}/°K$, while 304 stainless steel was around $18 \times 10^{-6}/°K$.

The PVR results from two different weld settings, as presented by Keil, are given in Figure 2.15. Note that lower critical velocity ($v_{cr}$) values indicate higher susceptibility to cracking in the PVR test. SC and LC in the figure stand for solidification crack and liquation crack, respectively, and designate which type of cracking was first identified.
using the PVR test. HAZ liquation cracking was most pronounced in the alloy with the highest P content (0.036 wt%), where P-rich eutectics were observed in the HAZ.

Figure 2.15: PVR test results of four high-Mn steels (denoted by FeMn-), Ni-based alloy 59 (2.4605), and austenitic stainless steels X15CrNiSi25-20 (1.4841), X8CrMnNi19-6-3 (1.4376), and X5CrNi18-10 (1.4301) at welding currents of 50 A (left) and 55 A (right) [68]; note that lower $v_c$ values indicate higher cracking susceptibility

Keil’s second investigation was focused primarily on the general weldability and characterization of the same four high-Mn base plates as the initial investigation, as well as two high-Mn, metal cored, gas metal arc welding (GMAW) consumables [69]. The chemical composition of pure weld metal samples of each filler materials were as follows (wt%): Fe-21.63Mn-0.48C-0.25Si-0.04Cr-0.04Ni and Fe-16.8Mn-0.29C-0.12Si-0.12Cr. Tests included a Gleeble®-based HAZ simulation study to investigate the precipitation
and hardening behavior of the base plates, creating butt welds with each base materials and consumable combination using GMAW and cold metal transfer (CMT) processes to identify general welding characteristics, and tensile testing of butt weld specimens. Optical microscopy was used to characterize representative samples. HAZ simulations showed significant grain growth in all base materials with increasing peak temperature and decreasing cooling rate. Ferrite growth was observed in the two base materials with the highest Al and Si levels following HAZ simulation even though they contained over 24 wt% Mn. Fine, discontinuous, precipitation existed along interdendritic regions of weld metal samples in an as welded condition. The authors indicated that it may be carbide precipitation ($M_3C$, $M_7C_3$, and/or $M_{23}C_6$), however they did not perform any further analysis to identify the precipitates. In general, tensile test results showed that base metal strength and ductility were higher than welded samples.

Mujica and various co-authors also published their work related to welding high-Mn steels that would be appealing to the automotive industry [70-73]. A review of their work and discussion of the various aspects of welding TWIP steels was then published [74]. In this work, particular attention was given to how chemical inhomogeneity in high-Mn steel welds can have a significant impact on phase stability and mechanical properties. The inhomogeneous nature of high-Mn steel fusion welds can originate from three sources as described by Mujica: weld pool metal vaporization, weld metal dilution, and solute redistribution. Weld pool metal vaporization is most concerning when considering Mn. Mn has a relatively high vapor pressure compared to other alloying elements. It was reported by Mujica that welding a Fe-25Mn-12Cr-0.24C-0.32N (wt%)
steel with a GTAW process operating at 1.13 kW and 0.4 m/min resulted in a weld metal vapor loss of nearly 1.5 wt% Mn [71]. Weld metal dilution would primarily be a concern when high-Mn steels are joined with dissimilar materials. For example, Mujica reported that laser welding a fully austenitic TWIP steel with a low-Mn TRIP steel resulted in the formation of martensite bands in the fusion zone [72]. The last source, solute redistribution, occurs as a result of weld pool solidification. Elements with partition ratios less than one segregate to interdendritic regions, leaving the dendrite cores depleted. An example is provided in Figure 2.16, where Thermo-Calc was used to perform a Scheil solidification simulation for a Fe-22Mn-0.6C (wt%) TWIP steel to show Mn and C enrichment in the solid and liquid as solidification takes place [74]. From a phase stability standpoint, chemical variations throughout the weld metal microstructure could lead to localized differences in SFE, potentially causing martensite formation and/or unfavorable modes of deformation.
Saha investigated the resistance spot weldability of a TWIP980 steel having a chemical composition of Fe-18Mn-0.6C-1.5Al (wt%) [75]. Specifically, cross-tensile testing, microhardness indentations, optical microscopy, and scanning electron microscopy were used to assess resistance spot welded specimens. It was found that the weld nugget which formed had a fully austenitic dendritic structure. The HAZ surrounding the weld nugget remained fully austenitic but experienced significant grain growth relative to the base metal. No ferrite or martensitic phases were observed. Softening in the HAZ and weld nugget was attributed to grain size effects. Cross-tensile testing indicated that increasing weld time resulted in increasing cross-tensile strength due to nugget growth until expulsion was observed. Many weld defects were observed.
during the investigation. These included interdendritic porosity in the weld nugget, shrinkage cavity formation at the faying surface, and HAZ liqutation cracking. Spot energy dispersive X-ray spectroscopy (EDS) scans were performed in the HAZ over an intergranular liquid film as well as the HAZ matrix. The authors indicated that the film was both C- and Mn-rich relative to the matrix. Comparing the two presented EDS scans, the relative height difference between the C peaks is quite subtle.

In 2011 POSCO hosted the 1st International Conference on High Manganese Steels (HMnS2011), where two presentations were given related to welding high-Mn steels \[76, 77\]. Unfortunately, the only available information regarding these talks is in the form of an abstracts booklet or from secondary sources which were present for the talks and have referenced them in some way. The first of these talks specifically addressed the hot cracking and segregation behavior of high-Mn steel welds through the use of a developed multiple bead Varestraint method \[76\]. Segregation of Mn and C to interdendritic regions and the formation of a divorced eutectic structure were observed. It was considered that the formation of a continuous austenite-M\(_3\)C eutectic along grain boundaries significantly impacted hot cracking behavior. As indicated by Mujica \[74\], the investigation found that a Fe-18Mn-0.6C (wt\%) alloy contained significant solute redistribution due to solidification. Areas within dendrite cores reportedly contained 14.7 wt\% Mn and 0.43 wt\% C, while boundaries contained 22.5 wt\% Mn and 2.29 wt\% C. The second presentation involved resistance spot welding of high-Mn steels \[77\], and appears to be very closely related to the investigation published by Saha et al. \[75\] since they contain the same authors.
In a similar fashion, at the recent International Welding/Joining Conference – Korea 2012 a presentation was given related to the hot cracking susceptibility of high-Mn Fe-Mn-C-Al steel [78]. In this investigation a Fe-18Mn-0.6C (wt%) steel was tested with varying levels of Al (0-6 wt%) using a multiple bead Varestraint technique. It was found in this study that the addition of Al to the austenitic high-Mn steel caused a decrease in hot cracking susceptibility. The decreased hot cracking susceptibility was attributed to the Al additions shifting primary solidification from an austenitic (A) mode to a ferritic-austenitic (FA) mode. It was also reported that the addition of Al suppressed any austenite-M3C eutectic formation.

Choi et al. recently tested the mechanical properties of a high-Mn metal-cored GMAW consumable with specific focus on cryogenic properties for LNG tank construction [2]. Due to what is assumed to be intellectual property restraints, the specific weld metal composition was not given. Instead, a chemical composition range was loosely defined and it was indicated that both the base metal and weld metal were compliant. The given composition range was indicated as follows (wt%): 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 tensile strength, CVN toughness, and contact tip opening displacement (CTOD) toughness were measured for various locations in the weld metal and HAZ, and then compared with the base metal behavior. A stable austenitic structure was obtained down to cryogenic temperatures. Tensile test specimens taken transverse to the weld seam demonstrated yield strengths of 460 MPa and 438 MPa, and ultimate tensile strengths of 640 MPa and 669 MPa, respectively. Both specimens failed in the weld
metal due to the as solidified microstructure. CVN impact energy was lowest for the weld metal at all test temperatures from room to -196 °C. The minimum observed impact energy was still higher than the target design criteria value set by the authors of 54 J. CTOD results given at -163 °C were comparable for all locations. No mention was given to any issues with solidification cracking or HAZ liquation cracking.

Table 2.2 summarizes the key influences that various alloying elements have on high-Mn steel weld metals as indicated by the various weldability studies reviewed here. Specifically, the effect of Mn, C, Al, P, and S on the weldability of high-Mn steels is presented.

