ADVANCED CHARACTERIZATION TECHNIQUES IN UNDERSTANDING THE
ROLES OF NICKEL IN ENHANCING STRENGTH AND TOUGHNESS OF
SUBMERGED ARC WELDING HIGH STRENGTH LOW ALLOY STEEL
MULTIPLE PASS WELDS IN THE AS-WELDED CONDITION

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Metallurgical and Materials Engineering).

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Striving for higher strength along with higher toughness is a constant goal in material properties. Even though nickel is known as an effective alloying element in improving the resistance of a steel to impact fracture, it is not fully understood how nickel enhances toughness. It was the goal of this work to assist and further the understanding of how nickel enhanced toughness and maintained strength in particular for high strength low alloy (HSLA) steel submerged arc welding multiple pass welds in the as-welded condition. Using advanced analytical techniques such as electron backscatter diffraction, x-ray diffraction, electron microprobe, differential scanning calorimetry, and thermodynamic modeling software, the effect of nickel was studied with nickel varying from one to five wt. pct. in increments of one wt. pct. in a specific HSLA steel submerged arc welding multiple pass weldment. The test matrix of five different nickel compositions in the as-welded and stress-relieved condition was to meet the targeted mechanical properties with a yield strength \( \geq 85 \) ksi, a ultimate tensile strength \( \geq 105 \) ksi, and a nil ductility temperature \( \leq -140^\circ F \). Mechanical testing demonstrated that nickel content of three wt. pct and greater in the as-welded condition fulfilled the targeted mechanical properties. Therefore, one, three, and five wt. pct. nickel in the as-welded condition was further studied to determine the effect of nickel on primary solidification mode, nickel solute segregation, dendrite thickness, phase transformation temperatures, effective ferrite grain size, dislocation density and strain, grain misorientation distribution, and precipitates. From one to five wt. pct nickel content in the as-welded condition, the primary solidification was shown to change from primary \( \delta \)-ferrite to primary austenite. The nickel partitioning coefficient increased and dendrite/cellular thickness was refined. Austenite decomposition temperatures into different ferrite products were also suppressed to refine the effective ferrite grain size with increasing nickel. Finally, dislocation density and strain increased and a more preferred orientation behavior was observed. At five

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wt. pct nickel, a precipitate in the form of MnNi₃ or FeNi₃ was observed. Its presence in both inter and intragranular regions enhanced strength and toughness by limiting the ferrite grain size and precipitation strengthening.
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CHAPTER 1
INTRODUCTION

Improvement in high strength low alloy (HSLA) steel weld metal mechanical properties could be achieved by controlling the type and amount of constituents within the microstructure of the weld metal. The microstructure of weld metal could be affected by weld metal composition, weld metal solidification and cooling rate, prior austenite grain size, and post weld heat treatment. The main factors that affect weld metal composition would be dilution of the weld wire, base metal composition, transfer of elements between the slag-metal interface, and minor contamination from the environment. Many aspects could be altered to achieve desired mechanical properties. Previous research has improved mechanical properties of low carbon structural steel welds via microstructural control by promoting acicular ferrite (AF) and minimizing Widmanstätten side plate ferrite (WF) and bainite.

Since the 1960s, gas tungsten arc welding of HSLA steels has been performed to produce welds with both good strength and toughness. With the growing demand for high strength steel welding in various applications, shielded metal arc welding (SMAW), fluxed cored arc welding (FCAW), and submerged arc welding (SAW) have been used to process flexibility and productivity. The demand for welds with higher strength (yield strength \(\geq 85\) ksi (586 MPa) and ultimate tensile strength \(\geq 105\) ksi (723 MPa)) using submerged arc welding has pushed toward more stringent criteria for toughness while maintaining the strength. Submerged arc welding is an advantageous and cost effective process with deposition rates four to ten times greater than SMAW when using high heat inputs with no spatter and minimal skill required to operate.

An HSLA-100 steel system was developed through an improvement program by the U.S. Navy in the 1980s through the early 1990s. Today, the continuation of improving shipbuilding materials and joining techniques to obtain enhanced mechanical properties endures. In
HSLA steels, toughness is achieved by designing alloys with selected combinations of alloying additions, for example, nickel, manganese, chromium, and molybdenum. Other minor additions such as titanium, aluminum, niobium, and vanadium are also used. Elements such as manganese and nickel have typically been added in controlled ratios to achieve the desired strength and impact properties. There are also accepted ratios for titanium and nitrogen reported in the literature. The continuous search for a better combination of alloying elements that minimizes cost and maximizes both weld strength and toughness was the driving force of this proposed research. Since there was no clear picture as to the effect of nickel additions between three to five wt. pct., the multiple pass weld metal based on the MIL-105S HSLA steel submerged arc welding was used to investigate the effects of nickel from one to five wt. pct. nickel at increments of one wt. pct.

1.1 Research Objectives

The goal of this research was to gain a fundamental understanding of the effects of nickel as an alloying agent on the strengthening and toughening mechanisms in specific HSLA steel submerged arc welding multiple pass welds. Nickel is known to improve toughness through empirical data with an unclear understanding [5, 17, 22–26, 38, 67]. Literature states one mechanism for nickel improving toughness was that it increases the stacking fault energy and allows for easier cross slip in body-centered cubic iron [3, 8]. This work used a variety of analytical techniques to further study the effects of nickel to improve mechanical properties of current HSLA steel submerged arc welding multiple pass welds. To assist in achieving this goal, an understanding in the relationships of the weld composition, weld microstructure, and mechanical properties was to be developed. The desired outcome of this program is to be able to better match the weld metal to a specifically designed pressure vessel base metal. Target mechanical properties set forth by the research program are as follows: yield strength (YS) \( \geq 85 \text{ ksi} (586 \text{ MPa}) \), ultimate tensile strength (UTS) \( \geq 105 \text{ ksi} (724 \text{ MPa}) \) and a nil-ductility temperature at 35 ft-lbs (NDT_{35ft-lbs}) \( \leq -140^\circ \text{F} (-95.6^\circ \text{C}) \). A more complete target of mechanical properties can be found in Table 1.1. The aim of this research was to
understand the effects of nickel on the strengthening and toughening mechanisms in HSLA steel submerged arc welding multiple pass welds. To understand the effects of nickel, this research looked at the following aspects:

- Primary solidification mode
- Nickel solute segregation
- Dendrite thickness
- Phase transformation temperatures
- Effective ferrite grain size
- Dislocation density and strain
- Misorientation distribution
- Precipitates

For comparison purposes, the mechanical properties of HSLA-100 steel have a YS of 100 to 120 ksi (690-827 MPa) with a 17 pct. elongation and a Charpy v-notch toughness of NDT \(_{28J}\) (NDT \(_{21ft-lbs}\)) at -18\(^\circ\)C (0\(^\circ\)F). Thus, a YS \(\geq 85\) ksi achieving a NDT \(_{35ft-lbs}\) \(\leq -140^\circ\)F (-96\(^\circ\)C) would be a difficult task.

<table>
<thead>
<tr>
<th>Yield Strength (ksi)</th>
<th>Ultimate Tensile Strength (ksi)</th>
<th>Pct. Elongation</th>
<th>Pct. Reduction of Area</th>
<th>NDT(_{35ft-lbs})</th>
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<tr>
<td>(\geq 85)</td>
<td>(\geq 105)</td>
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<td>(\geq 45)</td>
<td>(\leq -140^\circ)F</td>
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CHAPTER 2
LITERATURE REVIEW

This section will give some general background information regarding fluxes used in submerged arc welding, some basic concepts related to welding flux studies, the significance of oxygen, nitrogen, sulfur, and phosphorous in submerged arc welding, and the austenite decomposition behavior in steel weld metals. In addition, this Section will also give a brief fundamental review of some basic theories in solidification, thermodynamics, grain boundary energies, and energetic effects in microstructural development in research.

2.1 Submerged Arc Welding Fluxes and Basic Concepts Related to Welding Fluxes

A brief discussion on some fundamental aspects of submerged arc welding fluxes will be presented in this Section. If nickel is increased in the weld composition for mass production, the preferred methodology would be alloying through the submerged arc welding flux. There are three major types of submerged arc welding fluxes depending on the method of production: fused, bonded, and agglomerated. Fused welding fluxes are first crushed to ensure that all the mineral components are two to four millimeter in particle size. Dry mix is then melted in a furnace and quenched, crushed, sieved, dried, and packaged. Due to the manufacturing process, fused fluxes typically do not contain ferroalloys and deoxidizers. Bonded welding fluxes are ground to size and dry mixed together. Using a binder (usually potassium or sodium silicate), dry mix is bonded together and pelletized. The wet pellets are often contained and then dried at temperatures between 370°C and 800°C [6]. Flux is then sized and packaged. The low baking temperatures of bonded fluxes do contain ferroalloys and deoxidizers. Moisture is a problem for bonded and agglomerated fluxes thus a temperature and humidity controlled room should be used for storage of these fluxes.
Major flux ingredients are manganese oxide, silica (silicon dioxide), lime (calcium oxide), magnesium oxide, alumina, and calcium fluoride. The formulation of submerged arc welding fluxes are typically some complex combination in the form of the major flux ingredients listed above and may include various minor flux constituents such as titanium dioxide, barium oxide, iron oxide, potassium oxide, and sodium oxide. The main functions of the welding fluxes are to provide protection for the molten weld pool from the atmosphere, refine the weld pool, stabilize the plasma arc, and add alloying additions to the weld metal.

The basicity index (BI) is used to calculate whether the slag formed in submerged arc welding is basic or acid. Basicity of a flux can be described as the ratio of the total weight percent of the basic components over the total weight percent of the acid components. Silicate fluxes are considered acidic. Alkali and alkali-earth metal oxide fluxes are termed basic. Commonly used oxides in fluxes are listed from acidic to basic as follows: SiO$_2$, P$_2$O$_5$, Al$_2$O$_3$, TiO$_2$, FeO, MgO, MnO, CaO, Na$_2$O, and K$_2$O [20]. The most widely accepted and used BI equation is given in Eq: 2.1 [55]:

\[
BI = \frac{CaO + CaF_2 + MgO + K_2O + Na_2O + \frac{1}{2} (MnO + FeO)}{SiO_2 + \frac{1}{2} (Al_2O_3 + TiO_2 + ZrO_2)}
\] (2.1)

Even though the basicity concept originated from the iron and steel making industry to describe the sulfur refining behavior of a slag and it is not rigorous, it is still popular to use. A BI value of less than one is acidic, between 1.0 and 1.3 is neutral, and greater than 1.3 is basic. Higher welding flux basicity should produce cleaner welds with respect to sulfur, phosphorous, and non-metallic inclusions. Increasing flux basicity should cause decreasing silicon and oxygen contents [55]. However, basic fluxes have a greater tendency to absorb moisture.

Submerged arc welding fluxes used during the welding process affects the physical and chemical properties of weld metal. Improved welding fluxes can enhance the welding process thereby producing improved properties in weld metal. The ability of the welding flux to minimize gas and impurity pick up is critical to microstructural development and mechanical
properties of weld metal. Thus, it is essential that certain characteristics be met by the welding flux. The melting temperature of the welding flux should be 200°C lower than that of the filler metal and base metal [18]. The viscosity of the molten slag must be adequate to cover the molten weld pool to prevent atmospheric contamination, control slag-metal interactions, prevent weld porosity, retain alloying additions, and provide good weld bead morphology. Even though a low viscosity flux will allow for a greater bulk diffusion rate of chemical elements, i.e. a greater reaction rate at the slag-metal interface to absorb atoms and molecules into the molten slag and diffuse these species away from the slag-metal interface, the slag must still be viscous enough to protect the molten weld pool from the atmosphere [47]. The molten slag should be less dense than the molten weld metal to prevent slag inclusions.

Welding flux should also limit spatter during welding, refine the weld pool by removing impurities, and create a molten slag that is easily detachable. The arc stability of the welding process should be enhanced by the welding flux because of deliberate introduction of the ingredients that are easily ionized. The weld penetration is dependent on flux properties such as viscosity, arc stability, and capillarity [47]. SiO$_2$ is a flux addition used to increase viscosity and current capacity. CaO and MgO are similar in functionality which is to improve arc stability, but they can also decrease the viscosity of the molten slag. CaO is a better arc stabilizer than MnO [16]. Lighter fluorides such as MgF$_2$ and CaF$_2$ in fused submerged arc welding fluxes produces unstable arcs that may result in varied penetrations and irregular bead shape [43]. CaO, MgO, and Al$_2$O$_3$ additions increase the sensitivity of the welding fluxes to moisture pick up which can cause porosity in welds. MnO increases arc stability and therefore penetration but decreases sensitivity to porosity. MnO also decreases current capacity [16, 41].

The chemical interactions between molten slag and molten weld metal need to be considered because of oxygen control, loss of alloying elements via oxidation, and unfavorable elemental pickup from the molten slag. There are three major stages in the submerged arc
welding process where these chemical reactions are of importance: the electrode tip stage, the droplet stage, and the weld metal stage. Slag-metal reactions are most prevalent at the molten electrode tip because of the high surface-to-volume ratio of the molten metal and the intense stirring caused by the Lorentz force. The stirring motion induced by the Lorentz force brings the reactants in the molten slag and metal towards the slag-metal interface whereby diffusion through boundary layers in the slag and metal causes slag-metal reactions to occur. The extent of diffusion is determined by activity gradient which is a function of the thermodynamics of the reaction. Thus, a thermodynamically favorable reaction will have a high concentration of the reaction product at the interface with a high diffusion rate [43].

2.2 High Strength Low Alloy Multiple Pass Welds

The development of HSLA steels and welds has been driven by the need to reduce costs and the enhanced mechanical properties, specifically strength for certain applications. High strengths and high toughness can initially be achieved by refining the grain size.

2.2.1 Macro-Alloying Additions

Ferrite in HSLA steels is strengthened by grain refinement, precipitation hardening, and some solid solution strengthening. Alloying additions in HSLA steels assist in strengthening the ferrite by grain refinement, precipitation strengthening, and solid solution strengthening. Solid solution strengthening is related to alloying content whereas precipitation hardening and grain refinement is related to the interdependent relationship of the alloy design and the thermomechanical treatment. Alloying additions also lower the transformation temperatures from austenite to ferrite to produce finer microstructure to enhance strength. Some austenite stabilizers are given in the following in order of decreasing effectiveness: carbon, nitrogen, manganese, nickel, and copper. Higher carbon content decreases weldability and impact toughness, but at controlled amounts this deleterious effect can be minimized. In amounts greater than 1 wt. pct., manganese is the main strengthening element in HSLA steels [40]. As a mild solid solution strengthener in ferrite, manganese also decreases the transformation
temperature from austenite to ferrite. In high strength steels, manganese content greater than 1.6 to 1.8 wt. pct. degrades toughness [13]. Manganese also forms manganese sulfide inclusions.

Silicon is a deoxidizer in molten steel. It increases the strength of HSLA steels and is an effective solid solution strengthenener, Figure 2.1. Silicon oxides can form as weld metal inclusions thus decreasing hardness. Chromium is a relatively strong hardenability agent. Controlled amounts of chromium, copper, and phosphorous can enhance the corrosion resistance of steels. Nickel is also added into HSLA steels to enhance corrosion resistance to the atmosphere. It is also a mild solid solution strengthenener of ferrite and an austenite stabilizer which improves toughness in HSLA steels. Molybdenum is essential to increasing deformation resistance at elevated temperatures. Another carbide stabilizer also a carbide former, molybdenum is primarily added to HSLA steels to improve hardenability when transformation of microstructures other than ferrite-pearlite is required, i.e. acicular ferrite and bainite. In HSLA steels, molybdenum additions (0.15 to 0.30 wt. pct.) increase the solubility of niobium in austenite [40], which enhances the niobium carbide precipitates in ferrite. These precipitates also pin austenite grain boundaries thereby retarding grain growth. Nickel, chromium, and molybdenum are all effective substitutional hardeners [7]. Aluminum is added to control austenite grain growth and is also a deoxidizer. Aluminum has been shown to increase strength and decrease toughness in high strength steel weld metal.

It is generally accepted that nickel and manganese additions in controlled ratios in low carbon structural steels increase toughness. However, HSLA steel systems differ in composition, there is no clear picture as to the effect of nickel additions between two to five wt. pct., a range within which falls the specific HSLA steel system proposed for this research.

2.2.2 Second Phase Particles in Weld Metal

Second phase particles in HSLA steel submerged arc weld metal include sulfides, nitrides, carbides, carbonitrides, and oxides. These particles are complex in chemical and structural nature. They typically take the general form of MC, M_xC, M_xC_y, MN, M_xN, M_xN_y, and
Microalloying additions of vanadium, niobium, and titanium are all strong carbide, nitride, and carbonitride formers [19]. Chromium, molybdenum, iron, and zirconium also form carbide and nitrides. Silicon nitrides are sometimes formed. The origin of non-metallic inclusions can be divided into two groups: indigenous and exogenous. Indigenous inclusions form by precipitation as a result of homogeneous reactions in the steel and are mostly composed of oxides and sulfides. Exogenous inclusions are a result of slag and other contamination which contact the molten steel. Some features of exogenous inclusions are large in size, random in occurrence, irregular in shape, and complex in structure. The main mechanism for formation of non-metallic oxides inclusions is deoxidation [27]. Most exogenous inclusions are complex oxides of manganese, silicon, aluminum, and titanium along with manganese sulfides. In submerged arc welding with the basic Oerlikon OP121TT flux on steels with yield strength less than 690 MPa (100 ksi), twenty-one different inclusion types were identified and the nine major types are as following in highest to lowest occurrence [33, 34]: MnO-SiO₂-FeO-Al₂O₃-TiO₂, SiO₂-FeO-Al₂O₃, MnO-SiO₂-Al₂O₃-TiO₂, MnS-MnO-SiO₂-Al₂O₃-FeO-TiO₂, SiO₂-Al₂O₃, MnO-SiO₂-FeO-Al₂O₃, MnO-Al₂O₃-SiO₂, MnS-MnO-SiO₂-FeO-Al₂O₃, and MnS-MnO-FeO-Al₂O₃.
2.3 Fundamental Metallurgical Principles

In this section, a brief background on some fundamental theories needed for the understanding of the weld metal development sequence conveyed in this research will be presented.

2.3.1 Basic Solidification Concepts

As uniform liquid solidifies, solute atoms in the liquid are redistributed. This redistribution depends on both the thermodynamic and kinetic conditions. The partitioning coefficient of an element can be determined by Eq. 2.2 where $C_S$ and $C_L$ are the solid and liquid compositions determined from the initial composition of the alloy of interest, $C_O$. The value of $k$ depends on temperature but if the solidus and liquidus lines are assumed to be linear then $k$ can be assumed to be constant.

\[ k = \frac{C_S}{C_L} \]  

(2.2)

When $k$ is less than one, the content of alloy of the solid is less than the composition of the liquid thereby causing the solute to be rejected into the liquid. During solidification the solute content of the liquid continues to rise. The solute content of the solid also continues to rise during solidification since the solid grows from the higher solute liquid. Composition of a solidified alloy weld is not uniform. Concentrations of impurities and alloying elements are different in different parts of the weld. These differences are a result of different solubility of impurities in liquid and solid phases at the equilibrium temperature, thereby resulting in segregation.

During solidification, the S/L interface can be planar, cellular, columnar, and equiaxed dendritic depending on the processing condition and material involved. The thermodynamic aspect that quantifies constitutional supercooling is defined by the difference between the equilibrium liquidus temperature minus the actual liquidus temperature. As constitutional supercooling increases, the solidification mode transforms from planar to cellular, to columnar dendrite, and then equiaxed dendrite. At a high temperature gradient and low growth
rate, the solidification front will be planar. When growth rate increases and temperature gradient decreases, the planar solidification front breaks down. With perturbations in the planar solidification front, cellular mode which is characterized by elongated cells in a dense-packed pattern results. In a weldment, both elongated cells and honeycomb-like structures are termed cellular growth and a cross-sectioned specimen can contain both. In a planar front, the undercooling of the melt ahead of the interface is the driving force for solidification. The temperature distribution in the melt, which controls the solidification process and the stability of the interface is a function of position and distance from the interface. As undercooling increases with the distance from the interface, a temporary faster growth will occur at the interface forming a perturbation. The planar interface will now become unstable allowing the perturbation to grow until steady state is achieved. The concentration of solute around the base of the perturbation is higher than at the tip of the perturbation thus retarding solidification in the base minimizing the radial growth. The magnitude of the constitutional undercooling will dictate the structures with strong undercooling corresponding to honeycomb-like structures or hexagonal cells.

Solidification microstructure of alloys are affected by the temperature gradient, G, and the growth rate, R, as seen in Figure 2.2. A high G/R forms a planar solidification whereas a low G/R forms an equiaxed dendrite solidification microstructure. At higher cooling rates, the morphologies of solidification structure become finer since there is less solidification time. The slower the cooling rate during solidification, the coarser become the solidification structures since there is more time available for coarsening. Note that the morphology of solidification is determined by the ratio G/R while the size of the solidification structure is dictated by the product G*R [29].

During fusion welding, base-metal grains at the fusion line are the substrate for nucleation and epitaxial growth. While new grains can nucleate at random orientations, epitaxy occurs in the same crystallographic orientation of base-metal grains. For FCC and BCC crystal structures, the epitaxial growth continues in the <100> direction. In multiple pass welding,
this phenomenon can be observed at the fusion line of each new bead. As grain growth continues away from the fusion line, the mechanism known as competitive growth dominates in the bulk weld metal. In Figure 2.3, it can be seen that the solidifying grains will continue to grow in the preferred direction typically perpendicular to the weld pool (the melting temperature isotherm) and out-grow the less favorably oriented grains.

Figure 2.2: Effect of temperature gradient, G, and growth rate, R, on the dendrite morphology and size of solidification microstructures [29].

Figure 2.3: Epitaxial and competitive growth in the bulk weld metal fusion zone [29].

The nucleation of new grains during welding can occur via four different mechanisms: dendrite fragmentation, grain detachment, heterogeneous nucleation, and surface nucleation,
Figure 2.4. Dendrite fragmentation can occur due to weld pool convection where dendrite tips are broken off in the mushy zone along the back of the weld pool and carried into the bulk weld pool to act as nuclei for new grain formation. Grain detachments occur when partially melted grains detach from the S/L interface of the weld pool to act as new nuclei for new grain formation. Heterogeneous nucleation occurs when foreign particles in the weld pool provide substrate with favorable crystallography that can act as a nucleus. The last mechanism for nucleation of new grains during welding occurs at the weld pool surface that can be thermally undercooled to create nuclei. During welding these nucleation sites on the surface can grow new grains downward into the liquid metal in the weld pool [29].