<table>
<thead>
<tr>
<th>Element</th>
<th>Effect of Addition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Stabilizes austenite</td>
<td>[2],[64], [66-78]</td>
</tr>
<tr>
<td></td>
<td>Segregates to dendrite boundaries</td>
<td>[74], [76]</td>
</tr>
<tr>
<td></td>
<td>Can promote β-Mn formation</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>Readily evaporates from weld pool</td>
<td>[71]</td>
</tr>
<tr>
<td>C</td>
<td>Stabilizes austenite</td>
<td>[2], [64], [66-78]</td>
</tr>
<tr>
<td></td>
<td>Segregates to dendrite boundaries</td>
<td>[74], [76]</td>
</tr>
<tr>
<td></td>
<td>Promotes solidification cracking</td>
<td>[64], [68], [76]</td>
</tr>
<tr>
<td></td>
<td>Promotes HAZ liquation cracking</td>
<td>[64]</td>
</tr>
<tr>
<td>Al</td>
<td>Stabilizes ferrite</td>
<td>[66], [67], [78]</td>
</tr>
<tr>
<td></td>
<td>Reduces solidification cracking</td>
<td>[78]</td>
</tr>
<tr>
<td>P</td>
<td>Segregates to dendrite boundaries</td>
<td>[64], [67], [68]</td>
</tr>
<tr>
<td></td>
<td>Promotes solidification cracking</td>
<td>[64], [67], [68]</td>
</tr>
<tr>
<td></td>
<td>Promotes HAZ liquation cracking</td>
<td>[64], [68]</td>
</tr>
<tr>
<td>S</td>
<td>Little influence on solidification cracking</td>
<td>[64]</td>
</tr>
</tbody>
</table>
CHAPTER 3: OBJECTIVES

Based on the information provided in Chapter 2, it is apparent that solidification cracking of high-Mn steel weld metals could be problematic. The simultaneous presence of substantial austenite stabilizing elements in the weld pool, a relatively high coefficient of thermal contraction in the solid, and the potential for eutectic formation during solidification all point to solidification cracking being a serious concern. Moreover, the structures which are built to contain LNG are of a much larger scale than other applications that utilize high-Mn steels (automobile components, railway frogs, etc.). This implies that an additional solidification crack promoting factor would be present: a high degree of weldment restraint. With all of this in mind, solidification cracking susceptibility of high-Mn steel weld metals needs to be thoroughly investigated as part of the material design process preceding any potential implementation by the natural gas industry. The purpose of this investigation was to assess the solidification cracking susceptibility and solidification behavior of high-Mn steel weld metals, and to lay the groundwork for future metallurgical investigations of high-Mn steel welds. The following list presents the primary objectives of this research.

1) Evaluate the effects of chemical composition on the solidification behavior of a wide range of high-Mn weld metals through both laboratory thermal analysis and computational techniques.
2) Assess the solidification cracking susceptibility of various high-Mn steel weld metals as a function of composition using a newly developed CPT testing system. This also includes evaluating the suitability of the newly developed CPT system for testing solidification cracking of high-Mn steels.

3) Metallographically characterize high-Mn steel weld metal samples to identify relative phase stability and gauge solute redistribution resulting from solidification.

4) Relate composition, solidification behavior, solidification cracking susceptibility, and weld metal microstructural features to guide future research objectives related to high-Mn consumable development for LNG service.
CHAPTER 4: MATERIALS AND EXPERIMENTAL PROCEDURES

In this section, the techniques which were used to assess the solidification behavior and cracking susceptibility of various high-Mn steel weld metals will be reviewed. A description of the various compositions which were investigated, laboratory techniques, computational tools, and characterization methods will be described in detail.

4.1 MATERIALS

The tested chemical compositions were selected based on the availability of precursor materials which could be consolidated in various ratios using an arc melting system. The arc melting system consisted of a Cu hearth and GTAW torch contained within a sealed quartz chamber capable of maintaining an inert atmosphere to prevent atmospheric contamination. Materials were placed within the Cu hearth, the chamber was sealed, and high purity Ar was used to purge the system prior to melting. Once purged, Ar continued to flow through the chamber for the remainder of the melting process. The GTAW torch was then manually initiated and used to melt, stir, and consolidate the contained charge. Once sufficiently mixed in the liquid state, the arc was extinguished and solidification took place. All components of the system were continuously water cooled to prevent damage and promote heat extraction following melting. A Miller Dynasty 300 LX power supply was used to provide a constant current.
of 225 amps to the GTAW torch in a straight polarity configuration. Melting times were varied to ensure complete mixing of the molten sample. A picture of the arc melting system is provided in Figure 4.1. For the remainder of this document the samples created using the arc melting system will be referred to as “buttons”.

Figure 4.1: GTAW melting system for creating small charges of desired composition

Initially, efforts were taken to simply weigh and arc melt combinations of individual high-purity elements to achieve specific compositions. Unfortunately, the volatility of Mn and the lack of a convenient way to control C content proved to be problematic during initial trials. As a result, four master heats of high-Mn steel were used as a defining basis for the test composition matrix. The four master heats of
material were produced using a vacuum induction melting system courtesy of the Welding and Joining Research Group of POSCO, a South Korean steel developer and producer. The master heats contained various combinations of Mn and C which could be mixed to span a wide range of high-Mn steel compositions. In addition to the four master heats, two other materials were available to further expand the composition matrix. One material was a high-Mn steel bar commercially referred to as “Mangalloy,” which was provided courtesy of Ford Steel Company, a Missouri based wear resistant steel producer. The final precursor material was in the form of high-purity (99.9% metal basis) Al granules that were purchased from Alfa Aesar.

The chemical composition for each of the master heats of material were measured via unknown techniques and provided by POSCO. Chemical analysis of the Mangalloy bar was performed by Applied Technical Services of Marietta, Georgia using various optical emission and XRF-WD techniques calibrated via high-Mn standards. The chemical composition of the Al granules was obtained via a certificate of analysis from Alfa Aesar for the particular lot number which was used. The alloys contained within Table 4.1 define the composition matrix used for this study. The compositions provided in Table 4.1 are the nominal calculated values for each tested alloy obtained using the known precursor compositions and desired mixing ratios. The compositions were selected to provide a wide range of Mn and C conditions to determine their interactions, as well as two additional alloys containing Al. Although not directly included in the design matrix, observations from laboratory and computational tests provided clues to the influence of impurity elements (S+P).
Table 4.1: Calculated composition matrix for this investigation

<table>
<thead>
<tr>
<th>Designation</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>FeMnC-1</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-2</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-3</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-4</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-5</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-6</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-7*</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-8</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-9</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnC-10</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnCAI-1</td>
<td>Bal.</td>
</tr>
<tr>
<td>FeMnCAI-2</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

*Trace amounts of Si, Ni, and Cr detected through EDS analysis

Prior to weighing and melting buttons, surface scales were mechanically removed from all materials to expose the underlying clean base material. The surface scales on the master plates were removed via wet surface grinding. Small scale-free pieces of the Mangalloy bar were cut using a precision sectioning machine fitted with a wet abrasive cut-off wheel. The Al granules were mechanically ground using a standard bench grinder. The high-Mn master heats and Mangalloy bar were cut into small pieces (6 to 10 g) using a combination of a hydraulic metal shear and wet abrasive saw. Following surface scale removal and sectioning, materials were thoroughly cleaned using ethyl alcohol to remove any residue.

Materials were then weighed to the desired ratios using a high precision analytical balance capable of measuring to the nearest 0.01 mg. Minute amounts of material were removed from individual pieces of precursors using a bench top grinder and/or a wet belt...
grinder with SiC abrasive to reach the desired mass. Once the desired precursor ratio was reached, material pieces were given a final cleaning with ethyl alcohol, dried, and melted into button form.

4.2 CAST PIN TEAR TESTING

A newly developed levitation melting and casting system [63] was utilized to assess solidification cracking susceptibility of all alloys in the test matrix via CPT testing. In this test, a water cooled Cu levitation melting coil contained within a controllable atmosphere housing is used to melt small charges of material. A high-frequency induction power supply is used to energize the axisymmetric coil and excite eddy currents within the sample. Once excited, a repulsive Lorentz force exists between the induction coil and sample, causing sample levitation. The levitating specimen then heats and subsequently melts due to Joule dissipation. A two color optical pyrometer is used to monitor the surface temperature of the sample during testing. Situated below the induction melting coil, an Al fixture holds a two-piece axisymmetric Cu-Be pin mold. Flow valves at the top and bottom of the housing, as well as below the mold, allow for proper inert gas purging to prevent atmospheric contamination. Once the charge reaches a desirable casting temperature, the induction coil is shut off and the material casts into the mold. A schematic representation of the induction levitation coil and pin mold are provided in Figure 4.2. A quartz insert lines the inside of the induction coil to prevent any short circuiting. Not pictured in Figure 4.2b, a small Cu backing piece is situated under the mold to contain the charge within the mold cavity during casting. The head and foot features of the pin mold provide intrinsic restraint to the solidifying melt through
the gauge section. Various mold pin lengths are available ranging from 0.5 in (12.7 mm) to 2 in (50.8 mm) to provide varying levels of restraint during solidification. The gauge section diameter is 0.1875 in (4.76 mm). The head and foot dimensions are held constant across all molds. Longer mold / pin lengths represent higher degrees of restraint during solidification.

![Schematic representations of levitation melting coil used for CPT testing (a) and CPT test mold (b)](image)

Figure 4.2: Schematic representations of levitation melting coil used for CPT testing (a) and CPT test mold (b)

The approach for this investigation deviated slightly from the methodology of previous CPT testing. In general, CPT testing has been conducted by taking a single alloy and casting pins across the entire range of mold lengths. Solidification cracking responses would then be compared with previously tested materials as a function of pin length to provide a relative idea of solidification cracking susceptibility. Due to the size of the composition matrix which has been defined here, only two pin lengths were used.
Pin lengths of 1 in (25.4 mm) and 2 in (50.8 mm) were selected to represent low- and high-restraint conditions, respectively. The cracking behavior was then compared as a function of composition at fixed pin lengths.