Figure 2.4: Nucleation mechanisms during welding: (a) top view; (b) side view [29].

2.4 Austenite Decomposition in Steel Weld Metals

The main factors that influence microstructure of a steel weld are the following: weld chemical composition, austenite grain size, and cooling rate from 800°C to 500°C. The weld composition is determined from three contributing parts in submerged arc welding: submerged arc welding flux, filler metal wire, and base metal. The microstructure of steel weld metal is produced by weld metal solidification and subsequent austenite decompo-
sition. Products of austenite decomposition that can form include grain boundary ferrite (GBF), Widmanstätten ferrite (WF), acicular ferrite (AF), bainitic, martensite, and retained austenite (RA).

2.4.1 Ferrite Morphologies

During austenite-to-α-ferrite transformation, the austenite parent phase decomposes into the transformation products. These transformations continue until adjacent transformation products impinge neighboring transformations. By a nucleation and growth process, different morphologies of pro-eutectoid ferrite forms along austenite grain boundaries and interfaces. Using the Dubé classification, for a small undercooling, allotriomorphic ferrite forms along the austenite grain boundaries. During nucleation, the allotriomorphic ferrite crystals exhibit a preferred orientation relationship with one of the austenite grains which is usually of the Kurdjumov-Sachs (KS) type: \( \{111\}_\gamma // \{110\}_\alpha \) and \( <\overline{1}\overline{1}0>_{\gamma} // <\overline{1}\overline{1}1>_{\alpha} \). The KS relationship shows that the closed-packed planes and directions of austenite and ferrite are parallel to each other. Sometimes, ferrite orientation relationship may alter and not have close-packed parallel directions such as the one given by the Nishiyama-Wasserman (NW) type: \( \{111\}_\gamma // \{110\}_\alpha \text{ and } <101>_{\gamma} // <001>_{\alpha} \). The ferrite can grow into the adjacent austenite grain with no specific orientation. A grain boundary allotriomorph, grain boundary ferrite, or equiaxed ferrite is described as a crystal that is nucleated on and grows along the parent phase grain boundary, Figure 2.5(top). Allotriomorphic ferrite is often described as blocky ferrite nucleating on high angle boundaries. Grain boundary ferrite is not desirable for weld metal toughness because it provides a continuous crack path along the parent phase boundary through the ferrite [45].

Idiomorphic ferrite (ID) can also form within the austenite grains. For larger undercooling, the pro-eutectoid ferrite that forms from the austenite grain boundaries is WF. Needle-like or plate-like ferrite is termed WF or Widmanstätten sideplates that grow near the \( \{111\}_\gamma \) octahedral planes on a habit plane [10][45], Figure 2.5 (bottom-left and bottom-right). These side plates can be characterized by their aspect ratio ranging from 10:1 to as
high as 20:1 [62]. Through a displacive transformation mechanism, WF growth occurs by a para equilibrium (PE) mode. Paraequilibrium transformation is when the substitutional alloying elements cannot partition while carbon, the fast diffusing interstitial element, redistributes between phases until uniform chemical potential is reached. The growth rate is carbon diffusion controlled in the austenite ahead of the WF plate formation. Widmanstätten ferrite is also characterized by the K-S orientation relationship given above and grows with a habit plane close to \{111\}_γ.

Figure 2.5: Schematic diagram of grain boundary ferrite and Widmanstätten ferrite [1]. Reprinted from Krauss, 2005.

At high cooling rates, HSLA steel welds can form acicular ferrite. Figure 2.6 shows a continuous–cooling-transformation (CCT) diagram for HSLA 80 steel plate where the amount of AF decreases with decreasing cooling rates along with increasing microhardness.

The transformation temperature of acicular ferrite is close to that of Widmanstätten ferrite but the morphology differs. Acicular ferrite in HSLA steel welds are described as short, non-parallel arrays of ferrite laths that are arranged in an interlocking pattern, basket weave with a large number of laths growing close to each other and therefore impinging upon one another. The laths are typically 1 to 2 micron thick with an aspect ratio ranging from 4:1 to 10:1 [62]. Ferrite laths are shown to have high dislocation densities separated by high angle grain boundaries. The fine intragranular acicular ferrite morphology found in low-carbon steel welds are known to improve notch toughness, Figure 2.7.
Figure 2.6: Continuous-cooling transformation diagram for HSLA 80 plate steel [54]. Reprinted from Krauss, 2005.

Figure 2.7: Acicular ferrite in low-carbon weld metal. Nital etch, light micrograph at 500x. Courtesy of S. Liu, Colorado School of Mines. Reprinted from Krauss, 2005.
Acicular ferrite has been shown to nucleate on oxide particles in weld metal [34, 63]. Figure 2.8 shows a schematic of different ferrite morphologies that develop during the solidification of steel weld metal including acicular ferrite nucleation from intergranular and intragranular inclusions. Larger volume fraction of acicular ferrite increases strength and toughness due to the interlocking nature of the laths [62]. Thus, acicular ferrite is desirable ferrite morphology in HSLA steel submerged arc welding specifically to enhance lower shelf notch toughness.

![Figure 2.8: Schematic diagram of intragranular acicular ferrite (IAF), polygonal or primary ferrite (PF), bainitic ferrite (BF) or Widmanstätten ferrite (WF), and inclusions as nucleation sites in weld metal [31]. Reprinted from Krauss, 2005.](image)

It is well documented that the formation of acicular ferrite is associated with the distribution of non-metallic inclusions in steel weld metal since they provide preferential sites for nucleation. The efficiency of a nucleation site is related to the lattice disregistry between nucleating phase and the inclusion [42]. Research suggests that low mismatch between the inclusion and ferrite will promote acicular ferrite formation since the inclusions with the best lattice matching with acicular ferrite should be most effective in its nucleation [39]. This observation suggests that the specific phases with their respective lattice parameters within inclusions are responsible for nucleating acicular ferrite. Inclusions with galaxite (Al$_2$O$_3$·MnO), a spinel in face-centered cubic (FCC) structure with a lattice parameter of
0.82 nm, and TiO in a FCC structure with a lattice parameter of 0.42 nm seem to promote nucleation of acicular ferrite [36]. Sulfides have been debated as nucleation sites. Some researchers have dismissed MnS, but some think that sulfides play a critical role in acicular ferrite formation.

It has also been suggested that stress/strain fields around inclusions from differences in the thermal expansion coefficients between the inclusion and the matrix can promote nucleation of acicular ferrite at inclusion sites [11]. This suggestion of the difference between the coefficients of thermal expansion was contradicted by research that calculated resultant strain energy and found it minor relative to the transformation energy required for nucleation [9]. Being heterogeneous nucleation always more favorable than homogeneous nucleation, intragranular nucleation sites are always more favorable in developing acicular ferrite [34]. Other factors that affect the formation of acicular ferrite are the quantity and size distribution of the non-metallic inclusions.

In weld metal of low alloy steel, the average nucleus size is around 0.5 micron. Non-metallic inclusions with a distribution between the ranges of 0.4 to 0.9 micron are better nucleation sites for acicular ferrite. Inclusions with a bell curve size distribution from 0.1 to 0.5 micron are poor nucleation sites for acicular ferrite [32]. Studies have also shown that with weld metal oxygen content between 200 to 350 ppm with inclusion size ranging between 0.3 to 0.9 micron, acicular ferrite nucleation is favorable. At lower weld metal oxygen content (15-30 ppm), the inclusion sizes decrease to 0.35 to 0.75 micron: acicular ferrite nucleation is still shown to be favorable [66]. Even though refined acicular ferrite is used widely in industry to enhance toughness in steel weld metal, a clear understanding of the mechanism of acicular ferrite nucleation is not complete.

2.4.2 Bainite

Bainitic microstructure is composed of various phases, typically a mixture of ferrite and cementite morphologies. There are two distinct ferrite-cementite morphologies identified as upper bainite and lower bainite. In upper bainite, cementite forms between ferrite laths at
temperatures below 500°C. In lower bainite, cementite forms within ferrite laths at temperatures below 300°C. Aaronson et al. identified six morphologies of bainite, Figure 2.9 [1].

![Figure 2.9: Schematic drawings of the six morphologies of bainite according to Aaronson et al.: (a) nodular bainite, (b) columnar bainite, (c) upper bainite, (d) lower bainite, (e) grain boundary allotriomorphic bainite, and (f) inverse bainite [1]. Reprinted from Krauss, 2005.](image)

It is believed that the bainite transformation is more displacive in nature where a ferrite forms from austenite with complete supersaturation of carbon through displacive transformation. Note that the ferrite in bainite is termed bainitic ferrite. Carbon diffusion to austenite occurs through a post-transformation event. The overall transformation kinetics originates from the bainitic ferrite and should show surface relief, no substitutional partitioning, an incomplete reaction phenomenon because of subsequent carbon diffusion, and a KS and NW orientation relationship.

The bainite structure is transformed as aggregates of ferrite plates separated by thin films of austenite, martensite, or cementite. These aggregates of plates are called sheaves or subunits. The platelets within the sheaves tend to adopt a consistent orientation relationship. As each sheaf grows, new subunits will nucleate near the tips of the existing sheaf.
where austenite is unstable and carbon concentration is low. The incomplete transformation is described by two different mechanisms: composition-invariant growth and solute drag. For the composition-invariant growth using the displacive transformation model, initially bainitic ferrite and the parent austenite begin with the same composition and the carbon then partitions to austenite or forms carbides. Thus, the formation of bainitic ferrite is possible when a certain region of austenite has a lower carbon content than initial composition. Once the initial compositional temperature is reached again, bainitic ferrite growth stops. This process gives an incomplete reaction since ideally the reaction should continue to metastable equilibrium, $A_{c3}$. Using a diffusional model, bainite transformation is incomplete due to alloying elements at the transformation interface reducing mobility and creating an energy barrier requiring additional driving force to overcome the solute drag effect [10].

For this research, a combination of bainite morphologies will be considered: lower bainite (LB), upper bainite (UB), granular bainite (GB), and coalesced bainite (CB). Lower bainite has fine needle-like features at lower transformation temperatures. The carbides form in a single habit plane oriented approximately 55-60° to the $\gamma - \alpha$ habit plane. A high dislocation density should exist for LB. Upper bainite has a coarser needle-like structure at higher transformation temperatures and forms cementite as the carbide. For cementite, the orientation relationship in LB is $\{001\}_\theta$/$\langle211\rangle_\alpha$, $\langle110\rangle_\theta$/$\langle0\overline{1}1\rangle_\alpha$, and $\langle010\rangle_\theta$/$\langle1\overline{1}1\rangle_\alpha$. For GB, its ferrite laths are acicular in nature and possess martensite-austenite (M-A) constituents and retained austenite (RA) along with martensite [10]. Coalesced bainite are bainitic ferrite grains that have coalesced together with small carbides dispersed within the coarser bainitic ferrite grains [23, 24].

### 2.4.3 Martensite

Martensite is a diffusionless transformation from austenite due to a shear mechanism. The fast cooling rate does not allow for diffusion of carbon atoms but instead traps the carbon atoms within octahedral sites of a body-centered cubic (BCC) structure producing the martensitic phase. Due to the arrangement of carbon atoms in BCC, martensite takes on
a body-centered tetragonal (BCT) structure which is a distorted BCC structure where the c/a ratio is greater. There are two major morphologies in martensite, plate and lath. Plate martensite can be identified by its random arrangement of martensite plates and is limited in ductility and more crack-susceptible. Lath martensite occurs in low and medium carbon steels whereas plate martensite is formed in high carbon steels. In HSLA steel weld metal, only lath martensite will develop because of the lower carbon content. Lath martensite is transformed in large numbers whereby the individual laths are separated by low angle boundaries allowing them to align themselves parallel to each other known as packets [30].

The martensite transformation involves a shear parallel to the habit plane (interface between austenite and martensite phase) with expansion normal to the habit planes. Invariant plane strain (IPS) surface relief or tilt occurs due to the volume and shape change. The habit plane for low carbon (0-0.4 pct.) for steels is \(\{111\}_\gamma\) with orientation relationships as \(\{111\}_\gamma/\langle011\rangle_{\alpha'}, <10\bar{1}>\gamma/\langle1\bar{1}1\rangle_{\alpha'}\) [45]. The martensite transformation kinetics is nucleation-controlled rather than growth controlled with the internal structure either high in dislocation density (lath) or large amount of twins (plate).

### 2.5 Effect of Nickel

The literature review presented below demonstrates that past research has examined the effects of nickel on mechanical properties through microstructural characterization and mechanical testing without providing any clear explanation as to the mechanisms that dictate the formation of these microstructural constituents.

Research studies on HSLA steel systems with nickel contents between one to three wt. pct. has been conducted quite extensively for quantitative microstructural characterization and mechanical testing. For as-welded conditions, Evans and Bailey concluded that at one wt. pct. manganese, increasing nickel content increased the amount of acicular ferrite. Yield strengths for one wt. pct. manganese and increasing nickel amounts of 1, 2.25, and 3.5 wt. pct. were approximately 450, 460, and 475 MPa, respectively. Ultimate tensile strength for those same alloys gave values of approximately 525, 550, and 575 MPa, respectively.
Correspondingly, the ductile-brittle transition temperatures for 100 J (73.6 ft-lbs) for these alloys were approximately -60, -65 and -50°C, respectively. At 1.8 wt. pct. manganese, increasing nickel content up to 2.25 wt. pct. increased acicular ferrite. Above 2.25 wt. pct. nickel, martensite began to form and ferrite with second phase increased at the cost of acicular ferrite, which also reduced the impact toughness of the weld.

Yield strengths for alloys that contained 1.8 wt. pct. manganese and increasing nickel amounts of 1, 2.25, and 3.5 wt. pct. were approximately 550, 600, and 650 MPa, respectively. Ultimate tensile strengths for those alloys gave values of approximately 630, 675, and 725 MPa, respectively. Charpy v-notch temperatures for 100 J (73.6 ft-lbs) for 1.8 wt. pct. manganese alloys were approximately -40, -10, and 20°C, respectively. An increase in nickel generally increased the amount of acicular ferrite at the expense of both primary ferrite and ferrite with second phase. With the high manganese level of 1.8 wt. pct. and nickel above 2.2 wt. pct., the formation of martensite and increasing amounts of ferrite with second phase occurred at the expense of acicular ferrite and primary ferrite. The aspect ratios of acicular ferrite were increased with the addition of nickel and grain boundary carbides precipitated after stress relief. At low manganese content of 0.65 wt. pct., toughness improved as nickel additions increased. At high manganese content of 1.8 wt. pct., toughness decreased as nickel content increased above 0.5 wt. pct. Toughness was improved with low manganese content with nickel additions up to 3.5 wt. pct. For similar nickel content, Evans and Bailey also found the welds with 1 wt. pct. manganese have acceptable toughness [15].

Wang and Liu [60] demonstrated that increasing nickel content increased the amount of acicular ferrite and decreased grain boundary ferrite. Martensite formed at high nickel contents. Nickel additions initially decreased prior austenite grain size but additional nickel rapidly coarsened grain size. The best weld toughness had a composition of 1.6 wt. pct. manganese and 1 wt. pct. nickel or 0.7 wt. pct. manganese and 2.5 to 3.5 wt. pct. nickel. Welds with higher nickel contents (2.5 wt. pct. for 1.6 pct. manganese and 5.5 wt. pct. for 0.7 to 0.3 wt. pct. manganese) exhibited poor toughness from an increased presence of
For nickel contents of 3.14, 7.23, and 9.23 wt. pct. with a constant two wt. pct. manganese, Keehan et al. [23, 24, 26] have done extensive characterization and testing to examine the detrimental effect of the formation of coalesced bainite on mechanical properties. At two wt. pct. manganese and 3.14 wt. pct. nickel, the microstructure solidified predominately as $\delta$-ferrite which allowed less segregation and the microstructure was more homogenous with an absence of coalesced bainite. The microstructure of 7.23 and 9.23 wt. pct. nickel at two wt. pct. manganese was not much different from each other. The overall microstructure was very fine with a mixture of bainite, martensite, and films of retained austenite.

These welds solidified as austenite which resulted in significant segregation of manganese and nickel to interdendritic regions and promoting coalesced and upper bainite in the dendrite core regions with martensite at interdendritic regions. The reheated regions were a mixture of tempered bainite and martensite. Yield strength for the varying amounts of nickel of 3.14, 7.23, and 9.23 wt. pct. were determined as 756, 795, and 848 MPa, respectively. Ultimate tensile strength for those same compositions were determined as 945, 1006, and 1051 MPa, respectively. The impact toughness as a function of temperature was given for those same compositions as 50, 31, and 11 J at -40°C and 80, 38, and 17 J at 22°C, respectively. The optimal microstructure presented by Keehan et al. showed that a predominant mixture of upper and lower bainite with some martensite and no coalesced bainite gave the best combination of strength and toughness [22, 25].

Keehan et al. [22] demonstrated that in high manganese welds, high resolution microscopy showed that dendritic core regions consisted of a mixture of mostly upper bainite and some coalesced bainite. Interdendritic regions displayed mostly martensite. Additions of carbon content encouraged martensite formation and reductions of manganese promoted upper bainite in the microstructure. The mechanical properties and the neural networking predictions were often parallel. High manganese and high nickel improved strength but negatively impacted toughness while a decrease in manganese increased impact toughness greatly.
Mechanical properties can be related to the relative amounts of the different microstructural constituents. Martensite provided high strength and tolerable toughness, whereas upper and lower bainite gave both good toughness and strength. The combination of coalesced bainite and martensite gave the least desirable properties. $A_{c1}$ was lowered by the increasing contents of manganese and nickel which does not allow for tempering in the reheat regions and contributed to undesirable microstructural changes that lead to poorer impact toughness. The optimal strength and impact toughness possessed a fine mixture of upper and lower bainite with some martensite at the combined 0.5 wt. pct. manganese, 7 wt. pct. nickel, and intermediate carbon level which also gave a higher $A_{c1}$ for more tempering of reheated regions [22].

Additional research from Keehan et al. [23, 24, 26] showed that using both shielded metal-arc welding and submerged arc welding processes, a constant 7 wt. pct. nickel content with varying manganese content from 2 to 0.5 wt. pct. improved toughness which is explained by an increase in the amount of upper and lower bainite instead of coalesced bainite. At this high level of nickel, decreasing amount of manganese decreased the presence of coalesced bainite. From a microstructural standpoint, a higher proportion of upper and lower bainite provided good strength and great toughness whereas coalesced bainite was determined as a negative contribution to toughness. In addition, good strength and toughness can also be found in a martensite microstructure with coalesced bainite dispersed homogeneously throughout [23, 24, 26].

Research from Keehan et al. also used neural networking models that have predicted a loss in toughness with nickel additions for manganese content greater than 1.5 wt. pct and a gain in toughness for nickel additions for manganese content below 1.5 wt. pct. Increasing nickel additions at two wt. pct. manganese increased strength by solid solution hardening and increased amounts of martensite due to nickel and manganese segregation to interdendritic regions. For higher manganese content welds described above, the toughness decrease was attributed to the formation of coarse grained coalesced bainite [23, 24, 26].
Muruganath et al. [37] also used mathematical models to demonstrate improvement in toughness and strength using nickel as the primary alloying addition to ferritic weld metals. When manganese content is high, nickel is detrimental to toughness. However, when nickel is added to low manganese content impact toughness is increased. These findings through neural network modeling were confirmed with shielded metal-arc welding low-manganese and high-nickel consumables in physical experiments. It is still not understood why there are opposing effects of nickel with varying manganese content [37].

Bhole et al. [5] performed a literature review stating the confusion of the effects of nickel in HSLA steels. It is known that nickel and molybdenum play pivotal roles in microstructural control with no optimal nickel content established. Molybdenum additions in the range of 0.817-0.881 wt. pct. increased the impact toughness and decreased the fracture appearance transition temperature (FATT). An increase in acicular ferrite and granular bainite was also observed. Combined nickel (2.03-2.91 wt. pct.) and molybdenum (0.7-0.995 wt. pct.) in the weld metal increased acicular ferrite and toughness. Increasing only nickel resulted in lower weld metal toughness and higher FATT. A decrease in acicular ferrite and increase in ferrite with second phase aligned were observed [5].

Kim et al. [28] showed that there are two main ways to enhance mechanical properties: grain refinement and the control of alloying elements. For Steel A (0.193 C, 1.350 Mn, 0.482 Mo, 0.922 Ni), coarse cementite particles precipitated along the lath boundaries with a small number of fine M$_2$C carbides distributed within the laths. In Steels B (0.099 C, 0.701 Mn, 0.962 Mo, 2.500 Ni) and C (0.060 C, 1.550 Mn, 1.000 Mo, 1.460 Ni) where carbon content was reduced dramatically and molybdenum and nickel content were increased, the number of fine M$_2$C carbides was increased and the number of coarse cementite particles decreased. In Steels B and C, M-A constituents were formed but decomposed to carbides and ferrite after tempering. The tensile and fracture properties of B and C steels were better than those of Steel A [28].
CHAPTER 3
EXPERIMENTAL PROCEDURES

This section presents the details of the material compositions, welding fabrication process, post-weld heat treatment, sample extraction, mechanical testing methods, and analytical techniques employed during the characterization of the multipass weld mockups. All bulk chemical compositions presented below were analyzed using optimal emission spectroscopy (OES).

3.1 Preliminary Research Experimental Procedures

A detailed description of the experimental procedures performed in the first year of this research program to develop the direction of the thesis is presented in this section. The experimental procedure started with the welding and sample preparation performed by Knolls Atomic Power Laboratory along with the chemical compositions of the submerged arc welding fluxes, filler metal wires, base metal, and weld compositions. The metallographic procedure for both the macrophotographs and microphotographs are both presented. Next, the technique for the identification and development of the microstructural key using LOM is discussed.

3.1.1 Welding and Sample Preparation

A total of nine alloys/welds were studied. Table 3.1 gives the nine alloys/welds that were studied for the first year of this research program.

The multiple weld mockups for each of these alloys/welds were produced by Knolls Atomic Power Laboratory. An example of one of these multiple pass weld mockups is shown in Figure 3.1 and Figure 3.2. Table 3.2 gives a summary of the documented welding parameters for the multiple pass weld mockups. Note that only five alloys/welds are presented in Table 3.2 because the as-welded and stress-relieved were all fabricated with the same welding
### Table 3.1: Alloys/welds studied during the first year of this research program.

<table>
<thead>
<tr>
<th>Filler Metal Alloy</th>
<th>Flux</th>
<th>Welding Process</th>
<th>As-welded or Stress-relieved</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-105S</td>
<td>Oerlikon</td>
<td>GTAW</td>
<td>as-welded</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAW</td>
<td>as-welded</td>
</tr>
<tr>
<td>W11/W12</td>
<td>Oerlikon</td>
<td>SAW</td>
<td>stress-relieved</td>
</tr>
<tr>
<td>W13/W14</td>
<td>Oerlikon</td>
<td>SAW</td>
<td>stress-relieved</td>
</tr>
<tr>
<td>W13/W14</td>
<td>ESAB</td>
<td>SAW</td>
<td>as-welded</td>
</tr>
<tr>
<td>W11/W12</td>
<td>ESAB</td>
<td>SAW</td>
<td>as-welded</td>
</tr>
</tbody>
</table>

parameters. Post-weld heat-treatment consisted the difference between the as-welded and stress-relieved. With the exception of the as-welded and stress-relieved weld samples of W11/W12 and W13/W14, actual multiple pass weld mockups were provided for the initial study of the research program. As-welded and stress-relieved samples of W11/W12 and W13/W14 were provided in tested Charpy V-Notch samples.

#### 3.1.2 Chemical Compositions for Filler Metal Wires, Base Metal (Comp F), and Weld Metal

The chemical compositions of the filler metal wires MIL-105S, W11/W12, and W13/W14, the base metal known as Comp F, and the weld compositions for all the multiple pass welds are presented. Table 3.3, Table 3.4, Table 3.5, Table 3.6, and Table 3.7 give the chemical compositions related to each of the nine alloys/welds studied during the initial portion of the research program.

The chemical compositions for the submerged arc welding fluxes used are reported in Table 3.8 (Oerlikon OP121TT) and Table 3.9 (ESAB OK 10.62).

#### 3.1.3 Metallographic Procedures for Macrophotographs

A series of manual grinding steps using a hand wall sander and an automatic hand sander were utilized to grind up to 600 grit for macrophotographs. These sanders were used because of the very large surface of the weld mockups that needed to be prepared for examination.
Table 3.2: Welding parameters for the nine alloys/welds studied during first year of this research program.

<table>
<thead>
<tr>
<th>Alloys/Welds</th>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>Heat Input (kJ/in)</th>
<th>Travel Speed (ipm)</th>
<th>Wire Feed Rate (ipm)</th>
<th>Root Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTAW</td>
<td>330</td>
<td>13</td>
<td></td>
<td>6.5</td>
<td>150</td>
<td>4°±1°</td>
</tr>
<tr>
<td>SAW Oerlikon</td>
<td>420</td>
<td>30</td>
<td>≤55</td>
<td>16</td>
<td>110</td>
<td>8°±1°</td>
</tr>
<tr>
<td>SAW ESAB</td>
<td>420</td>
<td>31</td>
<td></td>
<td>16</td>
<td>117</td>
<td>14°±1°</td>
</tr>
<tr>
<td>W11/W12</td>
<td>420</td>
<td>32</td>
<td></td>
<td>16</td>
<td>110</td>
<td>8°±1°</td>
</tr>
<tr>
<td>W13/W14</td>
<td>420</td>
<td>32</td>
<td></td>
<td>16</td>
<td>110</td>
<td>8°±1°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloys/Welds</th>
<th>Preheat (°F)</th>
<th>Interpass (°F)</th>
<th>Electrode Diameter (in)</th>
<th>Electrode Extension (in)</th>
<th>Base Metal Thickness (in)</th>
<th>Root Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTAW</td>
<td>200</td>
<td>350</td>
<td>0.15625</td>
<td>0.625</td>
<td>3</td>
<td>N/A</td>
</tr>
<tr>
<td>SAW Oerlikon</td>
<td>200</td>
<td>350</td>
<td>0.09375</td>
<td>1.125</td>
<td>4</td>
<td>5/1 ± 1/16</td>
</tr>
<tr>
<td>SAW ESAB</td>
<td>200</td>
<td>350</td>
<td>0.09375</td>
<td>1.125</td>
<td>4</td>
<td>5/1 ± 1/16</td>
</tr>
<tr>
<td>W11/W12</td>
<td>200</td>
<td>350</td>
<td>0.09375</td>
<td>1.125</td>
<td>4</td>
<td>5/1 ± 1/16</td>
</tr>
<tr>
<td>W13/W14</td>
<td>200</td>
<td>350</td>
<td>0.09375</td>
<td>1.125</td>
<td>4</td>
<td>5/1 ± 1/16</td>
</tr>
</tbody>
</table>

Table 3.3: Gas-tungsten arc welding using MIL-105S filler metal wire in the as-welded condition

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cr</th>
<th>C</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Sn</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-105S</td>
<td>Bal.</td>
<td>0.91</td>
<td>0.51</td>
<td>1.6</td>
<td>0.09</td>
<td>0.13</td>
<td>&lt;0.002</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.21</td>
<td>0.002</td>
<td>0.008</td>
<td>&lt;0.002</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Comp F</td>
<td>Bal.</td>
<td>3.05</td>
<td>0.51</td>
<td>0.34</td>
<td>1.62</td>
<td>0.17</td>
<td>0.002</td>
<td>0.023</td>
<td>0.009</td>
<td>0.28</td>
<td>0.007</td>
<td>0.006</td>
<td>0.0042</td>
<td>0.0027</td>
<td>0.0097</td>
</tr>
<tr>
<td>Weld Metal</td>
<td>Bal.</td>
<td>1.16</td>
<td>0.52</td>
<td>1.28</td>
<td>0.32</td>
<td>0.1</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.18</td>
<td>0.008</td>
<td>0.008</td>
<td>&lt;0.01</td>
<td>0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table 3.4: Submerged arc welding using MIL-105S filler metal wire and Oerlikon flux in the as-welded/stress-relieved conditions

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cr</th>
<th>C</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Sn</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-105S</td>
<td>Bal.</td>
<td>0.91</td>
<td>0.51</td>
<td>1.6</td>
<td>0.09</td>
<td>0.13</td>
<td>&lt;0.002</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.21</td>
<td>0.002</td>
<td>0.008</td>
<td>&lt;0.002</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Comp F</td>
<td>Bal.</td>
<td>3.05</td>
<td>0.51</td>
<td>0.34</td>
<td>1.62</td>
<td>0.17</td>
<td>0.002</td>
<td>0.023</td>
<td>0.009</td>
<td>0.28</td>
<td>0.007</td>
<td>0.006</td>
<td>0.0042</td>
<td>0.0027</td>
<td>0.0097</td>
</tr>
<tr>
<td>Weld Metal</td>
<td>Bal.</td>
<td>0.92</td>
<td>0.54</td>
<td>1.26</td>
<td>0.12</td>
<td>0.11</td>
<td>&lt;0.018</td>
<td>0.012</td>
<td>0.012</td>
<td>0.16</td>
<td>0.008</td>
<td>0.003</td>
<td>0.004</td>
<td>0.021</td>
<td>0.008</td>
</tr>
</tbody>
</table>
Figure 3.1: Halved, angled aerial view of the submerged arc multiple pass weld mockup with ESAB flux (~18 cm (~7 inches) in width and length ~10 cm (~4 inches) in length).

Table 3.5: Submerged arc welding using MIL-105S filler metal wire and ESAB flux in the as-welded/stress-relieved conditions

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cr</th>
<th>C</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Sn</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-105S</td>
<td>Bal.</td>
<td>0.91</td>
<td>0.51</td>
<td>1.6</td>
<td>0.09</td>
<td>0.13</td>
<td>&lt;0.002</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.21</td>
<td>0.002</td>
<td>0.008</td>
<td>&lt;0.002</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Comp F</td>
<td>Bal.</td>
<td>3.05</td>
<td>0.51</td>
<td>0.34</td>
<td>1.62</td>
<td>0.17</td>
<td>0.002</td>
<td>0.023</td>
<td>0.009</td>
<td>0.28</td>
<td>0.007</td>
<td>0.006</td>
<td>0.042</td>
<td>0.0027</td>
<td>0.0097</td>
</tr>
<tr>
<td>Weld Metal</td>
<td>Bal.</td>
<td>0.96</td>
<td>0.51</td>
<td>1.52</td>
<td>0.12</td>
<td>0.11</td>
<td>0.005</td>
<td>0.011</td>
<td>0.006</td>
<td>0.18</td>
<td>0.002</td>
<td>0.011</td>
<td>&lt;0.001</td>
<td>0.025</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

Table 3.6: Submerged arc welding using W11/W12 filler metal wire and Oerlikon flux in the as-welded/stress-relieved conditions

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cr</th>
<th>C</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Sn</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-105S</td>
<td>Bal.</td>
<td>0.96</td>
<td>0.55</td>
<td>1.5</td>
<td>0.07</td>
<td>0.0103</td>
<td>0.022</td>
<td>0.002</td>
<td>-</td>
<td>0.154</td>
<td>0.003</td>
<td>0.008</td>
<td>-</td>
<td>0.0009</td>
<td>0.002</td>
</tr>
<tr>
<td>Comp F</td>
<td>Bal.</td>
<td>3.05</td>
<td>0.51</td>
<td>0.34</td>
<td>1.62</td>
<td>0.17</td>
<td>0.002</td>
<td>0.023</td>
<td>0.009</td>
<td>0.28</td>
<td>0.007</td>
<td>0.006</td>
<td>0.0042</td>
<td>0.0027</td>
<td>0.0097</td>
</tr>
<tr>
<td>Weld Metal</td>
<td>Bal.</td>
<td>1.01</td>
<td>0.57</td>
<td>1.31</td>
<td>0.1</td>
<td>0.01</td>
<td>0.009</td>
<td>0.012</td>
<td>0.003</td>
<td>0.21</td>
<td>0.0032</td>
<td>0.012</td>
<td>&lt;0.001</td>
<td>0.019</td>
<td>0.0014</td>
</tr>
</tbody>
</table>
Figure 3.2: Cross sectioned view of the submerged arc multiple pass weld mockup with ESAB flux (~10 cm [~4 inches] in depth).

Table 3.7: Submerged arc welding using W13/W14 filler metal wire and Oerlikon flux in the as-welded/stress-relieved conditions

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cr</th>
<th>C</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Sn</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-1058</td>
<td>Bal.</td>
<td>3.78</td>
<td>1.39</td>
<td>0.1</td>
<td>0.093</td>
<td>0.043</td>
<td>0.028</td>
<td>0.002</td>
<td>0.046</td>
<td>0.003</td>
<td>0.012</td>
<td>-</td>
<td>0.0005</td>
<td>0.0036</td>
<td></td>
</tr>
<tr>
<td>Comp F</td>
<td>Bal.</td>
<td>3.05</td>
<td>0.51</td>
<td>0.34</td>
<td>1.62</td>
<td>0.17</td>
<td>0.002</td>
<td>0.023</td>
<td>0.009</td>
<td>0.28</td>
<td>0.007</td>
<td>0.006</td>
<td>0.0042</td>
<td>0.0027</td>
<td>0.0097</td>
</tr>
<tr>
<td>Weld Metal</td>
<td>Bal.</td>
<td>3.73</td>
<td>1.45</td>
<td>0.15</td>
<td>0.11</td>
<td>0.02</td>
<td>0.006</td>
<td>0.0074</td>
<td>0.008</td>
<td>0.05</td>
<td>0.0025</td>
<td>0.014</td>
<td>&lt;0.001</td>
<td>0.038</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Table 3.8: Flux composition of Oerlikon OP121TT (in wt. pct.)

<table>
<thead>
<tr>
<th>MnO</th>
<th>TiO₂</th>
<th>CaO</th>
<th>CaF₂</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>1.00</td>
<td>7.10</td>
<td>25.2</td>
<td>1.04</td>
<td>13.7</td>
<td>18.0</td>
<td>30.3</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 3.9: Flux composition of ESAB OK 10.62 (in wt. pct.)

<table>
<thead>
<tr>
<th>SiO₂+TiO₂</th>
<th>Al₂O₃+MnO</th>
<th>CaO+MgO</th>
<th>Fluorides</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>20</td>
<td>35</td>
<td>25</td>
</tr>
</tbody>
</table>
Using the hand wall sander, the coarser grits of 60, 120, and 240 grits were performed with water. For 320, 400, and 600 grit, the automatic hard sander and physical manual sanding was performed with water to achieve a smooth surface for macrophotographs. A macro-etch of 1 part of nitric acid to 7 parts of water was swabbed and then immediately rinsed off with water to reveal the macrostructure of the multiple pass welds.

### 3.1.4 Metallographic Procedures for Microphotographs

After cutting and mounting the samples of interest, a series of manual grinding was performed for 240, 320, 400, 600, and 800 grit with water with a decreasing pressure from medium to light. The polishing process followed the sequence of 3 micron premium diamond slurry polish on an ultra silk pad with microid extender at medium pressure for two minutes at a wheel speed of 200 rpm, then a 1 micron premium diamond slurry polish on a red felt pad with microid extender at light pressure for 30 seconds at a wheel speed of 200 rpm. Lastly, a final polish using 0.05 micron colloidal silica on a light blue imperial cloth at light pressure for 30 seconds at a wheel speed of 150 rpm was performed. For all the polishing steps, a second round of each step can be performed strictly adhering to the time interval given as the maximum time allowed each round. An etchant of two pct. Nital (98 pct. ethyl alcohol and two pct. nitric acid) was used with immersion for five to seven seconds.

### 3.1.5 Identification and Development of Microstructural Key – Light Optical Microscopy

For weld microstructural characterization, it is of utmost importance to have consistent recognition and identification of a phase. For this purpose, the IIW classification system [63] has been adopted (with two modifications related to the FS phase), in which the major weld constituents are described as follows and illustrated in Figure 3.3:

1) Primary Ferrite (PF) – This phase can exist in two forms, grain boundary ferrite (PF(G)) and intragranular polygonal ferrite (PF(I)). Grain boundary ferrite is the ferrite veins or polygonal grains associated with prior austenite grain boundaries. Intragranular
polygonal ferrite are ferrite grains, typically polygonal and found within prior austenite grains, that are larger than three times the average lath width of surrounding acicular ferrite or ferrite with second phase laths.

2) Acicular Ferrite (AF) – Acicular ferrite are small non-aligned and randomly oriented ferrite laths found within prior austenite grains. Typical regions of AF will exhibit laths with a medium aspect ratio (length/width ratios between 3 and 10).

3) Ferrite with Second Phase (FS) – This microstructural constituent is divided into two forms, ferrite with aligned second phase (FS(A)) and ferrite with non-aligned second phase (FS(NA)). Aligned second phase consists of two or more parallel laths of ferrite and their aspect ratio is generally greater than 10:1 (The IIW document specified a ratio of 4:1). Fine FS(A) will be separated from coarse FS(A) during characterization. Non-aligned second phase consists of blocks of ferrite with unclear orientation. Boundaries between laths are often missing.

4) Ferrite carbide aggregate (FCA) – These constituents are described as fine ferrite/carbide structures, including ferrite with interphase carbides and pearlite. Often this constituent is not resolvable under a light optical microscope and appears as a dark patch dispersed in the microstructure.

5) Martensite (M) – In low carbon steel welds, martensite generally exists in the form of packets that contain ferrite laths oriented in a triangular geometry. The three orientations of the laths reflect the three major habit planes of martensite.

3.1.6 Procedure for Quantitative Microstructural Analysis – Light Optical Microscopy

A series of consecutively spaced micrographs were taken from representative regions from each of the weld sets. Every third micrograph from each series taken at 200X were used for quantitative microstructure analysis. Seventeen micrographs from each of the weld sets were analyzed. A 100 point square test grid was used and superimposed over the micrographs. Manual point counting according to ASTM E 562-08 [50] was conducted to determine volume
Figure 3.3: Schematic representations of microstructural constituents: a) Imaginary boundary joining ends of second phases (indicated by dotted line); bi) Ferrite under crosswire $\leq 3x$ average lath width; bii) Ferrite under crosswire $\geq 3x$ average lath width; ci) Two or more parallel laths and aspect ratio $\geq 10:1$; cii) Two parallel laths with aspect ratio $\leq 10:1$ or non-aligned laths or isolated high aspect ratio laths; di) Area of FC colony under crosswire less than individual ferrite lath area; dii) Area of FC colony under crosswire greater than individual ferrite lath area; Note: aspect ratio = major axis: minor axis [63].
fraction of the phases. A total of 1700 points were counted and used for the each of the nine weld sets. The images were analyzed using Image J software.

### 3.1.7 Law of Mixture for Estimating Weld Zones

Revealing the macrostructure of the multiple pass welds allowed for the separation and quantification of the as-solidified weld metal and the re-heated weld metal, Figure 3.4 and Figure 3.5. The law of mixture is given as the following Eq: 3.1:

\[
100\% = \%\text{AsSolidifiedWeldMetal} + \%\text{ReheatedWeldMetal}
\]  \hspace{1cm} (3.1)

Given the quantitative microstructure of the as-solidified weld metal and the reheated weld metal, the law of mixture can be applied to give a better analysis of the true microstructure of the multiple pass weld metal mockups.

![Figure 3.4: Macrophotograph of the submerged arc multiple pass weld mockup with ESAB flux stress-relieved.](image)

Figure 3.4: Macrophotograph of the submerged arc multiple pass weld mockup with ESAB flux stress-relieved.
3.2 As Received Material Compositions for Fabricating Test Matrix

Base metal, known as COMP F, had the dimensions of 12 inches by 4 inches by 1/2 inch. Submerged arc welding wire, known as MIL-105S, was 1/8 inch diameter. Chemical compositions of COMP F, MIL-105S, and the weld composition using ESAB OK 10.62 flux were presented above in Table 3.5. The composition of the Oerlikon OP121TT flux was given in Table 3.8 with a Basicity Index (BI) of 2.7. ESAB OK 10.62 is a high impact neutral bonded flux with a BI of 3.4 and the flux composition was presented in Table 3.9.

3.3 Testing Matrix and Nickel Additions

A testing matrix with ten weld mockups were fabricated with nickel content from one to five wt. pct. at one wt. pct. increment. All welding parameters were held constant with average welding parameter values given in Table 3.10. The preheat temperature of the base plate was 200°F and a maximum interpass temperature of 350°F was maintained. To systematically input nickel into the weld metal, several methods were tested. For example, the base metal was buttered with nickel, welding over a strip of nickel powder laid on the base metal, and using a soluble paste to hold the nickel in place prior to welding. These methods were all viable for bead-on-plate welds but not multipass welding. Direct mixing of nickel granules of comparable particle sizes of the submerged arc welding flux was also
used. Due to density differences of the granules, separation issues caused inconsistent weld metal compositions. The method of addition selected used a second wire feeding system. This process gave the most consistent and repeatable nickel content during the fabrication of multipass weld mockups.

The second wire feeding system added nickel at a controlled feed rate directly into the molten weld pool underneath the welding flux. It was adapted using a modified Profax II TIG machine with a custom built wire positioner. The wire positioner was secured onto the original wire feeder guide and the wire was angled into the molten weld pool behind the primary wire and perpendicular to the direction of welding, Figure 3.6.

<table>
<thead>
<tr>
<th>Welding Parameters</th>
<th>Average Values</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (A)</td>
<td>420</td>
<td>10</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>Wire Feed Rate (ipm)</td>
<td>55</td>
<td>1</td>
</tr>
<tr>
<td>Travel Speed (ipm)</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td>Heat Input (kJ/in)</td>
<td>47</td>
<td>1</td>
</tr>
<tr>
<td>Electrode Extension (in)</td>
<td>1.125</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 3.6: Second Wire Feeder

Modifications on the Profax II TIG included adapting the smallest wire liner, guide, and drive roll to consistently feed the 0.5 mm (0.02 in.) diameter pure nickel wire, 99.99 wt.
pct. Other modifications included decreasing the voltage to the drive roll to decrease the minimum wire feed rate and changing the wire feeder control to initiate with the main wire feeder. Welding fume and dust collected on the pure nickel wire during the multipass welding fabrication process caused feeding issues. Therefore, cleaning filters were added prior to the nickel wire entering the drive roll to eliminate feeding issues that occurred from an iron dust buildup adhering to the coil liner in the secondary wire feeder.

The Arc Agent 3000P was adapted to the submerged arc welding setup to collect voltage, current, heat input, and welding time to monitor and maintain consistent welding parameters. Other data were also collected during welding: weight of bead, length of bead, and wire feed rate of the main submerged arc welding wire. To determine the approximate wire feed rate required for the pure nickel wire to increase the weld metal content by one wt. pct. nickel assuming 100 pct. recovery of nickel in the weld pool, a series of calculations were performed with the welding data collected. With the average welding parameter values per weld presented in Table 3.11 and the composition of the MIL-105S multipass weld metal without nickel addition in Table 3.12, a calculation based on the weight of a single weld bead being 28 g will require nickel additions of 0.0122 g/cm to increase the nickel content of the weld by one wt. pct. Knowing that 0.28 g (0.0122 g/cm x 22.9 cm) of nickel was needed in an average single weld bead of 22.9 cm length, then it was calculated that 0.00875 g/s was required if the average single weld bead takes 32 s to weld. Given a 1.75 g/m (0.04442 g/in) for the 0.5 mm diameter pure nickel wire, a wire feed rate of approximately 12 ipm was determined as a starting point of testing for the second wire feeder. Final feed rates for the second wire feeder are presented in Table 3.13 along with the nickel content for each of the ten weld mockups fabricated. Note the large number of decimals in the calculated values above were only intended for demonstration purposes.

Multiple pass weld mockups with minimum length, width, and height of 23 cm, 7 cm, and 2.54 cm were expected for machining Charpy V-Notch (CVN) and tensile specimens for testing. The average number of welds deposited per multipass weld mockup was 110 with an
Table 3.11: Average values per weld in submerged arc welding multipass fabrication

<table>
<thead>
<tr>
<th>Variables</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (s)</td>
<td>32</td>
<td>2</td>
</tr>
<tr>
<td>Weight (g)</td>
<td>28</td>
<td>2</td>
</tr>
<tr>
<td>Length (in.)</td>
<td>9</td>
<td>0.5</td>
</tr>
<tr>
<td>Main WFR (ipm)</td>
<td>55</td>
<td>N/A</td>
</tr>
<tr>
<td>Main WFR (ips)</td>
<td>0.917</td>
<td>N/A</td>
</tr>
<tr>
<td>Weight per second (g/s)</td>
<td>0.875</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3.12: MIL-105S multipass weld metal composition without nickel additions (in wt. pct.)