A minimum of three pins were cast for each composition at the 2 in (50.8 mm) mold length. Only a single pin was cast for each composition at the 1 in (25.4 mm) mold length because no cracking was observed during initial trials. In the event of an unacceptable cast (such as incomplete filling of the mold) an additional pin was made. Sample masses for the 1 in (25.4 mm) and 2 in (50.8 mm) pins were 12 g and 14 g, respectively. Buttons were created using the previously outlined procedure. Following melting in the arc melting system, buttons were thoroughly cleaned using ethyl alcohol and dried.

The casting procedure began by loading a button of desired composition into the quartz insert through an access hatch in the casting chamber. The hatch was then sealed, and the chamber was purged with high-purity Ar. The purging procedure consisted of flowing Ar into the chamber with all valves closed until a chamber pressure of 10 psi (69 kPa) was reached. The exhaust valve at the top of the chamber would then be opened to release the chamber pressure. This was repeated a total of three times. Ar flow was then redirected to flow through the mold cavity. Once again, all valves would be shut to create a chamber pressure of 10 psi (69 kPa). Venting was then directed through an exhaust valve under the mold cavity. This was also repeated three times and completed the purging process. Following purging, Ar flow was adjusted to exhaust under the mold cavity at a flow rate of 10 cfh (4.7 lpm). The induction coil was then energized by an
Ambrell EasyHeat 10 kW induction power supply operating at 224 kHz and 430 amps. The induction heating system was controlled through LabVIEW™. The coil current was stepped from 0 to 430 amps over 0.5 s to prevent buttons from being ejected from the coil when starting. Heating was carried out until approximately 100 °C superheat was reached. This was possible through the use of the optical pyrometer in conjunction with a real-time temperature output using a graphical interface. Once the desired level of superheat was reached the coil current was stepped from 430 to 100 amps over 1 s and then turned off. This ramp down allowed for the smoothest possible transfer of the molten charge into the mold cavity. These operating conditions were selected following an initial trial period. An example thermal history of FeMnC-7 during levitation melting is provided in Figure 4.3 as measured from the optical pyrometer. Due to the somewhat turbulent nature of the levitating charge within the mold and a relatively slow sampling rate of the pyrometer system (1 Hz), accurately identifying transformation temperatures from such a curve was not feasible.
Following casting, mold halves were split apart to remove the solidified pin. Mold halves were then thoroughly cleaned using liquid dish soap and water, as well as 800 grit SiC paper to remove any oxidation. The quartz insert was also cleaned following casting using ethyl alcohol and a cotton swab. The mold and Al fixture were equilibrated to room temperature between sequential castings to ensure comparable cooling conditions between tests.

Pins were placed in a rotating fixture equipped with a graduated dial to allow the angular length of any cracks which formed to be measured. The fixture was used in conjunction with a binocular microscope operated at 10x to 70x magnification. The angular length of all cracks was then recorded. Equation 4.1 was then used to determine
the percentage of cracking around the outer circumference of individual pins, where $L_C$ is the angular length of individual cracks in degrees.

$$\%\ Cracking = \frac{\sum L_C}{360^\circ} \times 100\%$$

Equation 4.1: Equation for quantifying the amount of cracking in a cast pin sample

### 4.3 THERMAL ANALYSIS

Thermal histories were recorded for each of the compositions within the test matrix during non-equilibrium solidification conditions. The procedure previously described was used to create 16 g button samples for each composition. GTAW spot welds were placed on the buttons using the parameters listed in Table 4.2 under high-purity Ar shielding. The spot welds were made using a GTAW torch powered by a Miller Dynasty 300 LX power supply on a Jetline Side Beam Welding System. The Jetline system was equipped with a bolt-on Jetline Arc Length Control which allowed the GTAW torch to be quickly retracted once the arc was extinguished. The retracted distance was selected to allow a thermocouple to manually be maneuvered towards the weld pool following welding while still maintaining an inert atmosphere from the post flow. A high temperature type-C thermocouple (W-5%Re vs W-26%Re) was manually plunged into the weld pool immediately following arc extinction. Temperature data was then recorded for the solidifying weld pool using an instruNet model 100 high-frequency data acquisition system operating at a sampling rate of 1 kHz. Data was collected for approximately 50 s following plunging. A minimum of three thermal histories were
acquired for each composition. In the event of an unsatisfactory plunge, such as an abnormal amount of noise in the thermocouple signal, additional tests were conducted. Buttons were positioned on top of a room temperature Cu cooling block to assist in heat extraction for all tests. A schematic view of the thermocouple plunging setup prior to and following welding is provided in Figure 4.4.

Table 4.2: Welding parameters for thermocouple plunging experiments

<table>
<thead>
<tr>
<th>Current</th>
<th>Arc Gap</th>
<th>Weld Time</th>
<th>Shielding</th>
<th>Flow Rate</th>
<th>Pre-flow</th>
<th>Post-flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 A</td>
<td>0.08 in (2 mm)</td>
<td>4 s</td>
<td>100% Ar</td>
<td>20 cfh (9.4 lpm)</td>
<td>3 s</td>
<td>50 s</td>
</tr>
</tbody>
</table>

Figure 4.4: Schematic of thermocouple plunging experiments prior to (a) and immediately following welding (b)
Following thermal data acquisition, SS-DTA software was used to analyze phase transformation behavior through the end of solidification. SS-DTA stands for single-sensor differential thermal analysis, and is an in-situ technique for determining phase transformation temperatures in metals that has been developed at The Ohio State University [79]. SS-DTA diverges from traditional DTA in that a reference sample is not necessary to identify phase transformations. Instead, mathematical functions are used to generate a reference curve from the thermal history that was obtained from a single thermocouple. The acquired thermal data is then compared with the generated reference curve. Deviations between the measured data and reference curves occur as a result of the latent heat affects associated with phase transformations. The lack of a necessary reference sample allows SS-DTA to be employed in situations where DTA is not possible, such as when high heating and/or cooling rates are involved.

SS-DTA was specifically used to measure the liquidus ($T_L$) and solidus ($T_S$) temperatures of all alloys within the test matrix. Using this information, the solidification temperature range (STR) was then calculated as the difference between $T_L$ and $T_S$. The STR of austenitic alloys during weld solidification has been shown to relate well with solidification cracking susceptibility [80]. Thermal histories were also analyzed to determine the solidification sequence of all alloys, i.e. to detect any phase transformations which may occur prior to terminal solidification.

### 4.4 SOLIDIFICATION SIMULATIONS

Various solidification simulations were carried out using Thermo-Calc Classic version R (TCCR), a commercially available software package from Thermo-Calc.
Software AB of Sweden. TCCR is a powerful software platform that can be used for many thermodynamic calculations [48]. Thermodynamic calculations are performed using thermodynamic information taken from databases that have been developed by Thero-Calc Software. The various databases are suitable for a wide range of materials systems and simulations. Database selection is left to the discretion of the user depending on the particular application.

In this investigation, TCCR was used primarily to perform solidification simulations with the SCHEIL module and TCS Steels/Fe-Alloys database, version 5 (TCFE5). Simulations were performed to computationally identify the compositional influence of various alloying additions during solidification of high-Mn steels. Within the SCHEIL module, a modified Scheil-Gulliver model was used to simulate solidification [81]. TCCR also proved to be useful to quickly generate various equilibrium phase diagrams using the Equilibrium Calculation (POLY) module and TCFE5 database.

In conjunction with TCCR, JMP® version 10 was used to analyze thermodynamic simulation outputs. JMP® is a statistical analysis software package commercially available from SAS Institute Inc., headquartered in Cary, North Carolina. Using JMP®, a design of experiments (DOE) methodology was employed to assess the influence of chemical composition on STR for a wide range of hypothetical alloys. This allowed for interactions to be identified which might otherwise be difficult to see through running individual simulations.
4.5 CHARACTERIZATION

4.5.1 Optical Microscopy

Samples which were characterized via light optical microscopy (LOM) were prepared using standard metallographic supplies and procedures. Sectioning of samples was performed using a TechCut 5™ precision sectioning machine using a resin bonded alumina abrasive wheel and high speed cutting fluid. Blade speeds and feed rates varied depending on the material being section and sample geometry. Following sectioning, samples were mounted in Bakelite using a hot compression mounting system. Once mounted, samples were sequentially ground using 360, 600, and 800 grit SiC abrasive paper disks on a rotating platen with continuous water cooling. Polishing was then sequentially performed using 9 μm, 3 μm, and 1 μm diamonds in an oil-based suspension. A final polishing step of 0.05 μm colloidal silica was then used. Ultrasonic cleaning in 200 proof ethyl alcohol was performed between every step for a minimum of 2 minutes to prevent contamination between various abrasives. Once removed from the ultrasonic alcohol bath, samples were given a final rinse with ethyl alcohol and dried using cool air.

Following polishing, three chemical etching techniques were utilized independently or in conjunction with one another with varying levels of success. Table 4.3 contains a summary of the chemical etchants used. All etching was performed at room temperature. Nital was applied by saturating a cotton ball and swabbing. The other etchants are tint etchants and require submersion to develop a surface film without disturbance. Ethyl alcohol was used to rinse samples once finished etching, followed by cool air drying. Etching times varied depending on the sample chemistry and etchant
used. Times ranged from as low as only 2-3 s to as high as 75 s. Optimum results were obtained when etching was performed immediately following the final polishing and rinsing step. Freshly made etchants were always used. In the event of over etching or unsatisfactory results, samples were taken back to the 1 μm step and polished through colloidal silica.

Table 4.3: Etchants used to reveal microstructural features for optical microscopy

<table>
<thead>
<tr>
<th>Etch</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nital (2-5%)</td>
<td>95-98 mL ethyl alcohol</td>
</tr>
<tr>
<td></td>
<td>2-5 mL HNO₃</td>
</tr>
<tr>
<td>Klemm's I Reagent</td>
<td>50 mL saturated aqueous</td>
</tr>
<tr>
<td></td>
<td>Na₂S₂O₃</td>
</tr>
<tr>
<td></td>
<td>1 g K₂S₂O₅</td>
</tr>
<tr>
<td>Beraha's Sulfamic Acid Reagent No. III</td>
<td>100 mL H₂O</td>
</tr>
<tr>
<td></td>
<td>3 g K₂S₂O₅</td>
</tr>
<tr>
<td></td>
<td>2 g NH₂SO₃H</td>
</tr>
</tbody>
</table>

Etching was followed by LOM using an Olympus GX-51 inverted microscope equipped with an Olympus DP71 digital camera. The Olympus camera was connected to a PC with imaging software to allow for proper color balancing and to ensure optimum image quality for bright field imaging. Differential interference contrast (DIC) microscopy was also occasionally used with the given microscope.

4.5.2 Scanning Electron Microscopy

Sample preparation for scanning electron microscopy (SEM) samples was very similar to that previously described for LOM. Instead of Bakelite, a graphite containing
phenolic thermoset was used to mount samples in order to prevent sample charging during imaging. All grinding and polishing steps were the same for SEM samples as they were for LOM samples. SEM samples were often analyzed in both the etched and non-etched conditions.

SEM imaging was conducted on two different instruments. Fracture surfaces from CPT testing were analyzed using a Quanta200 general purpose tungsten source SEM. Images for fracture surface analysis were acquired using a secondary electron (SE) detector. Characterization of button samples was performed using a XL-30 ESEM. The XL-30 ESEM system was equipped with a high-brightness field emission gun (FEG). Images of button samples were acquired using the equipped back scattered electron (BSE) detector. The XL-30 ESEM was also fitted with an energy dispersive spectrometer (EDS) to allow for qualitative and semi-quantitative chemical analysis.
CHAPTER 5: CAST PIN TEAR TESTING

This section will provide an overview of the CPT testing results based on the effect of particular alloying additions. Specifically, the apparent influences of Mn, C, Al, and impurities (S+P) will be discussed. Attention will be given to the cracking behavior of the test compositions at the high-restraint condition, 2 in (50.8 mm) mold length, since no cracking was observed at the 1 in (25.4 mm) length.

Significant oxidation of the pin molds was observed when casting high-Mn steels. Samples containing Al demonstrated both oxidation of the mold walls and pin surfaces. The oxidation was likely a result of inadequate removal of O from the test chamber, which could not be improved through varying the purging sequence and appeared to be a factor of the chamber design itself. An attempt was made to reduce oxidation through the use of an Ar+5%H₂ gas mixture in the chamber, however this had little effect.

In addition to oxidation during casting, a significant amount of vapor formation was observed from molten charges in both GTAW button melting and levitation casting. This formation was likely due to the relatively high vapor pressure of Mn [74, 82]. Table 5.1 compares the calculated composition of FeMnC-7 to the measured composition following GTAW button melting and subsequent levitation casting. Chemical analysis was performed by Applied Technical Services of Marietta, Georgia using various optical emission and XRF-WD techniques calibrated with high-Mn standards. As can be seen in
Table 5.1, there is a 1 wt% drop in Mn due to the levitation casting step. Interestingly, the calculated composition indicates lower Mn and C values than those which were measured following GTAW melting. This indicates that either the measuring technique used to determine the chemical composition was inaccurate to some degree, or that the composition of one or more of the precursor elements was incorrectly reported. Regardless, the calculated chemical composition was relatively close to the measured composition.

Table 5.1: Comparison of the calculated composition of FeMnC-7 to measured values following GTAW button melting and subsequent levitation casting

<table>
<thead>
<tr>
<th>Condition</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td>Calculated</td>
<td>23.15</td>
</tr>
<tr>
<td>After GTAW Melting</td>
<td>23.5</td>
</tr>
<tr>
<td>After Levitation Casting</td>
<td>22.5</td>
</tr>
</tbody>
</table>

Liquid metal “dripping” during levitation casting was often observed when using 14 g specimens for the 2 in (50.8 mm) mold length. As a charge of material suspended in the electromagnetic field within the levitation coil began to melt, the charge would elongate and small droplets would separate from the bulk sample, prematurely casting into the mold cavity. Dripping was never observed in 12 g samples being cast into 1 in (25.4 mm) molds. This dripping behavior is associated with the axisymmetric nature of the levitation coil in addition to the surface tension of the molten charge [83]. A so-called “magnetic hole” exists in the system at the highest and lowest points of the levitating charge. A solution to the problem was never identified in this investigation as
decreasing the sample mass was not possible due to mold cavity geometry, and making any adjustments to the coil design itself was not an option. A decrease in mold length would allow for a smaller sample mass to be cast, however in this investigation this resulted in insufficient restraint to induce cracking. In the event of a dripping sample, that particular charge would be scrapped and a new one would be created to take its place. It was also consistently observed that levitating charges prior to casting were laterally unstable within the electromagnetic field, and often promoted dripping and/or resulted in turbulent transfer to the mold cavity.

5.1 INFLUENCE OF MANGANESE

Referring back to Table 4.1, the composition matrix which was selected for this investigation allows for comparisons to be made between various alloys in order to assess the influence of specific elements. For example, the alloys can be arranged in such a way to consider Mn additions at fixed levels of C. The following alloys can be compared to identify the effect of Mn additions on a low C condition: FeMnC-1, FeMnC-4, and FeMnC-8. This compares the alloys at Mn contents of approximately 14, 24, and 34 wt%, respectively, and a fixed C content of 0.01 wt%. Figure 5.1 presents the circumferential cracking data for the described set of alloys as a function of Mn content. The information is presented as both individual data points for each measured pin as well as an average value for each composition.
Figure 5.1: CPT test circumferential cracking data showing the effect of Mn on cracking behavior at a fixed C content of 0.01 wt%; 2 in (50.8 mm) mold length

Unfortunately, presenting the information in this way neglects any synergistic relationships between Mn and impurities (S+P) at a low level of C. The impurity levels in the alloys presented in Figure 5.1 are all quite similar, having S between 0.005-0.008 wt% and P between 0.003-0.005 wt%. This provides a first approximation to the influence of Mn on the solidification cracking behavior of high-Mn steel weld metals. As can be seen, increasing Mn content appears to have a very little, almost negligible, effect on solidification cracking behavior. The difference in average %Cracking across a 20 wt% increase in Mn content is less than 10%. Similar trends were observed at an intermediate C content (~0.27 wt%) and high C content (~0.53 wt%) with varying levels
of Mn. The difference in average %Cracking across a 20 wt% increase in Mn was less than 15% for both levels. There was, however, much more scatter in the data at these levels.

5.2 INFLUENCE OF CARBON

In a similar fashion to how the test matrix can be broken into groups to identify the influence of Mn on solidification cracking susceptibility, compositions can be paired to identify the effect of C. The CPT test results for fixed Mn levels of approximately 14, 24, and 34 wt % as a function of C content are presented in Figure 5.2 through 5.4, respectively. This data was generated using the compositions of alloys FeMnC-1 through FeMnC-10 of Table 4.1.
Figure 5.2: CPT test circumferential cracking data showing the effect of C on cracking behavior at a fixed Mn content of approximately 14 wt%; 2 in (50.8 mm) mold length
Figure 5.3: CPT test circumferential cracking data showing the effect of C on cracking behavior at a fixed Mn content of approximately 24 wt%; Note that the alloy with the highest C content also had substantially more P (0.026 wt%) than the other alloys (0.004 wt%); 2 in (50.8 mm) mold length
As can be seen, a general increase of average %Cracking is observed with increasing C content for the tested alloys at 14 wt% and 24 wt% Mn. At a Mn content of 34 wt% there is a slight increase and subsequent decrease in average cracking response with increasing C content. Considering the scatter in the data, however, the difference in %Cracking between an intermediate and high C level is negligible in the 34 wt% Mn system. Note that a caveat exists in the data when considering the influence of C on solidification cracking susceptibility in the Fe-24Mn (wt%) system (Figure 5.3). The alloy which exhibited 100% solidification cracking in each of the pins which were cast (FeMnC-7) had a significantly higher P content than the rest of the alloys. FeMnC-7 had
a calculated P content of 0.026 wt%, while the rest of the alloys contained in Figure 5.3 had a P content of 0.004 wt%.