<table>
<thead>
<tr>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cr</th>
<th>C</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Si</th>
<th>P</th>
<th>Sn</th>
<th>Cu</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.45</td>
<td>1</td>
<td>0.51</td>
<td>1.52</td>
<td>0.12</td>
<td>0.11</td>
<td>0.005</td>
<td>0.011</td>
<td>0.006</td>
<td>0.18</td>
<td>0.011</td>
<td>0.001</td>
<td>0.025</td>
<td>0.0034</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.13: Second wire feeder settings and compositions (in wt. pct)

<table>
<thead>
<tr>
<th>Expected Nickel Content (wt. pct.)</th>
<th>Actual Nickel Content in As-Welded Condition (wt. pct.)</th>
<th>Actual Nickel Content in Stress-Relieved Condition (wt. pct.)</th>
<th>Wire Feed Rate (ipm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>1.9</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>2.9</td>
<td>2.9</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>4.1</td>
<td>4.1</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>5.2</td>
<td>5.1</td>
<td>51</td>
</tr>
</tbody>
</table>
average total deposited weld metal weight per multipass weld mockup at approximately 3000 grams. It is important to clarify that two conditions exist for the multipass weld mockups. One was the as-welded condition in which no post-weld heat treatment was performed. The other was the stress-relieved (stress-relieved) condition where a post-welded heat treatment advised by Knolls Atomic Power Laboratory was executed on the multipass weld mockup. The post-weld heat treatment that relieved the stress induced during the fabrication process consisted of a ramp rate from room temperature to 565.6°C (1050°F) at 10°C (50°F) per hour and then a 30 hour hold at 565.6°C (1050°F) with a ramp rate of -6.67°C (20°F) per hour back down to room temperature.

3.4 Metallographic Examination and EBSD

Metallographic procedures followed the description above for microphotographs Section 3.1.4 except that the etchant was slightly modified. Etching of the specimens were conducted using a two to five pct. Nital solution from 5 to 15 seconds. Light optical microscopy (LOM) and scanning electron microscopy (SEM) was performed on selected specimens. Electron backscatter diffraction (EBSD) analysis was also done on selected samples. EBSD specimen preparation did not require an etch but instead a final polish using 0.05 micron colloidal silica on a Buehler VibroMet(R) vibratory polisher for a duration of 6 to 8 hours. The specimens were broken out of the Bakelite mount and glued onto an aluminum stub to ensure electrical conductivity and acquisition of good EBSD patterns. Meticulous sample preparation and good conductivity of the sample were critical to adequate collection of EBSD patterns. EBSD machine settings include a 20 kV accelerating voltage, a 70° tilt of the specimen, a working distance of 15 mm with a capture parameters using 4X4 binning and 0.1 µm step size for an area of approximately 25 µm by 25 µm. A minimum of 6 EBSD scans were performed for one, three, and five wt. pct. nickel in the as-welded condition. All metallographic examination locations were identified using microhardness indentations where values closer to maximum hardness was considered reheated weld metal and hardness values closer to average hardness was considered as-solidified weld metal.
3.5 Mechanical Testing

Tensile specimens were machined from the multipass weld mockups along the direction of welding according to ASTM E8 [51]. Round tension test specimens followed ASTM E8 [51] with a 10 mm gauge length, 2.5 mm diameter, 2 mm radius of fillet, and 16 mm length of reduced section. A displacement rate of 0.02 in. per min was used to 4 pct. and a displacement rate of 0.05 in. per min was used thereafter to speed up the remainder of the tensile test. The extensometer gauge length of 0.5 in. was used along with the final length to determine percent elongation.

CVN specimens were machined in standard size (10 x 10 x 55 mm) in accordance with ASTM E23[49]. Samples were extracted perpendicular to the welding direction and the notch was also in the direction of welding. A lateral expansion gauge was used to determine the lateral expansion of the CVN specimens. Visual comparisons were used to determine percent shear. Depending on the number of specimens that obtained from each of the multilpass weld mockups, a range of temperature 82.2°C (180°F) to -195.6°C(-320°F) were used to test the CVN specimens to determine both the upper shelf energy (USE), lower shelf energy (LSE), and the energy transition temperature (ETT). Five definitions of transition temperature were determined from the absorbed energy versus temperature curves constructed with the data. As the most conservative criterion for the transition temperature, the fracture transition plastic (FTP) value corresponded to the upper shelf in fracture energy and was the temperature at which the fracture was 100 pct. fibrous (0 pct. cleavage). Fracture transition plastic was the temperature at which the fracture shifts from completely ductile to brittle. The probability of brittle fracture occurrence was minimal. Another transition temperature definition was a fracture-appearance transition temperature (FATT) at which 50 pct. cleavage and 50 pct. shear occurred. Another similar definition was the transition temperature at the average of the upper and lower shelf energy values. One other transition temperature was that at which 35 ft-lbs of energy absorbed. This criterion was the preferred adopted by the Knolls Atomic Power Laboratory. The last transition temperature determined and
reported was the nil ductility temperature (NDT). At the NDT, fracture began with almost no prior plastic deformation, i.e. 100 pct. cleavage fracture. The fracture behavior of the Charpy specimens were examined according to the five criterion for the sake of completeness.

Microhardness profiles were obtained using a Leco(R) MHT Series 200 microhardness machine at 500 gf with a dwell time of ten seconds. Microhardness profiles traversed through as-welded and reheated weld metal regions in the multipass weld mockup specimens. It was subsequently found that the stress-relieved specimens did not meet the criteria initially established by Knolls Atomic Power Laboratory. Conversely, the as-welded specimens did satisfy the sponsor’s pre-established criteria. To better focus the research study, only one, three, and five wt. pct. nickel in the as-welded condition were pursued.

3.6 Electron Probe Micro-Analyzer (EPMA)

A JEOL-8600 electron microprobe (EMP), also known as an electron probe microanalyzer (EPMA), was used to acquire nickel composition changes through interdendritic regions to evaluate segregation effects during solidification. The EMP is a non-destructive analytical tool for small volume chemical compositions. Similar to the SEM, the sample is bombarded with a beam of electrons to cause the sample to emit x-rays at specific frequencies. These specific x-ray wavelengths are acquired and counted by a wavelength dispersive spectrometer (WDS). This technique is particularly successful in determining the composition of particles, grains, and even chemical changes over a region on the scale of a few micrometers to millimeters. The JEOL-8600 has capabilities of high spatial resolution (1 µm beam size) and relatively high analytical sensitivity. It is equipped with four WDS and an energy-dispersive spectrometer (EDS). Sample preparation techniques have been described earlier in this document. Good sample preparation is essential in obtaining quality scans for analysis. Samples were mounted in Bakelite and painted with conductive carbon paint and copper tape to ensure electrical conductivity.

Figure 3.7 gives the calibration curve for line scans performed on one and two wt. pct. nickel. Figure 3.8 is a graph of the second calibration curve used to calculate values for
four and five wt. pct. nickel. The calibration curves were created using the varying nickel weld metal mockups built at Colorado School of Mines as standards. A minimum of 25 data points for each nickel content were collected to create the calibration curves. The coefficient of determination, $R^2$, approximately 0.95 for both Figure 3.7 and Figure 3.8, was sufficient to determine reliable outcomes for the intensity data collected for one, two, four, and five wt. pct. nickel. A minimum of 100 data points were acquired for the several nickel contents in the as-solidified weld metal in the as-welded condition.

![EPMA calibration curve 1](image)

**Figure 3.7: EPMA calibration curve 1.**

### 3.7 Computational Software Simulation

The software JMatPro\(^{(R)}\) was utilized to simulate useful material properties for the nickel added multipass weld mockups. Phase transformations were simulated in the form of time-temperature transformation (TTT) diagrams and continuous cooling transformation (CCT) diagrams and microhardness values in VHN for specific cooling rates. The computational
Figure 3.8: EPMA calibration curve 2.
modeling software gave no distinction between the as-welded and stress-relieved condition or the as-solidified and reheated weld metal microstructure.

### 3.8 Differential Scanning Calorimetry

A Netzsch simultaneous thermogravimetry-differential scanning calorimetry-STA and a Setaram Evolution 16/18 were both used to acquire differential scanning calorimetry data on transformation temperatures and exothermic/endothermic events that occurred during the heating and cooling of the sample. Samples were prepared to sit flat in a ceramic crucible with dimensions of 6.8 mm in diameter and 4 mm in height for the Netzsch and 5 mm in diameter and 3 mm in height for the Setaram. Sample sizes were approximately one gram in weight. Helium was used as the inert gas for all experiments performed. Ramp rate of 10 K/min was used for heating up to 1600°C (2912°F) and then cooled back to room temperature at the same ramp rate. This cooling rate did not simulate the welding conditions thus no direct information on microstructural evolution can be extracted from the differential scanning calorimetry data. However, the differential scanning calorimetry data will allow for the examination of the effect of nickel on the reactions within the weld metal at a constant ramp rate. The analysis software with the Netzsch is Proteus and the Setaram analysis software is Calisto. Both of these softwares helped determine transformation temperatures and areas under the curve to determine the energy associated with the exothermic/endothermic reactions.

A DSC monitors energy evaluation associated with phase transitions and chemical reactions as a function of temperature. The difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an empty alumina crucible, in this case. Since DSC is a bulk analytical technique, results take into consideration the combined as-solidified and reheated regions within the weld mockup. At a preset constant rate of temperature change at constant pressure, heat flow is equivalent to enthalpy changes given by Eq: 3.2.
Here $\frac{dH}{dt}$ is the heat flow and the heat flow difference between the sample and the reference is presented in Eq: 3.3.

$$\Delta \frac{dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} - \left( \frac{dH}{dt} \right)_{\text{reference}}$$

The heat flow difference can be either positive or negative depending on whether it is an endothermic or exothermic process, respectively. When heat flows into the sample making the temperature higher than that to the reference, Eq: 3.3 is positive for endothermic processes such as melting and decomposition reactions. When heat flows out of the sample, exothermic processes such as crystallization and oxidation reactions occur. In addition, a Python code was created to assist in finer analysis of deconvoluting some of the curves. The code can be found in Appendix F.

### 3.9 X-Ray Diffraction

X-ray diffraction studies were carried out to characterize nickel alloying behavior for HSLA steel weld multipass weld mockups for one, three, and five wt. pct. nickel in the as-welded condition and five wt. pct. in the stress-relieved condition. A Philips Diffractometer (PW-3200) with a Cu Kα radiation tube was used. Data was acquired for the spectral range of 30 to 148° with a step size of 0.02° and a dwell time of one second. Total scan times were between one and a half to two hours long. Using the Bragg-Brentano geometry on the line focus side, the instrument set up also used a graphite monochromator in the diffracted beam arm.

X-ray diffraction peak profile analysis is often used to characterize microstructures. Peak profiling can detect decrease in second phase particle size and lattice defects that cause strain fields such as a linear defect that causes long-range strain fields. These strain fields affect Bragg reflection thereby affecting the broadness of the peaks. The Williamson-Hall (WH) and Warren-Averbach analyzes are widely used to investigate crystalline size and
strain contributions to peak broadening[61, 64]. If either the crystalline shape or strain is anisotropic, the broadening does not change linearly with the diffraction angle. Using a modified WH plot proposed by Ungar and Borbely [56] and a modified Warren-Averbach analysis, the anisotropic strain broadening and strain of dislocations of the crystals were analyzed, respectively, in this research.

Strain is diffraction-order dependent whereas size is diffraction-order independent from the peak broadening diffraction profiles. To separate size and strain contributions, WH plots were developed and the integral breadth, \( \beta \), of the XRD line profiles is given by Eq: 3.4.

\[
\beta^* = \frac{1}{D} + 2\varepsilon K
\]  

(3.4)

Average grain size is related to \( D \), \( \varepsilon \) is microstrain, \( \beta^* = \beta \cos \frac{\theta}{\lambda} \) and \( K = 2\sin \frac{\theta}{\lambda} \) where \( 2\theta \) is the diffraction angle and \( \lambda \) is the wavelength of the x-ray beam. Using the full-width value at half-maximum (FWHM) peak which is half the measured intensity as the breadth, \( \beta \), \( \frac{1}{D} \) is replaced with \( \frac{0.9}{D} \). Then a plot of \( \beta^* \) versus \( 4\sin \theta \) would give a graph in which the slope of the line will be the microstrain and the crystalline size is given by the intercept of the line [64]. The modified WH equation is derived by Ungar and Borbely [56] and given in Eq: 3.5

\[
\beta^* = \frac{1}{D} + \alpha (K\bar{C}^{\frac{1}{2}}) + O(K^2\bar{C})
\]  

(3.5)

where \( \alpha = (\pi A^2b^2)\frac{1}{2}\rho^{\frac{3}{2}} \) known as the normalized mean square strain and O denotes noninterpreted higher-order terms. The A is a constant that depends on the effective dislocation radius, b is the Burgers vector, \( \rho \) is dislocation density, and \( \bar{C} \) is the average contrast factor of dislocations [56]. If dislocations are the main source of strain, the breadth changes from K to \( K\bar{C}^{\frac{1}{2}} \). For untextured cubic polycrystalline specimen or one with varied slip systems, simple fourth-order polynomials of hkl can be used for values of average contrast factors using the following Eq: 3.6 where \( H^2 = \frac{(h^2k^2 + k^2l^2 + l^2h^2)}{(k^2 + k^2 + l^2)^2} \) and \( q = \frac{B}{A} \) with A and B as elastic constants of the crystal [57]. For further details for estimating theoretical and experimental q factors and \( \bar{C}_{h00} \) refer to Ungar et al. [58]. By squaring both sides of Eq: 3.5 from Ungar and Borbely [56] and then substituting Eq: 3.6, an experimental q can be estimated by varying value of
D versus $H^2$. Then the average contrast factors can be estimated and plotted to determine the modified WH plots.

\[ \bar{C}_{hkl} = \bar{C}_{h00}(1 - qH^2) \]  

(3.6)
CHAPTER 4
RESULTS AND DISCUSSION

This Section is divided into three main parts: 1) initial research to identify nickel as the major element to be investigated for its effects on HSLA steel multiple pass weld mockups, 2) analysis for HSLA steel multiple pass weld mockups with incrementing amounts of nickel, and 3) a discussion of the descriptive model proposed for the explanation of the metallurgical effects of nickel addition. The initial research presents the results that led to the development of specifically studying the effect of nickel in HSLA steel multiple pass weld mockups to enhance toughness at lower temperatures while maintaining strength. The analysis for the HSLA steel multiple pass weld mockups utilized a variety of advanced characterization techniques to investigate primary solidification mode, nickel segregation, cellular dendrite thickness, phase transformation temperatures, dislocation density and strain, precipitates, effective grain size, and grain misorientation. Lastly, using the results from the advanced characterization techniques, a descriptive model was proposed to explain the effects of nickel on the microstructural evolution which directly affects the weld strength and toughness.

4.1 Initial Research

This Section will begin with the macrophotographs for which the amount of as-solidified and reheated weld metal was determined. The microstructural key that was developed to characterize the different morphologies in the weld metal will be given and discussed. Using the microstructural key and estimations of the weld zones, the microstructures were quantified and reported. With the weld metal composition, quantified microstructures in the weld metal, and the mechanical properties of the weld metal, nickel was identified as the specific alloying element to further pursue for improving weld metal toughness.
4.1.1 Macrophotographs and Law of Mixture

Macrophotographs of the entire multiple pass weld were prepared for the submerged arc welding and gas-tungsten arc welding mockups received. Figure 4.1 is a macro-etched image of the cross-section of the submerged arc weld using an ESAB flux received from Knolls Atomic Power Laboratory. Figure 4.2 is the macro-etched image of the gas-tungsten arc weld using the MIL-105S wire. For the W11/W12 and W13/W14 welds, Charpy v-notch samples extracted from the weld mockups were used to conduct microstructural analysis and determine as-solidified and reheated weld metal percentages using LOM.

![Macro-photograph of the submerged arc welding mockup using ESAB flux after etching using nital.](image)

The equation and usage of the law of mixture in estimating the weld zones have already been presented in Section 3.1.7. The values of the as-solidified weld metal and the reheated weld metal determined using the macrophotographs and Charpy v-notch samples are given in Table 4.1. The gas-tungsten arc weld showed a lower as-solidified weld metal value of 47 pct. whereas the measured values of the as-solidified submerged arc welds ranged from 57
Figure 4.2: Macro-photograph of the gas-tungsten arc welding mockup after etching using nital.
pct. to 68 pct. Note that this difference in percentage was because submerged arc welding is a higher heat input and higher deposit rate process than gas-tungsten arc welding process. The gas-tungsten arc weld had 53 pct. reheated weld metal. The reheated zone in the submerged arc welds ranged from 32 to 43 pct. The as-solidified versus the reheated weld metal ratio was the lowest for the gas-tungsten arc weld at 0.89 as compared 1.6, 1.5, 2.1, and 1.3, respectively, for the submerged arc welds using the ESAB flux, submerged arc welds using an Oerlikon flux, W11/W12, and W13/W14.

Table 4.1: The percentages of as-solidified weld metal and reheated weld metal used for the application of the law of mixture in microstructural quantification.

<table>
<thead>
<tr>
<th>Welds</th>
<th>As-Solidified Weld</th>
<th>Reheated Weld</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-tungsten arc weld</td>
<td>47%</td>
<td>53%</td>
</tr>
<tr>
<td>Submerged arc weld with ESAB flux</td>
<td>62%</td>
<td>38%</td>
</tr>
<tr>
<td>Submerged arc weld with Oerlikon flux</td>
<td>60%</td>
<td>40%</td>
</tr>
<tr>
<td>W11/W12</td>
<td>68%</td>
<td>32%</td>
</tr>
<tr>
<td>W13/W14</td>
<td>57%</td>
<td>43%</td>
</tr>
</tbody>
</table>

4.1.2 Microstructural Key

The MIL-105S gas-tungsten arc weld and the submerged arc welds using the Oerlikon flux were used to identify all the different types of microstructural constituents in order to develop the key for microstructural quantification. Figure 4.3 is a photomicrograph that shows all the major constituents in the weld cap (top pass) with only as-solidified weld microstructure. Four major constituents were identified: fine FS(A), coarse FS(A), FS(NA), and LM. Using microhardness testing, aspect ratios, and visual differences, these major constituents were identified, Table 4.2. For example, thicker and longer laths may have similar aspect ratios as thin and short laths, yet microhardness gave a distinct difference between fine FS(A) and coarse FS(A). Ferrite with aligned second phase was shown as grains with fine, parallel features whereas FS(NA) was shown as grains with fine, non-aligned structures. Ferrite with aligned second phase could be further identified as sideplates, upper or lower bainite but it is difficult to clearly identify bainite under the LOM. Figure 4.3 was used as keys for
interpreting all as-solidified microstructures in the other welds in the initial research. These keys were also used as guidelines to perform quantitative metallography on all the welds. In addition to the four major constituents identified (fine FS(A), coarse FS(A), FS(NA), and lath martensite), the MIL-105S gas tungsten arc weld showed three more constituents: equiaxed ferrite (EF), ferrite carbide aggregates (FCA), and AF. Equiaxed ferrite was shown as a light colored grain that does not have any fine non-aligned structures within it. Ferrite carbide aggregates are the dark regions around the light colored grains, Figure 4.5. Figure 4.4 shows the acicular ferrite constituent in the microstructure of the as-solidified weld. Acicular ferrite was virtually absent from the MIL-105S gas tungsten arc weld, but was a major constituent in the MIL-105S submerged arc weld.

Figure 4.3: MIL-105S gas-tungsten arc weld cap micrograph with a key shown in Table 4.2 that identifies all the major constituents present. Acicular ferrite is virtually absent in this micrograph.
Table 4.2: Microstructural key for Figure 4.3.

<table>
<thead>
<tr>
<th>Number</th>
<th>Phase</th>
<th>Aspect Ratio</th>
<th>Microhardness (VHN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fine FS(A)</td>
<td>8:1</td>
<td>267</td>
</tr>
<tr>
<td>2,3</td>
<td>Coarse FS(A)</td>
<td>17:1, 10:1</td>
<td>284, 281</td>
</tr>
<tr>
<td>4</td>
<td>FS(NA)</td>
<td>N/A</td>
<td>291</td>
</tr>
<tr>
<td>5</td>
<td>LM</td>
<td>N/A</td>
<td>321</td>
</tr>
</tbody>
</table>

Figure 4.4: MIL-105S submerged arc as-solidified weld with Oerlikon flux displaying acicular ferrite as a major constituent. The percent acicular ferrite in this micrograph easily exceeds 90 pct.
Figure 4.5: Example of ferrite carbide aggregates and equiaxed ferrite from the MIL-105S gas-tungsten arc weld at 500X.
4.1.3 Quantitative Microstructural Analysis

The raw data for the quantitative microstructural analysis is given in Table 4.3. Both as-welded and stress-relieved conditions were examined to determine the effects of post-weld heat treatment had on the microstructure of the multiple pass welds. No consistent effects between the as-welded and stress-relieved conditions were determined except for the FCA. The FS(A) and EF phases showed an increasing trend from the as-welded to the stress-relieved for submerged arc welds using the ESAB and Oerlikon flux and W11/W12. The FS(NA) phase showed a decrease from as-welded to stress-relieved for all the submerged arc welds except for W13/W14. Lath martensite and AF did not display consistent trends. A decrease in the percentage of FCA from as-welded to stress-relieved could be noted with the exception of the gas-tungsten arc weld. An example of the LOM micrographs used for the quantitative microstructural analysis for each weld is given in Figure 4.6, Figure 4.7, Figure 4.8, Figure 4.9, Figure 4.10, Figure 4.11, Figure 4.12, Figure 4.13, and Figure 4.14.

Due to the complex nature of the solidification, cooling, and reheating of a multiple pass weld, the microstructure could become complex to decipher. Thus, Figure 4.6 to Figure 4.14 should be seen as specific examples, rather than a general overview of the weld metal microstructure. In multiple pass welds, the heat from subsequent passes promotes a tempering effect on previous passes causing these reheated regions to undergo partial or complete transformation to a different secondary microstructure. In addition, a post-weld heat treatment or stress-relief treatment could cause precipitates in the matrix to grow and coalesce thereby altering their effect on notch toughness. Post-weld heat treatment and welding conditions could reduce toughness if the precipitation kinetics of finely disperse coherent precipitates are favored [14]. In 1996, Johnson [21] concluded that multiple pass thermal history and weld metal chemical composition in high strength shielded metal-arc welding played a more pivotal role in the mechanical properties than the initial or as-deposited microstructure. Therefore, chemical composition should be the first venue for adjusting the mechanical properties of welds.
Table 4.3: Summary of the quantitative microstructural analysis in percentage.