The fracture surface of a 100% cracked pin (FeMnC-7) was analyzed to identify the presence of liquid films during crack formation. As can be seen in Figure 5.5, the fracture surface of the cracked pin demonstrated a dendritic “egg crate” morphology that is typical of solidification cracking. The dendritic fracture morphology is a direct result of crystallization along <100> type growth directions after liquid film rupture. Similar fracture surface morphologies were identified in partially cracked pins of FeMnC-6 and FeMnC-10, found in Figure 5.6 and Figure 5.7, respectively. Fracture surfaces of other cracked pins demonstrated the same fractographic features.
Figure 5.5: Appearance of a fully cracked pin after opening the mold (a), and resulting fracture surface of the lower portion of the pin (b and c); alloy FeMnC-7, 2 in length
Figure 5.6: Fracture surface of partially cracked pin; alloy FeMnC-6

Figure 5.7: Fracture surface of partially cracked pin; alloy FeMnC-10
Optical micrographs of cross sectioned pins of FeMnC-3, FeMnC-6, FeMnC-7, and FeMnC-10 are presented in Figures 5.8 through 5.11, respectively. Solidification morphologies demonstrated the same characteristics in each of the cross sectioned specimens. All pins showed primary austenite solidification. An equiaxed “chill zone” exists along the outer diameter of cast pins where the first solid begins to form following casting. Subsequent growth proceeds inward from this region transitioning from columnar dendritic to equiaxed dendritic growth. The observed solidification cracks in cross sectioned specimens were generally present along SSGBs oriented perpendicular to the pin axis. Both surface cracks and subsurface cracks were identified. Evidence of possible eutectic formations along solidification boundaries can be seen in each of the presented cross sections. Alloys with approximately 0.53 wt% C (FeMnC-3, FeMnC-6, and FeMnC-10) showed very small amounts of grain boundary eutectic. Examples of the apparent eutectic can be seen at the tips of solidification cracks in Figures 5.8c (FeMnC-3), 5.9c (FeMnC-6), and 5.11c (FeMnC-10) as very thin discontinuous light etching regions within the solute rich grain boundaries. Grain boundary eutectic is much more pronounced along the solidification boundaries adjacent to the cracked regions in alloy FeMnC-7 (Figure 5.10c). It appears as though no backfilling of cracks occurred in the investigated pins with the exception of a region in Figure 5.9c, where evidence of a small amount of backfilling is present in a subsurface crack. Higher resolution analysis is needed to characterize the grain boundaries surrounding cracked regions to further identify the presence of eutectic films.
Figure 5.8: Cross sectioned CPT specimen showing solidification morphology changes through the thickness of the pin (a and b), and higher magnification view of regions with solidification cracks (c and d); FeMnC-3
Figure 5.9: Cross sectioned CPT specimen showing solidification morphology changes through the thickness of the pin (a), and higher magnification views of a cracked region (b and c); FeMnC-6
Figure 5.10: Cross sectioned CPT specimen showing solidification morphology changes through the thickness of the pin (a and b), and the presence of a eutectic constituent adjacent to cracked regions (b and c); FeMnC-7
Figure 5.11: Cross sectioned CPT specimen showing solidification morphology changes through the thickness of the pin (a), and higher magnification views of regions with solidification cracks (b and c); FeMnC-10

5.3 INFLUENCE OF ALUMINUM

Comparing the solidification cracking behavior of alloys FeMnC-5, FeMnCAI-1, and FeMnCAI-2 provides insight into the effect of Al on solidification cracking in high-Mn weld metals. The addition of Al to the CPT test samples resulted in a significant increase in the amount of oxidation during casting. Although oxidation occurred, three
pins were able to be cast for each of the Al containing compositions. Unfortunately, the interaction between sample oxidation and casting characteristics is unknown for this test. Oxidation made it difficult to identify cracks on sample surfaces. As a result, pins containing Al were briefly cleaned using a bench top grinder fitted with a wire wheel. Doing so allowed for the sample surfaces to more easily be interpreted.

CPT test data for samples containing approximately 24 wt% Mn and 0.27 wt% C and varying levels of Al is presented in Figure 5.12. As can be seen, Al additions appear to have a very small effect on solidification cracking. This is especially true when considering that the alloy with no Al additions has a single pin which is well separated from the rest of the pins at that composition. Looking at these results, it can be said that Al does not increase solidification cracking susceptibility as identified through CPT testing.
Figure 5.12: CPT test circumferential cracking data showing the effect of Al on cracking behavior at fixed Mn and C contents of 24 wt% and 0.27 wt%, respectively; 2 in (50.8 mm) mold length

5.4 INFLUENCE OF IMPURITIES (S+P)

As indicated previously, the composition matrix which was used in this investigation did not directly test for the influence of S and P. From the CPT test results, no conclusions can be drawn about the influence of S on the solidification cracking susceptibility of high-Mn steels. It is believed, however, that S would have a negligible effect due to the presence of such a high percentage of Mn to act as a scavenging element in the molten weld pool. This thought is supported by the work of Kato, where it was
demonstrated through Trans-Varestraint testing that S had very little influence on the solidification cracking behavior of a Fe-15Mn-0.7C-1Ni (wt%) austenitic alloy [64].

It appears as though P is likely detrimental to solidification cracking behavior in high-Mn steel weld metals. The composition with an increased P content of 0.024 wt% cracked to 100% in each of the pins which were cast at a 2 in (50.8 mm) mold length. Unfortunately, the alloy with the highest P content also had the highest C content, so a definitive statement cannot be made regarding its behavior specifically. The influence of increasing P content on the solidification cracking susceptibility of austenitic high-Mn steel weld metals has been demonstrated to be detrimental in the past [64].

5.5 CAST PIN TEAR TESTING CONCLUSIONS

The CPT test circumferential cracking results reveal the following regarding the solidification cracking susceptibility of high-Mn steel weld metals:

1) Increasing Mn content has a negligible effect on solidification cracking behavior.
2) Increasing C slightly increases the solidification cracking susceptibility of high-Mn steel weld metals, although the effect is subtle in the tested composition matrix.
3) Al additions up to 3 wt% have a negligible influence on solidification cracking behavior in a Fe-24Mn-0.27C (wt%) alloy.
4) CPT testing of high-Mn steel weld metal compositions with impurity levels below 0.011 wt% S and 0.005 P show somewhat sporadic cracking responses at the upper limit of the available mold lengths; indicating that in general, solidification cracking susceptibility of these alloys is low as identified using the CPT test.
Comparatively speaking, all of the alloys except FeMnC-7 are more resistant to solidification cracking than many of the alloys previously subjected to CPT analysis as summarized by Alexandrov [62]. Specifically, the cracking response of the alloys tested here appears comparable to the behavior of Waspalloy and Alloy 600, which both did not exhibit consistent 100% cracking until a 2 in mold length was used.

5) Although not directly tested, increasing P appears to be detrimental to solidification cracking behavior, agreeing well with the work of Kato [64].

6) The consistent observation of oxidation during testing, as well as occurrences of melt “dripping” prior to casting, indicate that it would be beneficial to either modify the CPT system to solve these problems or employ a different weldability test in the future.
CHAPTER 6: SOLIDIFICATION ANALYSIS

Each of the alloys in this investigation exhibited primary austenite solidification through both Scheil solidification simulations and laboratory thermal analysis. The effect of elements on solidification behavior will be discussed here. Specifically, solute redistribution during solidification and its effect on STR will be reviewed for the high-Mn steel compositions found in Table 4.1.

6.1 PREDICTED SOLUTE PARTITIONING

As a first step in determining the influence of elements on the solidification behavior of high-Mn steels, it is useful to consider partitioning behavior. Thermo-Calc provides a convenient way to calculate partition coefficients for alloys in complex multi-component systems. The calculated partition coefficients for FeMnC-7 are presented in Figure 6.1. Partition coefficients were calculated by performing a solidification simulation using the nominal composition provided in Table 4.1, and plotting the weight fraction of elements in austenite as a function of fraction solidified. The composition of the calculated solid at a very small fraction solidified (<0.1) is then determined. Assuming that the liquid composition has not deviated significantly from the nominal composition, the partition coefficient (k) for each element in the alloy is calculated by taking the ratio of the solid composition of a particular elements at a very small fraction
solidified to the corresponding nominal elemental composition. Similar partition coefficients to those provided in Figure 6.1 were calculated for all alloys in the test matrix. As Figure 6.1 shows, each of the elements contained within the FeMnC alloys should partition to the liquid during solidification, resulting in interdendritic regions being enriched and dendrite cores being depleted in solute relative to the nominal base composition. Not shown, Al has a partition coefficient of approximately 1 when added to the Fe-Mn-C system within the ranges explored in this investigation. Also provided, Figure 6.2 presents simulated solute profiles from a dendrite core (x=0) to a dendrite boundary (x=1). Comparing the figures, it is interesting to note that while Fe, Mn, C, and P behave as expected, S does not. That is, elements with k-values less than 1 should segregate to the grain boundary. Even though S has the lowest k-value of all of the elements calculated, it is actually depleting as the simulated austenite grain forms. This appears to be an inaccuracy in the simulated profile, as the austenite should actually enrich in S as solidification progresses to the point that MnS forms, in which it would subsequently decrease.
Figure 6.1: Calculated partition coefficients; FeMnC-7
Thermo-Calc solidification simulations which were performed in this investigation utilized a modification the Scheil-Gulliver model that allows for solid state diffusion of interstitial elements [81]. The use of this model as opposed to the traditional Scheil-Gulliver model was selected due to the relatively high concentration of C which was being investigated. Since interstitial diffusion at high temperature is much faster than substitutional diffusion, the assumption of no solid (back) diffusion is not valid when interstitial elements are present in high concentration. Therefore, including solid diffusion of C can have a drastic impact on simulation results. Figure 6.3 presents the effects of interstitial solid diffusion on solidification with complete mixing in the liquid. As can be seen, the modified Scheil-Gulliver model represents an intermediate condition.
between equilibrium solidification (complete solid diffusion) and traditional Scheil-Gulliver solidification (no solid diffusion). Allowing back diffusion of C causes solidification to terminate prior to reaching the M₃C eutectic reaction in the simulation. As will be seen in the next section, this assumption appears to be representative of what actually occurs in high-Mn steel weld metals containing C.

Figure 6.3: Effect of interstitial diffusion on solidification; Fe-24Mn-0.8C-0.005S-0.01P
6.2 SOLIDIFICATION TEMPERATURE RANGE ANALYSIS

As will be seen, scatter in transformation temperature data was quite pronounced for each of the tested compositions using thermocouple plunging and SS-DTA. In an effort to combat this problem, between three to five thermal histories were recorded for each composition. The scattered data can be attributed to three sources to some degree as observed in this investigation: 1) fluctuations in chemistry resulting from button melting; 2) manual operation of the thermocouple following arc extinguishment; 3) variability in thermal history interpretation. Each of these factors will be discussed briefly below.

Fluctuations in sample chemistry can result from the GTAW button melting procedure. These fluctuations can stem from either incomplete mixing of precursor materials during consolidation, or from metal evaporation due to the high temperatures associated with the arc. Incomplete mixing of precursor materials is a direct result of operator judgment. Melting occurs due to the presence of a high temperature heat source, and stirring is made possible through the GTAW arc pressure. Ideally, buttons are melted and stirred until sufficient mixing has taken place to create a uniform composition distribution. If inadequate melting and mixing take place, local variations in button chemistry can occur as dissimilar precursor materials can exist in discrete pockets of the sample. A solution to this problem is to simply melt and mix the buttons for a longer period of time; however that can lead to excessive metal evaporation. As indicated previously in Table 5.1, melt loss is possible for elements which have a high vapor pressure in the material. This is particularly true in this situation when considering Mn.
Therefore, a balance is necessary to successfully melt and mix precursor elements while minimizing exposure to the heat source.

The second source of scatter in the data occurs during the thermal acquisition process. Since the plunging technique requires manual thermocouple insertion into the solidifying weld pool immediately following arc extinction, inconsistencies can arise when considering how quickly the thermocouple can be inserted, as well as the insertion location. The reaction time of the operator determines how quickly the thermocouple can be placed in the solidifying weld pool, which primarily influences the depth in which the thermocouple reaches the liquid-solid interface and how quickly the measurement system can react to record thermal data. In the event of a slow reaction by the operator, or a sufficient reaction by the operator but a slow reaction by the measuring system, insufficient thermal data will be acquired in the liquid state. This does not necessarily make the validity of the data questionable, but can make later analysis difficult. For example, a recurring problem in this investigation was that temperature data above the liquidus was infrequently acquired. This was attributed to the reaction time of the measurement system. The thermocouple junction is initially at room temperature prior to plunging. Once the junction is quickly plunged into the weld pool it must thermally equilibrate with its surroundings. If the thermocouple reaches the liquid-solid interface quickly enough, no liquid temperature data will be recorded while the system is reacting. Since the SS-DTA processing technique requires that sufficient data be present to generate a reference curve, determining liquidus temperatures proved to be difficult.
Considering this setback, efforts were taken to relate peak measured temperatures to liquidus temperatures which were calculated using Thermo-Calc. Table 6.1 contains a comparison for each of the FeMnC alloys and their difference (ΔT). As can be seen, there is relatively close agreement for most of the alloys. Differences are likely due more to the thermal measurements than the Thermo-Calc predictions. As a result, all STR values for the remainder of this document will utilize the Thermo-Calc liquidus predictions. Also note that simulated STR values using Thermo-Calc will always be taken from a cutoff point of 0.98 fraction solidified.

Table 6.1: Comparison of peak temperature measurements and corresponding calculated liquidus temperatures

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Thermo-Calc Liquidus (°C)</th>
<th>Maximum Measured Temperature (°C)</th>
<th>ΔT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeMnC-1</td>
<td>1468</td>
<td>1474</td>
<td>-6</td>
</tr>
<tr>
<td>FeMnC-2</td>
<td>1453</td>
<td>1430</td>
<td>23</td>
</tr>
<tr>
<td>FeMnC-3</td>
<td>1438</td>
<td>1410</td>
<td>28</td>
</tr>
<tr>
<td>FeMnC-4</td>
<td>1426</td>
<td>1426</td>
<td>0</td>
</tr>
<tr>
<td>FeMnC-5</td>
<td>1412</td>
<td>1411</td>
<td>1</td>
</tr>
<tr>
<td>FeMnC-6</td>
<td>1397</td>
<td>1378</td>
<td>19</td>
</tr>
<tr>
<td>FeMnC-7</td>
<td>1392</td>
<td>1395</td>
<td>-3</td>
</tr>
<tr>
<td>FeMnC-8</td>
<td>1384</td>
<td>1402</td>
<td>-18</td>
</tr>
<tr>
<td>FeMnC-9</td>
<td>1371</td>
<td>1347</td>
<td>24</td>
</tr>
<tr>
<td>FeMnC-10</td>
<td>1358</td>
<td>1341</td>
<td>17</td>
</tr>
</tbody>
</table>

The thermocouple also needs to be centered in the button once plunged. Deviations away from the button centerline can cause thermal effects to appear at lower temperatures than they actually occur. As exothermic processes (such as solidification) take place in the melt, the heat is dissipated through solid conduction in a general direction perpendicular to the liquid-solid interface. If a thermocouple is plunged away
from the central axis of the solidifying button, the heat of reactions from areas above the plunge area and towards the center of the button will flow through the thermocouple, depressing the apparent local reaction temperature. The solution to this problem is for the operator to plunge the thermocouple as quickly as possible, while still being careful to place it in the center of the molten weld pool.

The final source of scatter in the data originates during post-weld thermal analysis. The somewhat subjective nature of identifying phase transformations from thermal data obtained from a solidifying weld pool introduces some error in the measurements. Actually identifying the presence of a transformation event from the thermal data is quite easy; however finding the exact transformation temperatures can be subjective since the analysis depends on correctly identifying model parameters to create a reference curve. Regardless of the subjective nature of the analysis, SS-DTA proved to be useful for determining transformation behavior. Using a technique to acquire thermal data that is not so operator dependent would allow for more consistent analysis. An example of such a technique was demonstrated by Alexandrov et al. to determine the solidification behavior of high-Cr Ni-base filler materials [84], where a small 1 g button was melted over a stationary thermocouple situated within a hole of a larger 20 g button. Such a technique was not utilized in this investigation due to concerns with accurately controlling the chemistry of the 1 g sample.

The results from thermal analysis testing will be presented in an identical manner to the CPT test results which were discussed in Chapter 5. That is, the composition test matrix will be broken into small groupings to identify the influence of Mn, C, Al, and
impurities (S+P). Results from measured solidification thermal analysis via SS-DTA and calculated solidification simulations will be presented and compared. Additionally, optical and/or scanning electron photomicrographs, as well as results from EDS analysis will be provided when applicable.