<table>
<thead>
<tr>
<th>Weld</th>
<th>Fine FS(A) (pct.)</th>
<th>Coarse FS(A) (pct.)</th>
<th>FS(NA) (pct.)</th>
<th>Lath Martensite (LM) (pct.)</th>
<th>Ferrite Carbide Aggregate (PCA) (pct.)</th>
<th>Equiaxed Ferrite (EF) (pct.)</th>
<th>Acicular Ferrite (AF) (pct.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTAW - as-welded</td>
<td>26</td>
<td>5.2</td>
<td>42</td>
<td>3.4</td>
<td>5.3</td>
<td>18.1</td>
<td>-</td>
</tr>
<tr>
<td>SAW ESAB flux - as-welded</td>
<td>8.7</td>
<td>-</td>
<td>22.3</td>
<td>7.7</td>
<td>5.7</td>
<td>8.9</td>
<td>46.7</td>
</tr>
<tr>
<td>SAW ESAB flux - stress-relieved</td>
<td>11.4</td>
<td>-</td>
<td>20.5</td>
<td>7.6</td>
<td>3.8</td>
<td>10.6</td>
<td>45.5</td>
</tr>
<tr>
<td>SAW Oerlikon flux - as-welded</td>
<td>10.1</td>
<td>-</td>
<td>27.2</td>
<td>1.6</td>
<td>3.2</td>
<td>5.4</td>
<td>52.5</td>
</tr>
<tr>
<td>SAW Oerlikon flux - stress-relieved</td>
<td>14</td>
<td>-</td>
<td>29.1</td>
<td>4.6</td>
<td>2.4</td>
<td>11.2</td>
<td>38.7</td>
</tr>
<tr>
<td>W11/W12 - as-welded</td>
<td>30</td>
<td>-</td>
<td>52</td>
<td>-</td>
<td>6</td>
<td>8.6</td>
<td>3.4</td>
</tr>
<tr>
<td>W11/W12 - stress-relieved</td>
<td>35.6</td>
<td>-</td>
<td>32.9</td>
<td>6.7</td>
<td>3.3</td>
<td>10.4</td>
<td>11.1</td>
</tr>
<tr>
<td>W13/W14 - as-welded</td>
<td>30.8</td>
<td>23</td>
<td>23.3</td>
<td>-</td>
<td>14.3</td>
<td>8.6</td>
<td>-</td>
</tr>
<tr>
<td>W13/W14 - stress-relieved</td>
<td>30.6</td>
<td>9.3</td>
<td>39.3</td>
<td>-</td>
<td>13.8</td>
<td>7</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.6: LOM micrograph of the as-solidified weld metal of a submerged arc weld mockup using ESAB flux in as-welded condition.
Figure 4.7: LOM micrograph of the reheated weld metal of a submerged arc weld mockup using ESAB flux in stress-relieved condition.

Figure 4.8: LOM micrograph of the as-solidified weld metal of a submerged arc weld using Oerlikon flux in as-welded condition.
Figure 4.9: LOM micrograph of the as-solidified weld metal of a submerged arc weld mockup using Oerlikon flux in stress-relieved condition.

Figure 4.10: LOM micrograph of the as-solidified weld metal of a W11/W12 weld in as-welded condition.
Figure 4.11: LOM micrograph of the reheated weld metal of a W11/W12 weld in stress-relieved condition.

Figure 4.12: LOM micrograph of the as-solidified weld metal of a W13/W14 weld in as-welded condition.
Figure 4.13: LOM micrograph of the as-solidified weld metal of a W13/W14 weld in stress-relieved condition.

Figure 4.14: LOM micrograph of the as-solidified weld metal of a gas-tungsten arc weld mockup in as-welded condition.
4.1.4 Correlation Between Weld Composition and Microstructure

Weld composition played a pivotal role in the microstructure of the weld metal. Using Table 3.3, Table 3.4, Table 3.5, Table 3.6, and Table 3.7 in parallel with Table 4.2, the weld composition and the microstructure was correlated. For the initial research, chemical elements of interest are manganese, nickel, and molybdenum. Using a combination of literature findings and experimental data from the initial research, the amounts of the influence of these elements on the microstructure will be discussed. The quantitative microstructural analysis used for the following discussion are from the stress-relieved specimens since mechanical properties were provided only for these specimens with the exception of the gas tungsten arc welds in the as-welded condition. More specifically in phase transformation and microstructure, results from only the as-welded specimens will be used in the latter part of this thesis.

Manganese is the principal strengthening element and retards most austenite decomposition reactions. The transformational temperature ranges are lowered by manganese for ferrite and pearlite transformation [10]. In low carbon steel weld metal, increasing manganese progressively increased the amount of acicular ferrite at the expense of primary ferrite. Not only did acicular ferrite increased in amount with increasing manganese content, it was also refined [15]. Evans also established that manganese had an optimum influence at 1.5 wt. pct. with peak mechanical properties and minimal influence from the stress-relieving of the weld deposits. The MIL-105S weld using ESAB flux with a manganese content of 1.5 wt. pct. showed the highest acicular ferrite pct., Figure 4.15. However, this figure showed that there is a minimum amount of manganese of around 1.2 wt. pct. before acicular ferrite can be formed. Figure 4.16 reinforced the role of manganese as a strengthener since its addition increased the percent of lath martensite.

Nickel is an austenite stabilizer that moderately affects hardenability. The increase of nickel increased the stacking fault energy thus making it easier for partial dislocations to recombine to cross slip, i.e. increasing toughness. Controlled nickel additions with respect to
manganese for C-Mn steel weld metal has been shown to increase toughness via a decrease of grain boundary ferrite and an increase of acicular ferrite content [67]. Note all C-Mn steel weld metal in this section refers to shielded metal arc weld metal [15]. Evans also concurred that nickel increased the proportion of acicular ferrite but at the expense of both primary ferrite and ferrite with second phase. At a high manganese content of 1.8 wt. pct. with nickel content above 2.2 wt. pct., martensite began to form with an increased amount of ferrite with second phase also at the expense of acicular ferrite and primary ferrite, Figure 4.17. At lower manganese content of 1 wt. pct., acicular ferrite was maximized at 3.5 wt. pct. nickel. There was no martensite formation at the lower manganese content of 1 wt. pct. From experimental data, when the sum of nickel and manganese exceeded approximately 2.5 wt. pct., acicular ferrite dropped to a minimum, Figure 4.18. Conversely, FS(A) and FS(NA) were maximized at high nickel and manganese contents as shown in Figure 4.19 and Figure 4.20. Evaluating only the submerged arc weld mockups, more acicular ferrite was
present at lower nickel content of approximately one wt. pct. but no acicular ferrite existed at the high nickel content of 3.73 wt. pct.

Nickel also increased the acicular ferrite aspect ratio and minimized cementite and pearlite in C-Mn steel weld metal with the formation of M/A constituents which precipitated as grain boundary carbides after stress relief [15]. Evans and Bailey [15] reported an increasing yield strength and ultimate tensile strength with increasing nickel and manganese content, Figure 4.21. They also examined the effect of nickel on varying manganese compositions on the Charpy transition temperature, Figure 4.22. For both as-welded and stress-relieved conditions, impact toughness was optimized at approximately 1.5 wt. pct. manganese and 1 wt. pct. nickel. At a nickel content of 2.25 wt. pct., the Charpy transition temperature started increasing thereby decreasing the toughness. Experimental data for NDT\textsubscript{35ft−lbf} displayed in Figure 4.23 showed a large increase when nickel increased from approximately 1 to 3.73 wt. pct. content. This behavior has not been clearly discussed in the literature.
Figure 4.17: Effect of nickel on as-deposited microstructure of C-Mn steel welds with a) 1wt. pct. manganese; b) 1.8 wt. pct. manganese [15].
Thus, it would be beneficial to more closely examine the effects of nickel within the range of composition of the MIL-105S steel system.

Note that literature data only examined the effect of nickel on varying manganese amounts. In the MIL-105S system, molybdenum needed to also be considered. Thus based on literature and experimental data analysis, it seemed that a manganese composition of 1.5 wt. pct. was adequate, but the nickel content at which it is most beneficial for microstructure/mechanical properties was yet to be determined. Molybdenum depressed the formation kinetics of ferrite and pearlite and increased hardenability. In C-Mn steel weld metal, molybdenum up to 0.5 wt. pct. increased and refined acicular ferrite at the expense of primary ferrite, Figure 4.24. Increasing molybdenum content to greater than 0.5 wt. pct. could increase formation of Mo₂C when carbon content is at or above 0.1 wt. pct. which can detrimentally affect toughness. All the weld mockups in the initial studies had a consistent carbon content of 0.1 wt. pct. Additions of molybdenum up to 1.1 wt. pct. reduced acicular ferrite and primary ferrite
Figure 4.19: Ferrite with second phase aligned (FS(A)) as a function of nickel and manganese steel weld composition.
Figure 4.20: Ferrite with second phase non-aligned (FS(NA)) as a function of nickel and manganese steel weld composition.
Figure 4.21: Effect of nickel and manganese on strength of welds, as-deposited and after stress relief at 580°C: a) Yield strength; b) Tensile strength [15].
Figure 4.22: Effect of nickel on 100J Charpy transition temperature of weld metal of varying manganese level: a) As-welded; b) Stress relieved at 580°C [15].
Figure 4.23: NDT_{35ft-lbs} as a function of nickel weld composition.

and increased ferrite with second phase [15]. Weld W13/W14 with a molybdenum content of 1.45 wt. pct. and a manganese content of 0.15 wt. pct. had 79 pct. ferrite with second phase and no acicular ferrite. The lower molybdenum content of the submerged arc weld mockups gave a higher acicular ferrite percentage (38.7 pct., 45.6 pct., and 11.2 pct.) and a lower amount of ferrite with second phase, Table 4.3. Evans and Bailey [15] discovered that with no molybdenum, electron microscopy showed pearlite and bainite in the C-Mn weld deposit; but at 1.1 wt. pct. molybdenum, the ferrite with second phase was comprised of M/A constituents with Fe_{3}C as a grain boundary constituent. In another study, increasing molybdenum content has also been shown to decrease GBF and FS(A), while increasing acicular ferrite and granular bainite. The combination of nickel (2.03 to 2.91 wt. pct.) and molybdenum (0.7 to 0.995 wt. pct.) in the weld metal has been shown to give a higher volume fraction of acicular ferrite by decreasing FS(A) and GBF in a submerged arc welding HSLA lined pipe steel [5]. In 2005, Surian et al. [53] found that optimal weld metal
toughness was achieved at 0.25 wt. pct. molybdenum for 1.5 wt. pct. manganese and 1.8 wt. pct. nickel in Cr-free ferritic HSLA weld metal.

Figure 4.24: Effect of molybdenum on as-deposited microstructure of welds with one wt. pct. manganese [15].

In terms of mechanical properties, increasing molybdenum with increasing manganese showed an increase in both yield strength and ultimate tensile strength, Figure 4.25. As molybdenum was increased, acicular ferrite formation increased at the expense of primary ferrite which translated to higher strength. After 0.5 wt. pct. molybdenum at one wt. pct. manganese, acicular ferrite and primary ferrite components decreased while ferrite with second phase increased. A higher molybdenum content of one wt. pct. with increasing manganese content decreased the Charpy transition temperature in Figure 4.26. The best Charpy properties was shown for 0 wt. pct. molybdenum. Experimental data also showed that lower molybdenum content was more favorable in lowering the NDT_{35 ft-lbs}, Figure 4.27. In 2004, Kim et al. [28] stated that the combination of nickel and molybdenum gave a pre-
dominantly fine acicular ferrite matrix by decreasing the volume fraction of grain boundary ferrite. For the benefits described above, it was desirable to hold molybdenum content constant at 0.5 wt. pct. while adjusting the nickel content to achieve optimal microstructure and NDT$_{35ft-lbs}$.

Figure 4.25: Effect of molybdenum and manganese on strength of welds as-welded and after stress relief at 580°C: a) Yield strength; b) Tensile strength [15].
Figure 4.26: Effect of molybdenum on 100J Charpy transition temperature of weld metals of varying manganese level: a) As-welded; b) Stress-relieved at 580°C [15]).

Figure 4.27: NDT\textsubscript{35} as a function of molybdenum weld composition.
In 1991, Evans [15] reported that for C-Mn steel weld metal with a manganese content of 1.4 wt. pct., toughness dropped when nickel content exceeded 2.25 wt. pct. Since the MIL-105S with ESAB flux has a current weld composition of 0.96 wt. pct. nickel, further addition of nickel was made at one wt. pct. increments. It is in general agreement that the sum of the three elements (nickel, manganese, and molybdenum) was expected to be around 3 to 4 wt. pct. for high strength steels. In comparison, the current MIL-105S with ESAB flux gave a sum of approximately 3 wt. pct. for the three elements. Table 3.12 and Table 3.13 show compositions that result in a maximum sum of 4.45 wt. pct. for these elements of interest.

The effect of nickel optimizing high strength low alloy steel weld was not as clear as manganese and molybdenum. Using the weld composition with ESAB flux as the starting point, the manganese and molybdenum composition was 1.2 and 0.51 wt. pct., respectively, nickel was added at increments of one wt. pct. from one to five wt. pct. range. It was the goal of this matrix to explain how nickel in combination with manganese and molybdenum affected microstructure and NDT$_{35ft-lbs}$. Due to the refined microstructure observed in the welds, LOM may not be the most effective technique for microstructural analysis. Therefore, welds made in this test matrix will be analyzed using a number of different analytical techniques to give more definitive results as to why nickel might increase strength and toughness in HSLA steel weld metal.

4.2 Strategy for Analysis for HSLA Steel Multiple Pass Weld Mockups

Using a combination of different advanced characterization techniques, the submerged arc weld mockups were analyzed to determine the effects of nickel. Figure 4.28 is an example of the submerged arc weld mockups fabricated with incrementing nickel content. The first step to analyzing the weld mockups was to study the mechanical properties by acquiring data for hardness and performing both Charpy v-notch and tensile testing. The mechanical properties of these welds helped focus and select the specimens for further characterization. Electron probe micro-analyzer (EPMA) was used to study solute segregation.
and cell/dendrite thickness. Differential Scanning Calorimetry (DSC) was used to study the
effect of increasing nickel on primary solidification mode, phase transformation temperatures,
and enthalpy changes upon cooling. The simulation software, JMatPro, was used to predict
microstructure and phase transformation temperatures. X-ray diffraction (XRD) was uti-
lized to study the strain effects and precipitates with incrementing nickel. Lastly, electron
backscatter diffraction (EBSD) was used to characterize effective grain size, qualitative dis-
location density, and grain misorientation relationship. Results from these characterization
steps were used to formulate a descriptive model of the effects of nickel on the microstructural
development in these HSLA steel welds.

Figure 4.28: Weld mockup of five wt. pct. nickel.

4.2.1 Mechanical Properties: Vickers Microhardness, Charpy V-Notch Testing,
and Tensile Testing

The summary of all the mechanical properties from the varying nickel composition test
matrix described in Table 3.13 will be presented in this Section. Compiled data of Vickers
microhardness, Charpy v-notch testing, and tensile testing will be presented. Microhardness
data was acquired from regions that traversed as-solidified and reheated zones in the sub-
merged arc weld mockups. Figure 4.29 is a pictorial illustration of how the hardness profiles
were performed where the red lines are examples of hardness profiles taken. Figure 4.30
displays hardness profiles showing as-solidified regions with lower hardness and reheated regions with higher hardness. The range of Vickers microhardness values for the one to five wt. pct. nickel in the MIL-105S system varied from about 240 to 320 VHN. It can be seen that between one and two wt. pct. and three and four wt. pct. nickel in both the as-welded and stress-relieved condition, there was a definitive change in hardness. Table 4.4 showed the average hardness for two wt. pct. nickel as 266 VHN, approximately 20 VHN higher than the average hardness for one wt. pct. nickel weld. Between three and four wt. pct. nickel in the as-welded condition, the VHN value jumped from 275 to 308. In comparison, the hardness increased only 9 VHN between two and three wt. pct. nickel. The difference between four and five wt. pct nickel in the as-welded condition was 11 VHN. These changes with nickel addition will be discussed in a later section together with additional experimental evidence. The as-welded and stress-relieved conditions followed the same trend described above and can be seen in Figure 4.31. As nickel content increased, hardness values increased.

![Figure 4.29: Illustration of locations where hardness data were acquired.](image)

Charpy v-notch testing was performed on all ten specimens. Results were plotted to determine the transition-temperature curves. In mild steel, it is well-documented that nickel is generally accepted to be beneficial to notch toughness in amounts up to two percent and is beneficial for lowering the ductility transition-temperature. Results for one, three, and five wt. pct. nickel in both as-welded and stress-relieved condition will be displayed and
Figure 4.30: Vickers microhardness profiles.

Table 4.4: Vickers hardness numbers (VHN).

<table>
<thead>
<tr>
<th>Weld (wt. pct.)</th>
<th>5</th>
<th>5</th>
<th>4</th>
<th>4</th>
<th>3</th>
<th>3</th>
<th>2</th>
<th>2</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SR</td>
<td>AW</td>
<td>SR</td>
<td>AW</td>
<td>SR</td>
<td>AW</td>
<td>SR</td>
<td>AW</td>
<td>SR</td>
<td>AW</td>
</tr>
<tr>
<td>Avg. VHns</td>
<td>323</td>
<td>319</td>
<td>298</td>
<td>308</td>
<td>269</td>
<td>275</td>
<td>260</td>
<td>266</td>
<td>225</td>
<td>244</td>
</tr>
<tr>
<td>Avg. Max. VHns</td>
<td>331</td>
<td>335</td>
<td>313</td>
<td>320</td>
<td>278</td>
<td>281</td>
<td>272</td>
<td>280</td>
<td>233</td>
<td>252</td>
</tr>
<tr>
<td>Avg. Min. VHns</td>
<td>315</td>
<td>303</td>
<td>283</td>
<td>296</td>
<td>260</td>
<td>269</td>
<td>248</td>
<td>252</td>
<td>217</td>
<td>236</td>
</tr>
<tr>
<td>Avg. St. Dev.</td>
<td>8</td>
<td>16</td>
<td>15</td>
<td>12</td>
<td>9</td>
<td>6</td>
<td>12</td>
<td>14</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>
Figure 4.31: Average vicker hardness number as a function of nickel content (wt. pct.)

discussed below. Transition-temperature plots for two and four wt. pct. nickel can be found in Appendix A. The most important ductility transition-temperature to this research was the NDT<sub>35 ft-lbs</sub> since the target for these weld mockups was a NDT<sub>35 ft-lbs</sub> less than or equal to -140°F (-95.6°C).

Figure 4.32 gives the plotted transition-temperature curves along with the fracture-appearance curves for one wt. pct. nickel in both the as-welded and stress-relieved condition. Transition-temperature curves for three and five wt. pct. nickel are given in Figure 4.33 and Figure 4.34. The fractographs of the Charpy v-notch specimens for all ten specimens can also be found in Appendix A.

From Table 4.5, the FTP or the upper shelf transition temperature (T<sub>1</sub>) increased with increasing nickel content in both the as-welded and stress-relieved conditions. With increased nickel content, weld metal hardness increased, comparably, YS and UTS are expected to increase. Conversely, Charpy v-notch transition temperatures decreased, elongation and
Figure 4.32: Charpy v-notch curve for one wt. pct. nickel as-welded (left) and stress-relieved (right).

Figure 4.33: Charpy v-notch curve for three wt. pct. nickel as-welded (left) and stress-relieved (right).
the NDT or lower shelf energy (\(T_5\)) of the five wt. pct. nickel in the as-welded condition displayed a decrease from three wt. pct. nickel. In terms of NDT\(_{35\text{ft-lbs}}\) (\(T_4\)) less than or equal to \(-140^\circ\text{F}\), one, three, and five wt. pct. in the as-welded condition all satisfied the specific criterion. In the stress-relieved condition, \(T_4\) did not fulfill the targeted criterion.

In Figure 4.35, all determined transition temperatures were graphed with respect to nickel content in the as-welded condition. It was clear that \(T_4\), NDT\(_{35\text{ft-lbs}}\), for one through five wt. pct. nickel all fulfilled the less than or equal to minus 140°F criterion. A definitive decrease in transition temperature was observed between three and four wt. pct. nickel indicating an improvement in impact toughness at this level of nickel addition suggesting a more detailed characterization of the effect of nickel. Due to the complex nature of the weld mockup microstructure, in particular in the stress relieved samples, it becomes clear that the effect of nickel in the as-welded condition should be the focus of the remainder of this research. Understanding the effect of nickel at greater than three wt. pct. addition in enhancing low temperature impact toughness in the as-welded condition may demonstrate opportunities for
welding process simplification. For that reason, no further discussion on the stress-relieved condition will be developed, but experimental data for stress-relieved condition are compiled in Appendix A.

Plotting all transition temperature curves in one plot in the as-welded condition, it could be seen that increasing nickel not only affected the transition temperatures but also the shape of the transition curves. In Figure 4.36, one, two, and three wt. pct nickel displayed a more common S-curve characteristic observed in body-centered cubic material. Between three and four wt. pct. nickel, the S-curve shifts to a half S-curve found in high strength materials.

Table 4.5: Five transition temperatures for one, three, and five wt. pct. nickel in as-welded (AW) and stress-relieved (SR) condition.

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>1 wt. pct.</th>
<th>3 wt. pct.</th>
<th>5 wt. pct.</th>
<th>1 wt. pct.</th>
<th>3 wt. pct.</th>
<th>5 wt. pct.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AW</td>
<td>AW</td>
<td>AW</td>
<td>SR</td>
<td>SR</td>
<td>SR</td>
</tr>
<tr>
<td>T1</td>
<td>-39°F</td>
<td>80°F</td>
<td>180°F</td>
<td>30°F</td>
<td>180°F</td>
<td>200°F</td>
</tr>
<tr>
<td></td>
<td>(-39.4°C)</td>
<td>(26.7°C)</td>
<td>(82.2°C)</td>
<td>(-1.1°C)</td>
<td>(82.2°C)</td>
<td>(93.3°C)</td>
</tr>
<tr>
<td>T2</td>
<td>-99°F</td>
<td>-109°F</td>
<td>-125°F</td>
<td>-59°F</td>
<td>69°F</td>
<td>94°F</td>
</tr>
<tr>
<td></td>
<td>(-72.8°C)</td>
<td>(-78.3°C)</td>
<td>(-87.2°C)</td>
<td>(-50.6°C)</td>
<td>(25.6°C)</td>
<td>(34.4°C)</td>
</tr>
<tr>
<td>T3</td>
<td>-117°F</td>
<td>-111°F</td>
<td>-190°F</td>
<td>-32°F</td>
<td>9°F</td>
<td>-85°F</td>
</tr>
<tr>
<td></td>
<td>(-82.8°C)</td>
<td>(-79.3°C)</td>
<td>(-123.3°C)</td>
<td>(-35.6°C)</td>
<td>(-12.8°C)</td>
<td>(-65°C)</td>
</tr>
<tr>
<td>T4</td>
<td>-159°F</td>
<td>-172°F</td>
<td>-222°F</td>
<td>-95°F</td>
<td>-52°F</td>
<td>DNE</td>
</tr>
<tr>
<td></td>
<td>(-106°C)</td>
<td>(-113.3°C)</td>
<td>(-141.4°C)</td>
<td>(-70.5°C)</td>
<td>(-46.7°C)</td>
<td></td>
</tr>
<tr>
<td>T5</td>
<td>-270°F</td>
<td>-270°F</td>
<td>-320°F</td>
<td>-140°F</td>
<td>-140°F</td>
<td>-79°F</td>
</tr>
<tr>
<td></td>
<td>(-167.8°C)</td>
<td>(-167.8°C)</td>
<td>(-195.6°C)</td>
<td>(-95.6°C)</td>
<td>(-95.6°C)</td>
<td>(-61.7°C)</td>
</tr>
</tbody>
</table>

Four tensile samples were machined for each of the ten weld metal mockups fabricated. Figure 4.37, Figure 4.38, and Figure 4.39 showed stress-strain curves for all tensile samples for one, three, and five wt. pct. nickel in the as-welded condition, respectively. As nickel increased both the YS and UTS increased. Additional stress-strain curves for two and four wt. pct. nickel in the as-welded condition and all the stress-relieved condition stress-strain curves can be found in Appendix B. The yielding behavior changed as nickel was increased. At one wt. pct. nickel, a distinct yield point could be determined. For three and five wt. pct nickel, the yield point was less distinct with a more rounded elastic-plastic transition.
Figure 4.35: Determined transition temperatures in the as-welded condition.
Figure 4.36: Transition temperature curves for one through five wt. pct. in as-welded condition.
Figure 4.37: Stress-strain curves of one wt. pct. nickel in as-welded condition.
Figure 4.38: Stress-strain curves of three wt. pct. nickel in as-welded condition.
Figure 4.39: Stress-strain curves of five wt. pct. nickel in as-welded condition.
A summary of the YS and UTS data are presented in Figure 4.40. The three through five wt. pct. nickel specimens all met the YS and UTS criteria. Both uniform and total elongation can be seen in Figure 4.41. The total elongation criterion of greater than or equal to 18 pct. was sufficed by one through four wt. pct. nickel.

![Figure 4.40: Average YS and UTS values for one through five wt. pct. nickel.](image)

Another important piece of data extracted from tensile testing is the percentage reduction in area. The criterion stated a reduction in area of greater than or equal to 45 pct. would be required. Table 4.6 presents all data for reduction in area for one through five wt. pct. nickel. All nickel contents fulfilled this criterion.

Strain hardening, also known as work hardening, is the increase of strength of the metal as a result of permanent deformation. In plastic deformation, the dislocations move until they are stopped by other obstacles in the crystalline lattice. These obstacles can be grain boundaries, solid solution elements, precipitates, and other dislocations. Dislocation interaction is one of the most effective way to affect dislocations motions because when dislocations
Figure 4.41: Percent elongation versus nickel content.

Table 4.6: Percentage reduction of area for one through five wt. pct. nickel in both as-welded and stress-relieved conditions.

<table>
<thead>
<tr>
<th>Nickel content (wt. pct.)</th>
<th>as-welded</th>
<th>stress-relieved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>79.5</td>
<td>76.9</td>
</tr>
<tr>
<td>2</td>
<td>76.4</td>
<td>73.6</td>
</tr>
<tr>
<td>3</td>
<td>75.7</td>
<td>72.8</td>
</tr>
<tr>
<td>4</td>
<td>73.6</td>
<td>72.1</td>
</tr>
<tr>
<td>5</td>
<td>69.0</td>
<td>67.0</td>
</tr>
</tbody>
</table>
glide on different planes and intersect, they can interfere with each other to form kinks and jogs. The dislocations pile up against each other and become entangled which prevents further permanent deformation of that particular grain.

Calculation of the $\frac{d\sigma}{d\varepsilon}$ values immediately after yielding showed the different plastic deformation behavior of the three different nickel contents. An average $\frac{d\sigma}{d\varepsilon}$ for one, three, and five nickel were calculated as 200, 1100, and 1300 ksi, respectively. From one to three wt. pct. nickel, the calculated average slope increased tremendously demonstrating a increased rate of strain hardening for three wt. pct. nickel. From three to five wt. pct. nickel, the slope did increase but only by approximately 200 ksi.

Figure 4.42 gives the calculated instantaneous strain hardening ($n_{ins}$) from after yielding up to the UTS from true stress values. Beyond UTS, non-uniform elongation occurred. The break in the data points was a change in displacement rate of 0.05 cm per min. (0.02 inch per min.) up to 4 pct. deformation, then 0.13 cm per min. (0.05 inch per min) for the remainder of the test to speed up the testing process. The second graph on the right in Figure 4.42 gives the engineering stress and strain curves that were used to determine the $n_{ins}$. Figure 4.42 shows a definitive change in the trends for $n_{ins}$ from three to four wt. pct. nickel in the as-welded condition. In addition, the engineering stress-strain curves also showed a change in strain hardening behavior from three to four wt. pct. nickel. Additional data sets 2, 3, and 4 are included in Appendix C. Average values for the $n_{ins}$ in the as-welded condition were determined and presented in Table 4.7. As nickel content increased, the average $n_{ins}$ increased with larger increases between one and two wt. pct. nickel of 0.021 and between three and four wt. pct. nickel of 0.022. While it is possible to further pursue the plastic behavior of these welds, it was not deemed part of this work.

From the presented mechanical properties results above, one, three, and five wt. pct. nickel in the as-welded condition showed distinctive changes. Additional techniques including EPMA, DSC, XRD, and EBSD helped shed more light as to what are causing these distinctive changes. Largest change in microhardness measurements were found between one
Figure 4.42: Instantaneous strain hardening for one through five wt. pct. nickel in the as-welded condition Set 1 (left) and respective true stress-strain curves (right).

Table 4.7: Average values for instantaneous strain hardening in as-welded condition.

<table>
<thead>
<tr>
<th>Nickel (wt. pct.)</th>
<th>Average $n_{ins}$</th>
<th>Std. Dev. $\pm$ Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1116</td>
<td>0.0052</td>
</tr>
<tr>
<td>2</td>
<td>0.0908</td>
<td>0.0069</td>
</tr>
<tr>
<td>3</td>
<td>0.0824</td>
<td>0.0056</td>
</tr>
<tr>
<td>4</td>
<td>0.0604</td>
<td>0.0081</td>
</tr>
<tr>
<td>5</td>
<td>0.0498</td>
<td>0.0067</td>
</tr>
</tbody>
</table>
and two and then three and four wt. pct. nickel. The Charpy v-notch transition curves also changed in shape from one to five wt. pct. nickel. For YS and UTS, nickel content of three wt. pct. or greater satisfied the criteria. However, for total elongation, four wt. pct. nickel or below fulfilled the criterion. It should be noted that three and four wt. pct. nickel in the as-welded condition are the weld metal mockups that fulfilled all the criteria set forth in Section 1.1.

In EPMA and EBSD characterization only the as-solidified weld metal was studied. Using EPMA characterization, the effect of nickel on solute segregation and cell/dendrite thickness was addressed.

### 4.3 Electron Probe Micro-Analyzer

The data collected using EPMA assisted in determining experimental partitioning coefficient values of nickel and average dendrite thickness. Line scans were collected across as-solidified weld metal in one, two, four, and five wt. pct. nickel in the as-welded condition. Three wt. pct. nickel was not captured due to contamination issues on the surface of the prepared specimens. Since the mechanical properties of two and three wt. pct. nickel were similar, the two wt. pct. nickel specimen was used instead in microanalyses. An example of line scans performed for one and two wt. pct. nickel is given in Figure 4.43. An example of the measured nickel fluctuations for four and five wt. pct. nickel are shown in Figure 4.44 and Figure 4.45. Table 4.8 gives a summary of the measured values of the microanalyses used in the calculation of partition coefficients, $k$, and thickness of dendrites. Average values for peaks and valleys of the nickel profiles were determined and presented in Table 4.8 allowing for the calculation of average composition ratios. Partitioning coefficient, $k$, is defined as the ratio of the concentrations at the solidus, $c_S$, and liquidus, $c_L$, at a given temperature and is given in Eq: 4.1.

$$k = \frac{c_S}{c_L}$$ (4.1)
It determines the extent to which solute is rejected into the liquid during solidification. Since experimental k values were found to be less than one, the solid forming would have a lower nickel content than the liquid. Nickel atoms are rejected from the solid cell (dendrite cores) as it forms and accumulates in the intercellular liquid (interdendritic regions). Therefore, locations with higher nickel concentrations in the form of EPMA peaks were considered interdendritic regions; dendritic cores which solidified first would have lower nickel concentrations.

The average peaks, which correspond to average nickel composition in wt. pct. in the interdendritic regions, were 1.5, 2.4, 4.5, and 5.6 for one, two, four, and five wt. pct. nickel, respectively, in the as-solidified weld metal. The average nickel composition of the dendrite core regions as represented by the average valleys were 1.0, 1.8, 3.9, and 4.9. Partitioning coefficient values were calculated using Eq: 4.1. The partitioning coefficients increased with increasing nickel. Additionally, partitioning coefficients were determined using an Fe-Ni phase diagram for the compositions of one, two, four, and five wt. pct. nickel. The estimated values based on the Fe-Ni binary phase diagram compared well with the EPMA measured partitioning coefficient values for the steel weld compositions.

The distance between two peak compositions (or valleys) gave the thickness of the individual dendrites or cells. The decreasing average dendrite thicknesses of 38, 26, 20, and 14 µm were observed for one, two, four, and five wt. pct. nickel, respectively. An increase in nickel composition increased partitioning coefficient and decreased dendrite thickness.

Table 4.8: Measured cellular dendritic spacing from EPMA data.

<table>
<thead>
<tr>
<th>Nickel (wt. pct.)</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Peaks (wt. pct. Nickel)</td>
<td>1.5</td>
<td>2.4</td>
<td>4.5</td>
<td>5.6</td>
</tr>
<tr>
<td>Avg. Valleys (wt. pct. Nickel)</td>
<td>1</td>
<td>1.8</td>
<td>3.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Partitioning coefficient from EPMA data (k)</td>
<td>0.67</td>
<td>0.75</td>
<td>0.87</td>
<td>0.88</td>
</tr>
<tr>
<td>Avg. Distance btw Peaks and Valleys (µm)</td>
<td>19</td>
<td>13</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Avg. Dendrite Thickness (µm)</td>
<td>38</td>
<td>26</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>Partitioning coefficient from Fe-Ni Phase Diagram (k)</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Figure 4.43: EPMA line scans for 1 wt. pct. (left) and 2 wt. pct. (right) nickel in the as-welded condition in as-solidified weld metal.

Figure 4.44: EPMA line scan four wt. pct. nickel in the as-welded condition in as-solidified weld metal.
Figure 4.45: EPMA line scan for five wt. pct. nickel in as-welded condition in as-solidified weld metal.
A cellular dendritic structure was revealed using 10% nital and captured in LOM for the five wt. pct. nickel weld, Figure 4.46. The dark over-etched cell outlines defined the inter-cellular dendritic regions and the lighter regions were considered the cellular dendrite core regions. From the micrographs, the average cellular dendrite thickness for five wt. pct. nickel was $21.7 \pm 1.7 \mu m$. This value was slightly higher than the EPMA measured average dendrite thickness of $14\mu m$ for five wt. pct. nickel but comparable to the four wt. pct. value of $20 \mu m$.

The EPMA data showed a decrease in average dendrite thickness with an increase in nickel content. This observed change in the substructure drove the further study of the effect of nickel on primary solidification mode. Using DSC, the HSLA steel multiple pass weld mockups were further analyzed to determine additional effects on the solidification mode, phase transformation temperatures and exothermic reactions upon cooling.
4.4  Differential Scanning Calorimetry

DSC measurements were performed on one, three, and five wt. pct. nickel weld mockups in the as-welded condition. Figure 4.47 gives the DSC scans for one and five wt. pct. nickel using the Netzsch equipment. Shifts in the endo- and exothermic reactions were noticed as a function of nickel content in the bulk specimen that contained as-solidified and reheated steel weld metal. Using the five wt. pct nickel scan from Figure 4.47 as an example, several reactions were observed. Following the heating curve, the higher solid black line from the left of the graph, melting occurred at approximately 1530°C. Upon cooling to approximately 1425°C and 613°C, two exothermic reactions occurred.

For one wt. pct. nickel upon cooling, two higher temperature events were determined as B and C from Figure 4.48. The first event represented a primary delta-ferrite (δ-ferrite) solidification at point B at 1495°C (2723°F) which fits the Fe-C diagram range of the more stable BCC crystal structure from 1539°C (2802°F) to 1390°C (2530°F). The second event at point C represented the formation of austenite at 1391°C (2536°F) which was below the peritectic reaction at 1495°C (2723°F) on the Fe-C diagram. The five wt. pct. nickel scan in Figure 4.48 showed only one exothermic event occurring at 1425°C (2597°F), point D. Comparison of the two scans demonstrated a shift in the primary solidification mode from δ-ferrite to austenite. Figure 4.49 is similar to Figure 4.48 with the exception that Setaram equipment was used to perform the DSC experiments.

Individual scans for one, three, and five wt. pct. nickel using both Netzsch and Setaram equipment can be found in Appendix E. For the three wt. pct. nickel, the Netzsch scan displayed two high temperature events that occurred at closer temperature ranges than one wt. pct. nickel. For the Setaram, the three wt. pct. nickel showed only one event occurring at a lower temperature, close to 1400°C (2552°F), which signified a primary austenite solidification mode. Thus, the shift from primary δ-ferrite solidification to primary austenite solidification occurred somewhere between three and five wt. pct. nickel.
Figure 4.47: DSC for one and five wt. pct. nickel using Netzsch equipment.
Figure 4.48: DSC one and five wt. pct. nickel for high temperature events using Netzsch equipment.
Figure 4.49: DSC one and five wt. pct. nickel for high temperature events using Setaram equipment.
The cooling curves in the lower temperature region for one, three, and five wt. pct. nickel for both Netzch and Setaram are given in Figure 4.50 and Figure 4.51. The exothermic reactions associated with the lower temperature curves upon cooling described the ferrite phase transformations. Using portions of existing codes of a programming language called Python, a new logic was developed to deconvolute the lower temperature curves upon cooling. Implementing a peak finder and a sub peak finder, peaks were identified within the DSC data and a combination of Haar and Ricker wavelets were used to delineate the DSC curves. Haar wavelets are the simplest wavelets good for detecting sudden changes but not continuous and differentiable. Ricker wavelets are zero-phase wavelets with a central peak and two smaller side lobes. Ricker wavelets can be specified using the determined peaks with the peak finder function and used as a continuous wavelet transform. Also known as the Mexican hat wavelet, the Ricker wavelet function \( \psi \) is given by Eq: 4.2. The symbol, \( \sigma \), represents the width of the Ricker wavelet and x can be time or temperature depending on the data acquired.

\[
\psi = \frac{-2}{\sqrt{\pi} \sqrt{3\sigma}} \left( \frac{x^2}{\sigma^2} - 1 \right) \exp \left( -\frac{x^2}{2\sigma^2} \right) \tag{4.2}
\]

Using a Gaussian distribution fit for the continuous wavelet transforms, the DSC curves were deconvoluted to two main ferrite transformation events that occurred at high and low temperatures. High temperature ferrite transformations could consist of GBF (allotriomorphic ferrite), IF and pearlite. These are the Event 1 products. Low temperature ferrite transformations could consist of WF, AF, and bainite morphologies (bainitic ferrite, UB, LB, GB, and CB) Event 2 products. Using the Python code, a summary of the DSC data for one, three, and five wt. pct. nickel using the Setaram equipment is given in Table 4.9. The rows of 1 Nickel, 3 Nickel, and 5 Nickel gave the raw data obtained from the DSC experiments. Event 1 and Event 2 were extracted data from the deconvolution using the logic given in Appendix F.

The deduced amount of energy involved in Event 1 transformations were 24, 19, and 30 pct. for one, three, and five wt. pct. nickel, respectively. The percent energy distribution of
those ferrite transformation events are shown in Figure 4.52. Event 2 accounted for energy released during the low temperature ferrite transformations determined as 62 pct. for one wt. pct. nickel, 75 pct. for three wt. pct nickel, and 54 pct. for five wt. pct. nickel, also shown in Figure 4.52. From prior discussions on the onset of solidification for the alloys, one and three wt. pct. nickel should solidify as primary δ-ferrite whereas five wt. pct. nickel should solidify as primary austenite. For the one wt. pct. nickel, upon heating, melting occurred at approximately 1525°C. During cooling, solidification began at 1495°C. For the five wt. pct. nickel, the solidification temperature was lowered to 1425°C indicating a larger undercooling. The larger undercooling corroborated with the suppression of the δ-ferrite solidification and austenitic cellular structure observed in the as-solidified five wt. pct. nickel specimen using LOM, Figure 4.53.

To further discuss the austenite-ferrite transformation, Figure 4.52 shows that with an increase in nickel content from one to three wt. pct. the amount of the higher temperature ferrite transformation products (GBF (allotriomorph ferrite), IF, and pearlite) decreased. Instead, the amount of the lower temperature ferrite transformation products (WF, AF, and bainite morphologies) was observed to increase. It was clear that increasing nickel refined the ferritic weld metal microstructure. In Figure 4.54, the ferrite transformation temperature decreased with increasing nickel content. Additionally, the temperature range of the higher temperature ferrite transformation products became narrower with increasing nickel content as compared to the temperature range of the lower temperature ferrite transformation products. Increasing nickel content favored lower temperature ferrite transformation products.

Additional data related to the DSC experiments can be found in Appendix E. Using JMatPro, simulated CCT and TTT diagrams and hardness were obtained to validate some of the experimental data.
Figure 4.50: DSC one, three, and five wt. pct. nickel for last curve upon cooling using Netzsch equipment.

Table 4.9: Python deconvolution for one, three, and five wt. pct. nickel in as-welded condition using the Setaram equipment.

<table>
<thead>
<tr>
<th></th>
<th>Onset (°C)</th>
<th>Offset (°C)</th>
<th>Energy (µV·s/mg)</th>
<th>Temp. Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Nickel</td>
<td>854</td>
<td>658</td>
<td>-4.61</td>
<td>196</td>
</tr>
<tr>
<td>Event 1</td>
<td>824</td>
<td>750</td>
<td>-1.09</td>
<td>74</td>
</tr>
<tr>
<td>Event 2</td>
<td>780</td>
<td>670</td>
<td>-2.85</td>
<td>110</td>
</tr>
<tr>
<td>3 Nickel</td>
<td>685</td>
<td>590</td>
<td>-7.43</td>
<td>95</td>
</tr>
<tr>
<td>Event 1</td>
<td>680</td>
<td>630</td>
<td>-1.4</td>
<td>50</td>
</tr>
<tr>
<td>Event 2</td>
<td>665</td>
<td>595</td>
<td>-5.56</td>
<td>70</td>
</tr>
<tr>
<td>5 Nickel</td>
<td>649</td>
<td>541</td>
<td>-7.8</td>
<td>108</td>
</tr>
<tr>
<td>Event 1</td>
<td>640</td>
<td>600</td>
<td>-2.3</td>
<td>40</td>
</tr>
<tr>
<td>Event 2</td>
<td>630</td>
<td>550</td>
<td>-4.21</td>
<td>80</td>
</tr>
</tbody>
</table>
Figure 4.51: DSC one, three, and five wt. pct. nickel for last curve upon cooling using Setaram equipment.
Figure 4.52: Energy percentage of high and low temperature ferrite transformations.

Figure 4.53: LOM image of cellular dendritic structure of five wt. pct. nickel in the as-solidified weld metal in the as-welded condition.
4.5 Simulated Continuous Cooling Transformation Curves

To study the phase transformations of the alloys, thermodynamic calculations were conducted using a commercial software, JMatPro, that simulated continuous cooling transformation (CCT) and time-temperature transformation (TTT) behavior of alloys. The simulation, however, did not take into account the reheated weld metal of the multipass mockups since the software does not consider post-weld heat treatment. Continuous cooling transformation and TTT diagrams were helpful in determining the temperature-time processing history that could achieve defined mechanical properties. Continuous cooling transformation diagrams measured the extent of transformation as a function of time for a continuously decreasing temperature. The CCT diagrams for one, three, and five wt. pct. nickel are presented in Figure 4.55, Figure 4.56, and Figure 4.57. The phase fields identified on these diagrams were ferrite, pearlite, bainite, austenite, and martensite. Only the martensite start temperature was identified. From one, three, and five wt. pct nickel CCT diagrams, the ferrite transformation start curves decreased in temperature range from approximately 760-593°C.
(1400-1100°F), 677-538°C (1250-1000°F), and 538°C (1000°F), respectively. The increase in nickel content also showed a decrease in $A_{c1}$ and $A_{c3}$. Thus, the CCT diagrams showed that ferrite phase transformation was suppressed to lower temperatures with the increase of nickel. This behavior was to be expected since nickel is an austenite stabilizer. The bainite transformation curves were shown to be suppressed and shifted to longer delay times. For one, three, and five wt. pct. nickel, the bainite curves ranged from 593-427°C (1100-800°F), 538-371°C (1000-700°F), and 510-371°C (950-700°F), respectively. As expected, martensite start temperatures were also suppressed further increasing the strength of the expected as-solidified weld metal in the as-welded condition. The cooling rate of the weld mockups were experimentally determined with a small number of measurements during welding and was found to be similar to the cooling curves furthest right in the CCT calculated figures.

The calculated VHNs using JMatPro for the one and three wt. pct. nickel were consistent with values determined experimentally for the as-solidified weld metal given as 236 and 269 VHNs, respectively. The 236 VHN data fell between the 218 VHN of the first cooling curve furthest right and 251 VHN of the second cooling curve for one wt. pct. nickel. Three wt. pct. nickel experimentally averaged a value of 269 VHN which was closer to 267 VHN of the first cooling curve of Figure 4.56. The measured average of five wt. pct. nickel was 303 VHN which was lower than 361 VHN of the cooling curve furthest right in Figure 4.57.