6.2.1 Influence of Manganese

The influence of Mn on the STR of high-Mn steel weld metals was determined to be insignificant through both Scheil simulations and SS-DTA measurements. The STR results for alloys with approximately 0.01 wt% C are presented in Figure 6.4 as a function of Mn content. As can be seen, increasing Mn does not have a strong effect. This result is in close agreement with the CPT test results that indicated that Mn had a negligible effect on solidification cracking behavior. It can also be seen in Figure 6.4 that calculated and measured STR values are in close agreement with one another for the presented alloys.
Evidence of Mn segregation during solidification can be found in Figure 6.5. EDS analysis was used to semi-quantitatively determine the composition across dendrite cores and boundaries in a cross-sectioned button sample which had been used to gather thermal data for SS-DTA analysis. The alloy was FeMnC-10 from Table 4.1. The image and composition data were taken from an area immediately adjacent to the thermocouple plunge site in the fusion zone. As can be seen, interdendritic regions are Mn-rich, while the dendrite cores are Mn-lean. Additionally, Figure 6.6 is provided to show a qualitative representation of Mn segregation to interdendritic regions.
Figure 6.5: Evidence of Mn segregation in the FZ of a high-Mn steel sample; BSE image (left) and EDS line scan (right) showing Mn-rich interdendritic regions; FeMnC-10

Figure 6.6: SEM micrograph and corresponding EDS maps showing Mn segregation in an as solidified high-Mn steel weld metal; FeMnC-3

Mn segregation has a negligible influence on expanding the STR of high-Mn steel weld metals based on STR calculations and measurements at all C levels. This is in good agreement with the thermodynamic assessment of the Fe-Mn-C system by Djurovic et al. [18]. In their assessment, it was shown that the liquidus slope, solidus slope, and relative
separation of the liquidus and solidus lines changed very little between the hypoeutectic portions of a Fe-20Mn-C system and a Fe-40Mn-C system. In other words, increasing the Mn content from 20 wt% to 40 wt% in the Fe-Mn-C system would not cause a significant change in the difference between the liquidus and solidus temperatures at C contents which are applicable here. The increase in Mn does, however, shift the liquidus and solidus temperatures to lower values.

6.2.2 Influence of Carbon

The influence of C on solidification behavior in high-Mn steel weld metals appears to be significant from the analysis which was performed. It was found through both modified Scheil simulations and thermal analysis that increasing C caused a substantial shift in the STR of all Fe-Mn-C alloys tested here. The STR plots of tested Fe-Mn-C alloys are provided in Figure 6.7, Figure 6.8, and Figure 6.9. The results are broken into groups of approximately 14%, 24%, and 34 wt% Mn, respectively. The figures show that in general, increasing C results in an increase in STR. No eutectic carbide reactions were observed through SS-DTA analysis or solidification simulations. To highlight the effect of C on STR expansion Figure 6.10 is provided, showing simulated STR contours at various levels of Mn and C. As can be seen, C has a much larger effect on expanding the STR than Mn.
Figure 6.7: STR data showing the effect of C at a fixed Mn content of 14 wt%; both data sets utilize Thermo-Calc $T_L$ values, while $T_S$ values come from Thermo-Calc (Calculated) and SS-DTA (Measured).
Figure 6.8: STR data showing the effect of C at a fixed Mn content of 24 wt%; both data sets utilize Thermo-Calc T_L values, while T_S values come from Thermo-Calc (Calculated) and SS-DTA (Measured)
Figure 6.9: STR data showing the effect of C at a fixed Mn content of 34 wt%; both data sets utilize Thermo-Calc $T_L$ values, while $T_S$ values come from Thermo-Calc (Calculated) and SS-DTA (Measured).
Figure 6.10: Simulated STR contours in the Fe-Mn-C system using a modified Scheil-Gulliver Model to account for interstitial diffusion of C; contour line units are in °C

Unfortunately, SEM EDS analysis is not viable for low atomic number (low-Z) elements such as C [85]. Consequently, no direct observations or semi-quantitative analysis of C segregation could be made in the manner in which Mn segregation was identified. As indicated previously, solidification simulations indicate that C partitioning should be quite strong to interdendritic regions. There are features within the Fe-Mn-C system that can provide evidence that C segregation occurs. When considered together,
Figure 6.11a and Figure 6.11b can be used to identify the tendency for C to segregate to grain boundaries during solidification.

The two photomicrographs presented in Figure 6.11 are from FeMnC-1 (a) and FeMnC-2 (b). Both materials were polished using the procedure previously outlined and etched with Klemm’s I reagent, a common tint etchant used for steels. The key difference between these alloys is their C content. FeMnC-1 contains 0.01 wt% C while FeMnC-2 contains 0.27 wt% C. As can be seen, the weld metal of FeMnC-1 contains very fine martensitic features spread throughout the microstructure with some austenite formation along grain boundaries. Referring to the FeMnC-2 weld metal, martensite formation is still pronounced, however much more austenite formation occurs along interdendritic regions as a result of apparent C segregation. Note that the etching response of the alloys differs slightly and that color/phase associations do not completely match. Additional characterization would need to be conducted such as electron microprobe analysis (EMPA) with wavelength-dispersive spectroscopy (WDS) in order
to verify that C segregation was responsible for the observed increase in austenite stability.

Evidence of a very fine discontinuous 2nd phase along dendrite boundaries was found in alloys with approximately 0.53 wt% C (FeMnC-3, FeMnC-6, and FeMnC-10). The size, distribution, and alloys which they were found in lead the author to believe the 2nd phase could be carbides (likely M₃C). This would be in agreement with the findings of Yoo et al. [76], who indicated the presence of M₃C along solidification boundaries in high-Mn steel weld metals containing 0.6 wt% C. Yoo indicated that carbides appeared as a divorced austenite-M₃C eutectic as a result of weld solidification. The claim by Yoo could also be supported by considering the Fe-Mn-C liquidus projection as described by Djurovic [18]. In the Fe-Mn-C system an invariant line for the L→austenite+M₃C reaction exists in the approximate vicinity of the compositions considered. If the eutectic reaction is not reached it may also be possible for the precipitates to nucleate in the solid state during cooling if sufficient C segregation occurs along solidification boundaries (see the Fe-20Mn-C equilibrium phase diagram in Figure 2.2). Figure 6.12 presents SEM micrographs of FeMnC-6 and FeMnC-10 with arrows indicating examples of the described 2nd phase. Assuming they are carbides, it is unclear if they formed during a eutectic reaction since it was not detected through SS-DTA in multiple samples for each composition. EDS analysis of the 2nd phase was inconclusive as no significant changes in composition were detected between the particles and grain boundaries. The lack of composition change between the particles and grain boundary does, however, provide some evidence of carbide formation since C cannot be definitively identified using this
technique, although it could also be a result of their size. These precipitates differ significantly in size from the larger inclusions which were also found along grain boundaries in many samples (such as the large white particle in the upper right portion of Figure 6.12b). The inclusion formations are believed to be MnS, and will be discussed later in detail. Due to size, further characterization of the 2nd phase was not performed here and should be investigated further.

Figure 6.12: Evidence of possible carbide formation (arrows) along interdendritic regions in plunged buttons of FeMnC-6 (a) and FeMnC-10 (b)

6.2.3 Influence of Aluminum

Solidification temperature range analysis through SS-DTA testing was not in good agreement with simulated solidification behavior of high-Mn steel weld metals when Al was included. The STR results at a fixed Mn content of 24wt% and C content of 0.27 wt% with varying levels of Al are presented in Figure 6.13. As can be seen, alloy FeMnCAI-1 (1.5 wt% Al) shows a measured STR much higher than that which was calculated. On the other hand, the average measured STR of FeMnCAI-2 (3 wt% Al)
matches well with the calculated STR, but there is a significant amount of scatter in the data.

Figure 6.13: STR results demonstrating the influence of Al at fixed Mn and C contents of 24 wt% and 0.27 wt%, respectively; both data sets utilize Thermo-Calc $T_L$ values, while $T_S$ values come from Thermo-Calc (Calculated) and SS-DTA (Measured)

Unfortunately, these results provide little useful insight into the solidification behavior of high-Mn steels containing Al. The inconclusive data is attributed to two factors. First, as was observed in the CPT testing of Al-bearing high-Mn steel weld metals, significant oxidation was observed in plunged FeMnCAI buttons. Apparent oxides floated to the top of the molten weld pool prior to plunging, requiring penetration of the formed layer to retrieve solidification thermal data. The second, and more likely,
reason for these variations stems from inconsistent mixing of the Al precursor additions during the GTAW button melting step. Evidence of this can be found in Figure 6.14, where signs of incomplete mixing exist along the bottom side of a cross sectioned button sample containing 1.5 wt% Al. The Al likely comes into contact with the Cu hearth and conducts heat so efficiently that it solidifies and does not fully mix while stirring is applied from the GTAW arc pressure. A solution around this problem would be to use a higher welding current or continually flip and remelt the sample until complete mixing is achieved. However, this may introduce additional problems as elements with high vapor pressure, such as Mn, will tend to vaporize from the melt and adjust the composition away from that which was desired [74, 82].
Evidence of impurity segregation will be considered strictly from microstructural characterization standpoint below as S and P levels were not directly included in the test matrix. Evidence was found that S is likely scavenged by Mn at high temperature in the melt, while P segregation can lead to phosphide formation along interdendritic regions.