Using the first cooling curve furthest right on the figure, ferrite transformation began at approximately 677°C (1250°F) and then bainite transformation began at approximately 593°C (1100°F) for one wt. pct. nickel. For three wt. pct. nickel, the first cooling curve did not intersect the ferrite transformation curve, but the bainite transformation curve was intersected at 538°C (1000°F). Lastly, the first cooling curve for five wt. pct. nickel intersected the bainite transformation curve at 510°C (950°F) and then intersected martensite start temperature at 316°C (600°F). The VHNs simulated using JMatPro corroborated well with the measured VHNs for one and three wt. pct. nickel, but not for five. wt. pct. nickel. However, the trend of increased hardness with increasing nickel was verified using both mea-
sured and JMatPro simulations. In addition, bainite transformation was more dominant with increased nickel content shown in the CCT diagrams using the cooling curve furthest right (closest to the experimentally measured weld cooling rate). The corresponding TTT diagrams are presented in Appendix D and will not be discussed here.

Figure 4.55: Continuous cooling transformation curves for one wt. pct. nickel in as-welded condition with VHNs.

The simulated transformation temperatures using JMatPro were summarized in Table 4.10 for one, three, and five wt. pct. nickel. An increase in nickel decreased $A_{C_3}$ delaying ferrite transformation, in turn decreasing the duration of ferrite transformation and minimizing time for growth of ferrite grains. Increasing nickel content should decrease ferrite grain size thereby increasing strength and toughness. In the next Section, results from the XRD analysis technique should help further explain the effect of nickel on mechanical properties through strain and precipitates.
Figure 4.56: Continuous cooling transformation curves for three wt. pct. nickel in as-welded condition with VHNs.

Table 4.10: Transformation temperatures from JMatPro simulations.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_C_3$</td>
<td>814.9°C (1498.8°F)</td>
<td>763.3°C (1405.9°F)</td>
<td>725.3°C (1337.5°F)</td>
</tr>
<tr>
<td>$A_C_1$</td>
<td>680.4°C (1256.7°F)</td>
<td>640.7°C (1185.3°F)</td>
<td>612.8°C (1135°F)</td>
</tr>
<tr>
<td>Martensite Start ($M_s$)</td>
<td>403.1°C (757.6°F)</td>
<td>363.4°C (686.1°F)</td>
<td>329.1°C (624.3°F)</td>
</tr>
<tr>
<td>Martensite 50% ($M_{50}$)</td>
<td>369.8°C (697.6°F)</td>
<td>328.9°C (624.1°F)</td>
<td>293.8°C (560.8°F)</td>
</tr>
<tr>
<td>Martensite 90% ($M_{90}$)</td>
<td>292.4°C (558.4°F)</td>
<td>249.3°C (480.7°F)</td>
<td>211.8°C (413.2°F)</td>
</tr>
</tbody>
</table>
Figure 4.57: Continuous cooling transformation curves for five wt. pct. nickel in as-welded condition with VHNs.
4.6 X-Ray Diffraction (XRD)

The XRD spectra for the one, three, and five wt. pct. nickel are shown in Figure 4.58, Figure 4.59, and Figure 4.60, respectively. The peaks for all the XRD profiles prominently displayed all the BCC planes of (110), (200), (211), (220), (310), and (222). In Figure 4.60, additional peaks were seen consistent with MnNi$_3$ and FeNi$_3$. Previous structural and neutron diffraction studies [48] have shown that the intermetallic compound MnNi$_3$ crystallizes in the cubic AuCu$_3$ structure type, with a lattice parameter of $a=3.5\AA$. The peaks for the MnNi$_3$ intermetallic compound were seen at 43° (111), 51° (200), 75° (220), and very small peaks can be detected at 91° (311) and 97° (222) which were consistent with literature results for the intermetallic compound [46]. Research for the FeNi$_3$ intermetallic compound in Fe-Ni alloys has been of particular interest due to its ordered nature below a critical temperature of 765K (492°C). In the ordered state, FeNi$_3$ also has the well know AuCu$_3$ structure, which corresponded to L$_{12}$ FCC phase (Pm3m space group), with iron atoms located in the corners and nickel atoms at the center of the faces. Disordered FeNi$_3$ showed peaks at 43° (111), 49° (200), and 75°(220). Ordered FeNi$_3$ should also show the superlattice peaks associated with the single cubic form of the intermetallic compound with additional (100), (110), (210), and (211) peaks [59]. The measured data showed the first peak of (111) overlapped with the (110) peak of the BCC matrix thus only one peak was seen. Additional distinct peaks were seen at 51° (200) and 75° (220). An intermetallic compound was determined to exist from the five wt. pct. nickel XRD data, but without further investigation it could not be determined whether it was MnNi$_3$ or FeNi$_3$.

In an iron lattice, the presence of nickel could also result in FeNi$_3$ as well as MnNi$_3$ given the right conditions. Local nickel concentration has to be sufficient to form the stoichiometric compound. Regarding the detection of the intermetallic compound for the five wt. pct. nickel welds, the formation temperatures of MnNi$_3$ was 530°C and for FeNi$_3$ was 490°C [46, 59]. Assuming that the same temperatures hold true in a steel, these intermetallic compounds could form both along interdendritic regions (solute-rich zones) and heterogeneously in the
ferrous matrix. Typically, lower transformation intermetallic compounds could assist in minimizing ferrite grain size and strengthening the material. It may be of interest to further pursue more detailed characterization to clarify this point in the future.

Figure 4.58: XRD profiles for one wt. pct. nickel.

Figure 4.59: XRD profiles for three wt. pct. nickel.

Using the equations and explanation of the analytical procedure provided in Section 3.9, a Williamson-Hall (WH) plot of one wt. pct. nickel was developed using data from Figure 4.58 and shown in Figure 4.61. In Figure 4.61, the y-axis is defined as $\beta^* = \beta \cos\left(\frac{\theta}{\lambda}\right)$ where $\beta$ is the full width at half maximum intensity and the x-axis is $K = 2\sin\left(\frac{\theta}{\lambda}\right)$. When the
peak broadening did not change linearly with the diffraction peak, the material exhibited anisotropic behavior in terms of strain. This relationship can be seen in Figure 4.61 since the breadth of the XRD profile increased with diffraction angle and then decreased. To account for this anisotropic strain broadening, Ungar and Borbely’s [56] modified WH plot was used to determine the average strain. In Figure 4.62, the modified WH plot was shown with the breadths of the peaks including an estimated average contrast factor, $\bar{C}$. Plotting a best fit linear line with a high coefficient of determination, 0.983, the slope was determined as $3.96 \times 10^{-3}$ which was the average strain for one wt. pct. nickel.

Using this modified WH plot approach to decipher anisotropic strain broadening, average strain results for three and five wt. pct nickel were calculated. The results are summarized in Table 4.11. An increase in nickel showed an increase in average measured strain. This increase in strain could be attributed to lattice strain caused by the nickel atom in the iron matrix. Additionally, the increase in average measured strain can also be related to dislocation density. Similar application of XRD profile analysis has been used to characterize aging behavior of maraging steel (M250). Williamson-Hall plots showed anisotropic broadening with diffraction angle and the modified WH plots calculated the normalized mean square
Figure 4.61: Williamson Hall plot for one wt. pct. nickel.

Figure 4.62: Modified Williamson Hall plot for one wt. pct. nickel.
strain. The amount of strain was used to observe the effects of isothermal aging for different
lengths of time \cite{35}. To verify the increase in average measured strain from the XRD data,
existing mathematical models were used to calculate bainite start temperatures and their
respective dislocation densities. Bainite start temperature, Eq: 4.3 from Stevens and Haynes
\cite{52}, was used and given as follows:

\[ B_s (^\circ C) = 830 - 270C - 90Mn - 37Ni - 70Cr - 83Mo \]  \hspace{1cm} (4.3)

Bhadeshia’s \cite{4} dislocation density calculation based on phase transformation start tem-
perature, T, 4.4 was used and given as follows:

\[ \log \rho_d = 9.28480 + \frac{6880}{T} + \frac{1780360}{T^2} \]  \hspace{1cm} (4.4)

Using the values calculated from the above mathematical equations, Figure 4.63 was
plotted using the calculated dislocation density values for the y-axis and the bainite start
temperature values for the x-axis. As nickel increased from one to five wt. pct. in increments
of one wt. pct., the bainite start temperature decreased from 577$^\circ$C, 539$^\circ$C, 502$^\circ$C, 465$^\circ$C,
and 428$^\circ$C, respectively, and the dislocation density increased. This calculated trend from
validated mathematical equations reinforced that as nickel increased, dislocation density and
strain increased.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Average Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Nickel</td>
<td>3.96×10^{-3}</td>
</tr>
<tr>
<td>3 Nickel</td>
<td>4.14×10^{-3}</td>
</tr>
<tr>
<td>5 Nickel</td>
<td>9.79×10^{-3}</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis did further substantiate increasing nickel increased strength
and toughness through strain increase and a formation of a low temperature intermetallic
compound. The last analysis technique pursued was EBSD which should help determine the
effect of nickel on effective grain size, qualitative dislocation density, and grain misorientation
relationship.
Figure 4.63: Dislocation density of bainite as a function of the transformation start temperature.
4.7 Electron Backscatter Diffraction (EBSD)

Electron backscatter diffraction scans were performed for one, three, and five wt. pct. nickel in the as-solidified weld metal, Figure 4.64, Figure 4.65, and Figure 4.66. These examples of orientation image maps (OIM) along with the inverse pole figure (IPF) maps showed a distinct trend of grain refinement and a more preferred crystallographic orientation as nickel wt. pct. was increased. In Figure 4.64 and Figure 4.65, the inverse pole figures showed a more random distribution of the crystallographic directions of the grains at one wt. pct. nickel. In Figure 4.66 at five wt. pct. nickel, the inverse pole figure showed a more preferred crystallographic directions of the grains in the [111] and the [001] directions. An increase in nickel content beyond three wt. pct. promoted the preferred orientation.

Using the same three EBSD scan examples for one, three, and five wt. pct nickel, kernel average misorientation (KAM) maps were created to demonstrate strain effects, i.e. dislocation density, in Figure 4.67, Figure 4.68, and Figure 4.69. The kernel average misorientation (KAM) showed local misorientation of each point in the microstructure with respect to its neighboring points. Assuming that local misorientation gradients were formed from dislocation...
Figure 4.65: Example of orientation image map for three wt. pct. nickel in the as-solidified region.

Figure 4.66: Example of orientation image map for five wt. pct. nickel in the as-solidified region.
tions, the KAM map could be used as a qualitative measure of stored energy to characterize the distribution of dislocation density. With the white regions being areas of stored energy, i.e. high dislocation densities, with increasing nickel, dislocation density increased. The KAM maps verified the measured average strain determined using XRD peak profiles, that is i.e. increasing nickel increased strain.

It could be seen that as nickel increased ferrite grains were refined, Figure 4.70, thus increasing the total length of grain boundaries available in the matrix. The average effective ferrite grain size for one, three, and five wt. pct. nickel were 2.9, 2.4 and 1.7 μm with standard deviations of ±0.28, 0.24, and 0.22 μm. In Figure 4.71, Figure 4.72, and Figure 4.73, high angle grain boundaries (HAGBs) were shown in red. Average values were extracted from the EBSD scan for one, three, and five wt. pct. nickel in total grain boundary length as 2.37, 2.65, and 3.07 mm with standard deviations of ±0.25, 0.2, 0.31 in mm, respectively. The effect of nickel on increasing HAGBs grain refinement can be seen in Figure 4.74.

Figure 4.67: Examples of KAM map for one wt. pct. nickel in the as-solidified region.
Spatial orientation distributions were also extracted from the EBSD scans and plotted to demonstrate the change in misorientation distribution. In more recent literature [22–26, 30], different types of bainite have been proposed beyond the classical upper bainite and lower bainite. Bainite morphologies today include lath-like upper bainite, lower bainite, bainitic ferrite, granular bainite, and coalesced bainite. Better characterization and distinction of these different types of morphologies in the present welds and as a function of nickel content would be desirable. Microstructural components like martensite, upper bainite, lower bainite, and granular bainite showed distinct misorientation distributions due to their displacive formation mechanism. The crystallographic relationship determined by Kurdjumov and Sachs were followed to differentiate transformed variants of bainite. In ferritic transformations, a more random distribution existed with a maximum misorientation at $45^\circ$ [2]. Thus, the shape of the misorientation distribution function should be an indicator of the type of microstructure, but a quantification of the phase fractions should not be based on
the misorientation distribution alone. Figure 4.75, Figure 4.76, and Figure 4.77 shows the bar graphs of the misorientation distribution for the OIM maps from Figure 4.64, Figure 4.65, and Figure 4.66. Using Figure 4.78 and Figure 4.79 from Zajac et al.’s work [65], Figure 4.75, Figure 4.76, Figure 4.77 were graphed similarly with the x-axis as the misorientation angle in degrees and the y-axis as the number of pixels. One wt. pct. nickel showed a misorientation distribution similar to three wt. pct. nickel with the exception that the number of pixels between 40° to 60° went from an average 27,037 to 29,433 pixels. Additionally, using Zajac et al.’s work [65], both one and three wt. pct. nickel misorientation distribution were consistent to granular bainite. The five wt. pct. nickel displayed a misorientation distribution with a larger number of pixels less than 10° and greater than 40°. The number of pixels between 40° to 60° was averaged at 37,345 pixels. According to Zajac et al.’s work [65], five wt. pct. nickel gave a mixture of upper, granular, and lower bainite as compared to one and three wt. pct. nickel of mostly granular bainite.
Figure 4.70: Effect of nickel in wt. pct. in as-solidified region on effective ferrite grain size.
Figure 4.71: Example of KAM map with high angle grain boundaries (red) and coincidence site lattice (green) for one wt. pct. nickel in the as-solidified region.
Figure 4.72: Example of KAM map with high angle grain boundaries (red) and coincidence site lattice (green) for three wt. pct. nickel in the as-solidified region.
Figure 4.73: Example of KAM map with high angle grain boundaries (red) and coincidence site lattice (green) for five wt. pct. nickel in the as-solidified region.
In summary from the IPF maps, a more preferred orientation was clear as nickel was increased. Kernel average maps verified calculated XRD strain values in which dislocation density increased with nickel additions. As nickel increased, the effective ferrite grain size was decreased which can also be seen in Figure 4.80 of SEM images of one and five wt. pct nickel. Increase in nickel also increased the total average length of HAGBs making it more difficult for dislocation motion. Misorientation distributions showed that an increase in nickel content increased misorientations between 40° to 60°. Using Zajac’s theory on the shape of misorientation distributions to identify bainite types, at one and three wt. pct nickel, granular bainite was the dominant bainitic morphology. For five wt. pct nickel, a combination of upper, lower, and granular bainite was determined which was demonstrated in the finer microstructure.

4.8 Descriptive Model

Using the one wt. pct. as the low nickel content and five wt. pct. as the high nickel content, a brief discussion incorporating all the results presented above was discussed. Figure 4.81 gave the pictorial version of the descriptive model that summarizes the effect of
Figure 4.75: Bar graph for misorientation distribution for one pct. nickel in as-solidified region from Figure 4.64.
Figure 4.76: Bar graph for misorientation distribution for three pct. nickel in as-solidified region from Figure 4.65.
Figure 4.77: Bar graph for misorientation distribution for five pct. nickel in as-solidified region from Figure 4.66.
Figure 4.78: EBSD orientation maps and distribution of the misorientation angles of ferritic grains in (a) granular bainite, (b) upper bainite, and (c) lower lath-bainite [65].

Figure 4.79: Misorientation distribution for lower bainite, upper bainite, and granular bainite [65].
nickel on strengthening and toughening mechanisms through understanding the differences in solidification, solute segregation, and all phase transformations. Starting from the top of the schematic of the descriptive model, the low and high nickel content was compared and differences were clearly indicated and described to explain the higher strength and better toughness. For the low nickel content, primary solidification mode was $\delta$-ferrite which began at approximately 1490°C. For the high nickel content, primary solidification mode was austenite and began at approximately 1390°C. During solidification, nickel segregated to the interdendritic regions of the primary dendrite phases. As temperature decreased to 1400°C, austenite transformation occurred at low nickel content which nucleated from the solute-rich interdendritic regions. Austenite transformation did not occur for high nickel content welds because the primary solidification mode was austenite. The next transformation was the ferrite transformation Event 1 defined from the DSC deconvolution. For low nickel content, this transformation occurred at approximately 820°C and most likely in the form of grain boundary ferrite; for high nickel content, this transformation occurred at 650°C and most likely in the form of idiomorphic ferrite which formed intragranularly. The next step was the ferrite transformation Event 2 which included Widmanstätten ferrite, acicular ferrite, bainitic ferrite, upper bainite, lower bainite, coalesced bainite, and granular bainite. For

Figure 4.80: SEM images for one (left) and five (right) wt. pct nickel in the as-solidified region.
low and high nickel content, this transformation occurred at 780°C and 640°C, respectively. For high nickel content, an intermetallic compound precipitated in either the form of MnNi$_3$ or FeNi$_3$ at 520°C or 490°C, respectively. These precipitates can form both inter and intragranularly within the iron matrix. Whether the precipitates are MnNi$_3$ or FeNi$_3$, the strengthening of the lattice will occur.

In summary, the strengthening and toughening mechanisms could be separated into the following: mechanical properties, grain size, solid solution, microstructure, and precipitates. First, mechanical properties (YS, UTS, NDT$_{35 ft-lbs}$, and VHN) were determined with respect to increasing nickel content to evaluate if nickel did in fact increase strength and toughness and then weld specimens that satisfied the criteria were selected to be further investigated. One critical strengthening and toughening mechanism attributed to the increase in nickel was grain size. Through characterization using EPMA and EBSD, it was determined that the size of the cellular dendrite decreased and that the effective grains were refined with increasing nickel content. Solid solution strengthening and toughening was demonstrated with an increased bulk specimen strain through XRD and qualitative KAM showing an increase in dislocation density. Using microstructure strengthening and toughening, it was determined that primary solidification mode changed from δ-ferrite to austenite. Also, ferrite transformation temperatures were depressed with the temperature range for high temperature ferrite transformation products shortened. A mixed upper, lower, and granular bainitic structure promoted a more preferred grain misorientation. Lastly, the formation of an intermetallic compound at five wt. pct. nickel could have enhanced the strength and toughness. The transformation mechanisms outlines above clearly demonstrated that as nickel increased in the MIL-105S HSLA steel submerged arc welding mockup, the strength and toughness both increased.
Figure 4.81: Descriptive model for low and high nickel content.
CHAPTER 5
CONCLUSIONS

In the MIL-105S HSLA steel system, submerged arc welding multiple pass weldments were manufactured at one, two, three, four, and five wt. pct nickel in the as-welded and stress-relieved conditions. Mechanical properties in the form of Vicker microhardness, Charpy v-notch testing, and tensile testing were performed to determine which weld mockups fulfilled the main desired properties of $Y_S \geq 85$ ksi, $UTS \geq 105$ ksi, and $NDT_{35ft-lbs} \leq -140^\circ F$. The three and four wt. pct. nickel weld metal mockups in the as-welded condition meet all the criteria.

Focusing the study on the as-welded condition for one, three, and five wt. pct. nickel, advanced techniques were used to give a more detailed understanding of the primary solidification, solute segregation, dendrite thickness, austenite decomposition temperatures and different ferrite transformation products, effective ferrite grain size, dislocation density, grain misorientation distribution, and precipitates. The results from the advanced characterization are summarized in the following:

- Dendrite thickness was refined with increasing nickel content with one and five wt. pct. nickel having values of 38 and 14 $\mu$m, respectively.

- DSC scans showed the change of primary solidification modes between one and five wt. pct nickel from primary $\delta$-ferrite to primary austenite with the increase in nickel. This change in primary solidification mode changes the location of the solute segregation during solidification thereby affecting the location of the lower ferrite transformation products.

- Ferrite transformation temperatures for one, three, and five wt. pct. nickel are 854°C, 685°C, and 649°C. This decrease in ferrite transformation temperature with increasing nickel content shortened the amount of time for the overall transformation to occur.
• For one and three wt. pct nickel, high temperature ferrite transformation products (Event 1) expended a lower percentage of energy than low temperature ferrite transformation products (Event 2). A lower amount of energy was required for GBF, IF, and pearlite formation along the austenite grain boundaries. For five wt. pct nickel, Event 1 required more energy than for one and three wt. pct nickel because the intragranular IF required more energy since the ferrite grain boundaries are solute-rich due to the change in primary solidification mode. Event 2 required less energy since the amount of undercooling was larger helping to drive the WF, AF, and bainite transformations to nucleate and grow in the solute-rich regions.

• JMatPro simulations verified Vicker microhardness values decreasing with increasing nickel. In addition, the depression of ferrite, bainite, and martensite temperature was verified.

• X-ray diffraction results using modified Williamson Hall plots showed an increase in strain of $3.96 \times 10^{-3}$, $4.14 \times 10^{-3}$, and $9.79 \times 10^{-3}$ for one, three, and five wt. pct nickel. Diffraction peak profiles also revealed a MnNi$_3$ or FeNi$_3$ intermetallic compound that existed at five wt. pct. nickel and transformed at 530°C or 490°C, respectively. These intermetallic compounds minimized grain growth to enhance both strength and toughness.

• Electron backscatter diffraction data in the form of IPF maps concluded that increasing nickel gave the bainitic ferrite a more preferred orientation. In addition, KAM maps qualitatively verified the increase in strain, i.e. dislocation density, with the increase in nickel content with the XRD results.

• Average effective ferrite grain size decreased with increasing nickel content. Total average length of HAGBs increased with increasing nickel content. Grain misorientations above 40° increased with increasing nickel giving the grains higher volumes of misorientation within the grains making it more difficult for dislocations to slip thereby
increasing toughness. Using Zajac et al.’s approach in deciphering grain misorientation distribution trend, one wt. pct nickel had a dominant granular bainite structure whereas five wt. pct nickel had a combination of upper, lower, and granular bainite.
CHAPTER 6
FUTURE WORK

The research presented in this thesis has created additional questions of merit to be further pursued. The following is a short list of some of the topics that were derived that will further the understanding of submerged arc welded high strength low alloy steels and the development of microstructures and mechanical properties in these steel welds.