Evidence of possible MnS formation along a dendrite boundary is provided in Figure 6.15. As indicated previously, the presence of Mn and S in the solidifying weld pool results in the formation of apparent MnS inclusions which get swept to solidification boundaries. Therefore, it is likely that the presence of S in high-Mn steel weld metals
will have little influence on depressing solidification temperatures and promoting solidification cracking. The presence of high-Mn concentrations having this effect on austenitic weld metals has been show in the past. For example, in 1975 Brooks showed that the presence of high-Mn concentrations in fully austenitic stainless steel (type 21-6-9) weld metal promoted MnS formation, thereby reducing the effect of S on solidification cracking [86].

Evidence of P segregation was only observed in one of the compositions tested in this investigation, FeMnC-7. This is likely due to the fact that FeMnC-7 had a significantly higher P content the other alloys investigated. Figure 6.16 and Figure 6.17

Figure 6.15: SEM micrograph and EDS analysis showing the presence of a MnS inclusion along a solidification boundary; FeMnC-10
present SEM and OM analysis of the alloy, respectively. As can be seen in Figure 6.16, EDS analysis of the eutectic formation along an interdendritic region shows an abrupt spike in P content along with enrichment of Mn. Figure 6.17a presents the as solidified microstructure following GTAW button melting, which shows the presence of the eutectic formation (white interdendritic regions). Figure 6.17b presents evidence of liquation crack formation which occurred along the fusion boundary of a FeMnC-7 button during SS-DTA thermocouple plunging experiments. The liquation cracks likely formed as a result of P-rich interdendritic regions being present in the microstructure prior to applying the GTAW spot weld. The presence of this eutectic transformation was likely not identified through SS-DTA analysis due to a very small volume fraction.
Figure 6.16: SEM image showing the formation of a P-rich eutectic along a solidification boundary through EDS analysis; FeMnC-7

Figure 6.17: Optical micrographs presenting evidence of phosphide formation in FeMnC-7; (a) as melted button sample tint etched with Beraha’s sulfamic acid reagent no. III; (b) fusion boundary of an SS-DTA sample showing liquation cracking, tint etched with Klemm’s 1 reagent and viewed under DIC
The exact eutectic formation is unknown through the analysis techniques used here, but referencing the literature provides some insight. The most likely P-containing eutectic reactions which would occur in the high-Mn steel compositions explored in this investigation are either austenite-M$_3$P or austenite-M$_2$P, based on the ternary Fe-Mn-P liquidus projection published by Tokunaga [87]. Similarly, Chojecki indicated that a pseudoternary eutectic, austenite-M$_3$C-M$_3$P, could form in the Fe-Mn-C-P system [88]. Regardless of the phosphide reaction, it appears as though the P content is critical to hot cracking susceptibility for high-Mn steel weld metals, which agrees well with the findings of Kato [64].

The interactions between C, Al, and P and their effect on STR in a Fe-20Mn alloy were briefly evaluated using Thermo-Calc and a DOE methodology. Figure 6.18 presents the predicted first-order interactions of these elements within the following ranges (wt%): C (0-0.8), Al (0-3), and P (0-0.05). S was left out of this analysis since it appears as though the formation of MnS prevents it from having any effect. It should be noted that the only eutectic reaction observed in this analysis was a very small fraction (<1%) of austenite-M$_2$P that formed at high P levels (0.05 wt%), while fully austenitic solidification was predicted in all other simulations. It is predicted that while increasing P content in the Fe-Mn alloy increases the STR, this effect is minimal. This can be seen in Figure 6.18 by looking at the slopes of the lines in the far right column (shallow slopes indicating a small effect) and the proximity of the lines in the bottom row (parallel / tightly spaced lines indicating a small effect). The influence of C (far left column and top
row) is predicted to be much more significant on STR than other additions in the Fe-20Mn system.

Figure 6.18: DOE interaction plot showing the predicted STR behavior of a Fe-20Mn alloy with varying additions of C, Al, and P

6.3 CONCLUSIONS

The analysis performed here reveals the following regarding the solidification behavior of high-Mn steel weld metals:
1) The compositions considered in this investigation all demonstrated primary austenite solidification as determined through SS-DTA and solidification simulations.

2) SS-DTA analysis and simulated solidification behavior are in close agreement with one another when considering STR; although neither technique identified the formation of a P-eutectic in FeMnC-7.

3) Predictions and measurements of Mn segregation to interdendritic regions were in good agreement.

4) C appears to have the most influential effect on expanding the STR of these alloys during austenitic solidification due to segregation.

5) The influence of Al on solidification behavior in this investigation was inconclusive as oxide formation and incomplete Al mixing in button samples were observed.

6) The simultaneous presence of S and high levels of Mn in solidifying melts results in the formation of MnS inclusions, thereby preventing S segregation to grain boundaries.

7) The presence of a P-rich eutectic formation and apparent liquation cracking in a plunged button sample of FeMnC-7 indicate that P can have a detrimental effect on hot cracking.
CHAPTER 7: FINAL CONCLUSIONS

Based on the analysis presented in Chapter 5 and Chapter 6 the following conclusions can be drawn regarding the solidification behavior and cracking susceptibility of high-Mn steel weld metals:

1) CPT test analysis correlated well with trends observed from both measured and simulated STR values in the Fe-Mn-C system.

2) Solidification of all alloys in the test matrix exhibited primary austenite solidification.

3) Mn has little influence on solidification cracking susceptibility, which is attributed to Mn segregation having little effect on expanding the STR.

4) C additions increase the solidification cracking susceptibility of high-Mn weld metals, resulting from C segregation and STR expansion.

5) Al additions below 3wt% in the Fe-24Mn-0.27 alloy have little effect on solidification cracking susceptibility.

6) S impurities have little effect on solidification cracking susceptibility as they form MnS inclusions prior to terminal solidification.

7) P segregation has a detrimental effect on hot cracking (both liquation and solidification) susceptibility due to segregation and possible phosphide eutectic formation, although the analysis here cannot identify a practical P limit.
8) In general, the solidification cracking susceptibility of the alloys investigated here is relatively low as identified through the CPT test since inconsistent cracking behavior was pronounced at the upper restraint threshold. As a comparison, the cracking behavior of the tested alloys is expected to be similar to Waspalloy and/or Alloy 600 [62].
CHAPTER 8: FUTURE WORK

Following the findings of this investigation, there are areas in which further research would be beneficial for the development of high-Mn steel weld metals:

1) It seems as though a more thorough investigation of the influence of C and P on hot cracking would be beneficial. It is proposed that such an investigation should be conducted using a more severe hot cracking weldability test, such as the Varestraint test, considering that cracking could only be induced at the highest available level of restraint in the CPT test. Coupling this proposed study with higher level characterization techniques such as electron microprobe analysis and TEM could provide a better understanding of solute segregation and grain boundary precipitation, eutectic or otherwise. This would provide a better indication of the synergistic effects of Mn, C, and P in the system as well as developing a better understanding of practical chemical limits to avoid hot cracking.

2) Considering the use of high-Mn steel weld metals for LNG service, it would be beneficial to identify the influence of solute segregation on austenite stability at cryogenic temperatures. Since Mn and C are the principal alloying additions in these steels and both partition to interdendritic regions during solidification, it is possible that composition gradients which exist in fully austenitic high-Mn steel
weld metals at room temperature could result in martensite formation in solute-lean regions (dendrite cores) at low temperature. Such a characterization study could be completed using arc button melting to create high-Mn steel samples with varying Mn and C levels. Characterization could be performed via electron backscatter diffraction (EBSD) analysis or two-dimensional XRD analysis. It is believed that this procedure could lead to the formation of a constitution diagram similar to those which are commonly used for stainless steel weld metals.

3) As the desirable microstructure for low-temperature service would be fully austenitic, grain boundary mobility due to welding could lead to ductility dip cracking (DDC). Therefore, a DDC investigation is proposed. Such an investigation could be conducted using the Gleeble-based strain-to-fracture (STF) test to identify the susceptibility of fully austenitic high-Mn steels.

4) Another proposed investigation is to consider the influence of multi-pass welding conditions on precipitation in high-Mn steel weld metal. The solute segregation resulting from weld solidification can lead to solute profiles which promote precipitation due to subsequent weld passes. Such an investigation could be conducted by creating as-solidified weld metal tensile samples and utilizing the Gleeble thermo-mechanical system to simulate multi-pass welding conditions. Following simulation, samples could be characterized using SEM / TEM techniques as well as performing mechanical testing.

5) Lastly, further development of thermodynamic and kinetic databases which can accurately describe high-Mn steel compositions is proposed. As there is an
increased interest in high-Mn steels for a variety of applications (LNG storage, automotive components, etc.), it would be beneficial to have steel databases which are capable of confidently simulating various aspects of complex multi-component high-Mn alloys to aid in material design and analysis.
REFERENCES

8. BS EN 14620 - Design and manufacture of site built, vertical, cylindrical, flat-bottomed steel tanks for the storage of refrigerated, liquefied gases with operating temperatures between 0°C and -165°C. 2006.