- A thorough analysis should be pursued using advanced techniques to investigate reheated weld metal zones in the multipass weld metal mockup in the as-welded condition. The role that reheated weld metal zones play in the overall mechanical properties development in a multiple pass welds should be better understood.

- The specimens in the stress-relieved condition should be investigated to determine why a deterioration of toughness occurred while strength was retained. Detailed characterization of the microstructure evolution during the stress relief heat treatment should be conducted. Findings in this research topic can assist in creating a more effective post-weld heat treatment for the MIL-105S steel welds.

- Transmission electron microscopy can be performed in both interdendritic and dendrite core regions for one, three, and five wt. pct. nickel to verify the formation of MnNi$_3$ or FeNi$_3$ precipitates and their locations.

- The different types of bainite should be further identified, differentiated and quantified using different advanced tools including transmission electron microscopy. This work will assist in determining if increasing nickel increases or decreases certain types of bainite. The different morphologies of the bainites will determine the strength and toughness combinations in the different microstructures at different nickel additions.
The different phase transformations described in this research can also be further characterized by in-situ, real-time monitoring. For example, laser confocal microscopy can be used to examine the onset and progress of these transformations.

- Additional analysis of the different yielding along with the changes in plastic deformation behavior, e.g. strain hardening, in the specimens with different nickel additions should be conducted. It is important to better understand the differences between the welds with the four and five wt. pct. nickel additions from the lower nickel welds.
REFERENCES CITED


APPENDIX A - ADDITIONAL CHARPY V-NOTCH RELATED GRAPHS AND IMAGES

Additional transition-temperature curves for both the as-welded and stress-relieved conditions for two and four wt. pct. nickel are presented below in Figure A.1 and Figure A.2.

Figure A.1: Charpy v-notch curve for two wt. pct. nickel as-welded (left) and stress-relieved (right).

The Charpy v-notch fracture surface specimen images are presented below for all ten weld metal mockups. Figure A.3, Figure A.4, Figure A.5, Figure A.6, and Figure A.7 are specimen images for one through five wt. pct. nickel in the as-welded and stress-relieved conditions.

The transition temperature curves for one through five wt. pct. nickel for the stress-relieved condition was combined and presented below in Figure A.8. The determined transition temperatures, $T_1$ through $T_5$, were graphed together with respect to nickel content in the stress-relieved condition, Figure A.9. Note that the NDT$_{\text{35 ft- lbs}}$ criterion of $\leq -140^\circ$F was not obtained for any of the stress-relieved condition specimens.
Figure A.2: Charpy v-notch curve for four wt. pct. nickel as-welded (left) and stress-relieved (right).

Figure A.3: Charpy v-notch specimens for one wt. pct. nickel as-welded (left) and stress-relieved (right).
Figure A.4: Charpy v-notch specimens two wt. pct. nickel as-welded (left) and stress-relieved (right).

Figure A.5: Charpy v-notch specimens three wt. pct. nickel as-welded (left) and stress-relieved (right).

Figure A.6: Charpy v-notch specimens four wt. pct. nickel as-welded (left) and stress-relieved (right).
Figure A.7: Charpy v-notch specimens five wt. pct. nickel as-welded (left) and stress-relieved (right).

Figure A.8: Transition temperature curves for one through five wt. pct. nickel in stress-relieved condition.
Figure A.9: Determined transition temperatures in stress-relieved condition.
Upon further investigation into effect of the NDT\textsubscript{35ft-lbs}, the ratio of the stress-relieved over the as-welded condition was determined and plotted against the nickel content to determine whether or not they are related, Figure A.10. Without a determined value for five wt. pct. nickel in the stress-relieved condition at T\textsubscript{4}, it was difficult to see if the distinction between three and four wt. pct. existed. An additional graph using the NDT, T\textsubscript{5}, was determined for the ratio of the two conditions and plotted against nickel content, Figure A.11. A clear distinction can be seen between three and four wt. pct. nickel with five wt. pct. nickel behaving similarly to four wt. pct. nickel. Greater than four wt. pct. nickel led to a different behavior that should be investigated.

![Figure A.10: Ratio of stress-relieved over as-welded condition of NDT\textsubscript{35ft-lbs}, T\textsubscript{4}, as a function of nickel content in wt. pct.](image)

Lateral expansion data, i.e. the lateral change in dimensions of a Charpy impact specimen due to fracture, was measured and collected to characterize plastic deformation. The lateral expansion is the thickening of the specimen during fracturing and was measured as the difference between the initial width parallel to the notch and the final width parallel to the
Figure A.11: Ratio of stress-relieved over as-welded condition of NDT, T₅, as a function of nickel content in wt. pct.

notch after impact testing. It can be seen in the as-welded condition that the trends are similar to the transition temperature curves, Figure A.12.

The lateral expansion data for one through five wt. pct. nickel in the stress-relieved condition with similar trends to the transition temperature curves in the same condition can be seen in Figure A.13.
Figure A.12: Lateral expansion for one through five wt. pct. nickel in the as-welded condition.
Figure A.13: Lateral expansion for one through five wt. pct. in the stress-relieved condition.
APPENDIX B - ADDITIONAL STRESS-STRAIN GRAPHS

The stress-strain curves for one, three, and five wt. pct. nickel in the Sr condition is presented in Figure B.1, Figure B.2, and Figure B.3. Additional stress-strain curves for both two and four wt. pct. nickel in both as-welded and stress-relieved condition is given in Figure B.4 and Figure B.5.

Figure B.1: Stress-strain curves of one wt. pct. nickel in stress-relieved condition.
Figure B.2: Stress-strain curves of three wt. pct. nickel in stress-relieved condition.
Figure B.3: Stress-strain curves of five wt. pct. nickel in stress-relieved condition.

Figure B.4: Stress-strain curves for two wt. pct. nickel in both as-welded (left) and stress-relieved (right) condition.
Figure B.5: Stress-strain curves for four wt. pct. nickel in both as-welded (left) and stress-relieved (rig) condition.
The instantaneous strain hardening graphs for Set 2, Set 3, and Set 4 in the as-welded condition are shown in Figure C.1, Figure C.2, and Figure C.3, respectively. The respective stress-strain curves used to determine the instantaneous strain hardening data were presented in Appendix B with respect to the nickel content.

Figure C.1: Instantaneous strain hardening for one through five wt. pct. nickel in the as-welded condition Set 2.

For the stress-relieved condition, instantaneous strain hardening graphs for Set 1 along with the respective stress-strain curves used, Set 2, Set 3, and Set 4 are given in Figure C.4, Figure C.5, Figure C.6, and Figure C.7, respectively. The respective stress-strain curves used to determine the instantaneous strain hardening data were presented in B with respect to the nickel content.
Figure C.2: Instantaneous strain hardening for one through five wt. pct. nickel in the as-welded condition Set 3.
Figure C.3: Instantaneous strain hardening for one through five wt. pct. nickel in the as-welded condition Set 4.

Figure C.4: Instantaneous strain hardening for one through five wt. pct. nickel in the stress-relieved condition Set 1 (left) and respective engineering stress-strain curves (right).
Figure C.5: Instantaneous strain hardening for one through five wt. pct. nickel in the stress-relieved condition Set 2.
Figure C.6: Instantaneous strain hardening for one through five wt. pct. nickel in the stress-relieved condition Set 3.
Figure C.7: Instantaneous strain hardening for one through five wt. pct. nickel in the stress-relieved condition Set 4.
The average instantaneous strain hardening graphs for the stress-relieved condition is presented in Figure C.8.

Figure C.8: Average values for instantaneous strain hardening in stress-relieved condition versus nickel content.
APPENDIX D - TIME-TEMPERATURE TRANSFORMATION DIAGRAMS

The TTT diagrams measure the rate of transformation at a constant temperature. Figure D.1, Figure D.2, and Figure D.3 are TTT diagrams for one, three, and five wt. pct. nickel as-solidified weld metal in the as-welded condition.

Figure D.1: Time-temperature transformation curves for one wt. pct. nickel in as-welded condition.
Figure D.2: Time-temperature transformation curves for three wt. pct. nickel in as-welded condition.
Figure D.3: Time-temperature transformation curves for five wt. pct. nickel in as-welded condition.
APPENDIX E - DIFFERENTIAL SCANNING CALORIMETRY GRAPHS

Additional DSC graphs are presented in this section to show one, three, and five wt. pct. nickel in the as-welded condition using both Netzsch and Setaram equipment. These graphs are presented in Figure E.1, Figure E.2, and Figure E.3. In addition, the DSC curves for the first curve upon heating is also given for one, three, and five wt. pct. nickel to determine the $A_{C1}$, Figure E.4.

![DSC Graphs](image)

Figure E.1: Differential scanning calorimetry one wt. pct nickel in as-welded condition using Netzsch (left) and Setaram (right).
Figure E.2: Differential scanning calorimetry three wt. pct nickel in as-welded condition using Netzsch (left) and Setaram (right).

Figure E.3: Differential scanning calorimetry five wt. pct nickel in as-welded condition using Netzsch (left) and Setaram (right).
Figure E.4: Differential scanning calorimetry one, three, and five wt. pct nickel in as-welded condition using Netzsch (left) and Setaram (right) for 1st curve upon heating.
APPENDIX F - DIFFERENTIAL SCANNING CALORIMETRY DECONVOLUTION

PYTHON CODE

#!/usr/bin/env python3

from os import listdir
import numpy as np
from matplotlib.pyplot import figure, show, text, twinx, savefig
from scipy.signal import find_peaks_cwt, fftconvolve, argrelmax, argrelmin, decimate
from scipy.integrate import simps
from scipy.optimize import leastsq

def chunks(l,n):
    for i in range(0, len(l), n):
        yield l[i:i+n]

def find_nearest(array,value):
    idx = (np.abs(np.array(array)-value)).argmin()
    return idx

def lorentz(points, a):
    x = np.arange(0, points) - (points - 1.0)/2
    #xsq = x**2
    num = a*(2*a**2-6*x**2+(a**2+x**2)**2)
    den = np.pi*(a**2+x**2)**3
    return num/den

def gauss(params, x):
    #y = np.zeros_like(x)
    b, m = params[0:2]
    b = m = 0.
\[ y = x \cdot m + b \]

for i, paramset in enumerate(chunks(params[2:], 3)):

# for i, paramset in enumerate(params):

# \( T = Ts[i] \)

t, h, s = paramset

h = abs(h)

gau = np.exp( -(x-t)**2/2/s**2 )

y += gau*h #abs(h)

return y

def residual(params, x, y,):

res = gauss(params, x,) - y

return res

def ricker(points, a):

Also known as the mexican hat wavelet,
models the function:

\[ A \left( 1 - \frac{x^2}{a^2} \right) \exp\left( -\frac{t^2}{a^2} \right), \]

where \( A = \frac{2}{\sqrt{3a}} \pi^{1/3} \)

Parameters

———-

a: scalar

Width parameter of the wavelet.

points: int, optional

Number of points in ‘vector’. Default is “10*a”

Will be centered around 0.

Returns

———

vector: 1-D ndarray
array of length ‘points’ in shape of ricker curve.

\[ A = \frac{2}{\sqrt{3 \cdot a} \cdot (\pi^{0.25})} \]

\[ \text{wsq} = a^2 \]

\[ \text{vec} = \text{np.arange}(0, \text{points}) - \frac{(\text{points} - 1.0)}{2} \]

\[ \text{tsq} = \text{vec}^2 \]

\[ \text{mod} = (1 - \text{tsq} / \text{wsq}) \]

\[ \text{gauss} = \text{np.exp}(-\text{tsq} / (2 \cdot \text{wsq})) \]

\[ \text{total} = A \cdot \text{mod} \cdot \text{gauss} \]

return total

def haar(points, a):
    \[ \text{vec} = \text{np.arange}(0, \text{points}) - \frac{(\text{points} - 1.0)}{2} \]
    \[ \text{vec}[0: \text{len(vec)} / 2] = -0.5 \]
    \[ \text{vec}[\text{len(vec)} / 2:] = 0.5 \]

    return vec

def peakfinder(array):
    pk = []
    pval = array[0]
    lind = 0
    for i, val in enumerate(array):
        if (val > 0.) and (pval <= 0):
            lind = i
        elif (val <= 0.) and (pval > 0):
            uind = i
        pk.append((lind, uind))
        pval = val
    return pk

def subpeakfinder(array, inds):

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pks = []
lind, uind = inds
pki = argrelmax(array[lind:uind], order=5)
for pk in pki:
yield pk + lind
def peakinfo(xarray, yarray, inds):
lind, uind = indsarea = simps(yarray[lind:uind], xarray[lind:uind])
centroid = simps(yarray[lind:uind]*xarray[lind:uind], xarray[lind:uind])/area
variance = simps(yarray[lind:uind]*(xarray[lind:uind]-centroid)**2, xarray[lind:uind])/area**2
return np.abs(area), np.abs(centroid), np.sqrt(np.abs(variance))

#CONSTANTS
filename = '5 -SR_1.txt'
mass = 161.2 #mg
cooling = 1
wavelet = ricker
rwdt = 650 #100
Tlow = 500 #550
Thig = 850 #900
logb = 1.2 #logarithmic base for consecutive widths for find_peaks_cwt
width = 2000 #200 #base width for find_peaks_cwt
wtdt0 = 3
wtdt1 = -3
opt = 1

#PLOTTING
fig = figure(figsize=(6,6), dpi=150)
pl1 = fig.add_subplot(311)
pl2 = fig.add_subplot(312)
pl3 = fig.add_subplot(313)

if (cooling == 1):
    mul = -1.
    mat = 2
else:
    mul = 1.
    mat = 1

#DATA IMPORT

data = []
head = []
infile = open(filename, encoding='utf-16le', mode='r')

for line in infile.readlines():
    sline = line.split()
    try:
        newdata = map(float, sline)
        #data.append(np.fromiter(newdata, dtype='float64'))
        data.extend([val for val in newdata])
    except ValueError:
        print(line)
infile.close()

ndata = np.array(data, dtype='float64')
ndatar = np.reshape(ndata, (5, len(ndata)/5), order='F')
index, time, temp1, temp2, dsc = ndatar

#DATA PREPARATION

dsc = mul*dsc/1000. #change sign (if necessary) and convert to watts

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time = time*60 #convert to seconds
temp = temp2 #sample temperature
if cooling == 1:
time = time[0:len(time)//2]
temp = temp[0:len(temp1)//2]
dsc = dsc[0:len(dsc)//2]
else:
time = time[len(time)//2:]
temp = temp[len(temp1)//2:]
dsc = dsc[len(dsc)//2:]
temp = temp[::-1]
dsc = dsc[::-1]

#ATTRIBUTES OF THE DATA
lowi = find_nearest(temp, Tlow)
higi = find_nearest(temp, Thig)
if (lowi > higi):
  swap = lowi
  lowi = higi
  higi = swap
N = len(dsc)
dt = (time[-1]-time[0])/N
dT = abs(temp[-1]-temp[0])/dt/N #Approximate (avg) ramp rate (degC/s)
#CONVOLVE WITH WAVELET FUNCTION TO MAKE IT PEAKABLE?
Dsc = fftconvolve(dsc, haar(rwdt, min(10 * rwdt, len(dsc))), mode='same')
Dsc_r = fftconvolve(dsc, ricker(rwdt, min(10 * rwdt, len(dsc))), mode='same')
#TRUNCATE TO REGION OF INTEREST
time = time[lowi:higi]
dsc = dsc[lowi:higi]
temp = temp[lowi:higi]
Dsc = Dsc[lowi:higi]
Dsc_r = Dsc_r[lowi:higi]
interest = Dsc

print(Truncating data to region of interest between {0:4n} and {1:4n}.format(min(temp[0],temp[-1]), max(temp[0],temp[-1]))))

# PEAK DETECTION
wdtt = wdth
wdts = wdtt*logb**np.arange(wdt0, wdt1, -1)

pkis = argrelmax(interest, order=rwdt)[0]
print(len(pkis))

#pkis = np.concatenate((pkis, argrelmin(interest, order=rwdt)[0]))
#print(len(pkis))

#find_peaks_cwt(interest, wdts, ricker, noise_perc=10, #, max_distances=None, gap_thresh=None, min_length=None, min_snr=1, noise_perc=10)

# LEAST SQUARES FITTING
params0 = []
m = (dsc[-1]-dsc[0])/(time[-1]-time[0])
b = dsc[0]-time[0]*m
print(m, b)
dsc = dsc - m*time - b
params0.append(b)
params0.append(m)

print(Initial Peak Detection

for pki in pkis:
    print({0:.4e}\t{1:6.2f}\t{2:.6e}.format(time[pki], temp[pki], dsc[pki]))

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params0.extend([time[pki], dsc[pki], dt*rwdt]) #dsc

if opt == 1:

answer, *rest = leastsq(residual, params0, args=(time, dsc)) #dsc

b, m = answer[0:2]

print(After least squares (Gaussian) fit

\nTime/s \nDSC/W \nWidth/s \nTemp/C \nArea/mJ)

print(m: {0:.4e} tb: {1:.4e}.format(m, b))

for paramset in chunks(answer[2:], 3):

t, d, s = paramset

pki = find_nearest(time, t)

T = temp[pki]

ener = d*np.sqrt(2.*np.pi)*s

pl2.plot(temp, abs(d)*np.exp(-(time-t)**2/2/s**2)) #abs(d)

print({0:.2e} {1:.4e} {2:.4e} {3:6.2f} {4:.6e}.format(t, d, s, T, ener*1000)) #abs(d)

abs(s)

pl1.plot(temp, interest)

#pl2.plot(temp, interest)

pl3.plot(temp, dsc, 'k') #dsc

if opt == 1:

pl3.plot(temp, gauss(answer, time), 'r')

show()

temp, time, dsc, sensi, segment = datafolder[dataind]

print filenames[dataind]

T, D, S, t = zip(*filter(lambda x: x[2]==mat, zip(temp, dsc, segment, time)))

ltrunc = find_nearest(T, Tmin)

utrunc = find_nearest(T, Tmax)

if (ltrunc > utrunc):

swap = ltrunc
ltrunc = utrunc

utrunc = swap

T = np.array(T[ltrunc:utrunc])

D = mul*np.array(D[ltrunc:utrunc])

t = np.array(t[ltrunc:utrunc])

pl1.plot(T, D, 'k-', linewidth=0.75)

pl1.set_xlim((Tmin, Tmax))

hig = 1.2 #0.08

low = 0.5 #0.11

sep = -0.1 #0.01

width = 100*np.abs(uind-lind) #100 75 is interesting on 2awC

widths = width*np.arange(hig, low, sep)

Til = 400.

Tiu = 850.

lind = find_nearest(T, Tiu) #1490

uind = find_nearest(T, Til) #1500

#DETREND

detwid = 400

i = 3

detcon = peakfinder(fftconvolve(D, wavelet(min(10*detwid, len(D)), detwid), mode='same'))

detui = detcon[i][0]

detli = detcon[i][1]

print T[detui], T[detli]

pt0 = (T[detui], D[detui])

pt1 = (T[detli], D[detli])

m = (pt0[1]-pt1[1])/(pt0[0]-pt1[0])
\[ b = pt1[1]-m*pt1[0] \]
\[ D = D - m*T - b \]
\[
\#D = \text{detrend}(D)
\]
\[ Dt = \text{np.concatenate}((\text{np.diff}(t), [t[-1]-t[-2]])) \]
\[ ddD = \text{np.gradient}(\text{np.gradient}(D)/Dt/2.)/Dt/2. \]
\[ \text{for } w \text{ in } \text{widths}:#\text{np.arange}(\text{low}, \text{hig}, \text{sep}): \]
\[ \text{dec} = \text{fftconvolve}(D, \text{wavelet}(\text{min}(10*w, \text{len}(D)), w), \text{mode}='\text{same}') \]
\[ \text{pl3.plot}(T[lind:uind], \text{Dmap}[lind:uind], \text{color}='b') \]
\[ \#\text{dec} = \text{convolve}(D, \text{wavelet}(\text{len}(D), m*\text{width}), \text{mode}='\text{same}') \]
\[ \text{pks} = \text{filter}(\lambda x: x \text{ if } \text{dec}[x] > \text{tolerance} \text{ else None}, \text{argrelmax}(\text{dec}, \text{order} = 10)[0]) \]
\[ \text{vls} = \text{filter}(\lambda y: y \text{ if } \text{dec}[y] < \text{tolerance} \text{ else None}, \text{argrelmin}(	ext{dec}[lind:uind], \text{order} = 10)[0]) \]
\[ \text{vali} = \text{vls}[\text{np.argmin}(\text{dec}[\text{vls}])] + lind \]
\[ \#\text{pks} = \text{peakfinder}(\text{dec}) \]
\[ \text{Ts} = [] \]
\[ \text{Ds} = [] \]
\[ \text{decs} = [] \]
\[ \text{subpks} = [] \]
\[ \text{params0} = [] \]
\[ \text{T0} = [] \]
\[ \#\text{T0.append}(T[\text{vali}]) \]
\[ \#\text{params0.extend}([\text{D[\text{vali}], w}]) \]
\[ \text{for } \text{pk} \text{ in } \text{pks}: \]
\[ \text{if } (T[\text{pk}] > \text{Ti}) \text{ and } (T[\text{pk}] < \text{Tiu}): \]
\[ \text{params0.extend}([\text{D[pk], w}]) \]
\[ \text{T0.append}(T[\text{pk}]) \]
\[ \text{Ts.append}(T[\text{pk}]) \]
decs.append(dec[pk])
Ds.append(D[pk])
Ts = np.array(Ts, dtype='float64')
Ds = np.array(Ds, dtype='float64')

decmap = map(lambda x: x if x > 0 else 0., dec)
Dmap = map(lambda x: x if x > 0. else 0., D)

print Fitting %i peaks % (len(T0))
answer = leastsq(residual, params0, args=(T[lind:uind], Dmap[lind:uind], T0))
for i, ans in enumerate(chunks(answer[0], 2)):
    #print T: %.1f \ tD: %.3e \ tW: %.2f % (ans[0], ans[1], ans[2])
    print T: %.1f \ tD: %.3e \ tW: %.2f % (T0[i], ans[0], ans[1])
for i, ans in enumerate(answer[0]):
    print T: %.1f \ tD: %.3e \ tW: %.2f % (T0[i], decs[i], ans)
pl3 = fig.add_subplot(212)
pl3.plot(T[lind:uind], gauss(answer[0], T[lind:uind], T0), color='r')
pl3.plot(T[lind:uind], dec[lind:uind])  
pl3.plot(T[lind:uind], Dmap[lind:uind], color='b')