DEVELOPMENT OF THERMOELECTRIC POWER AND ELECTROMAGNETIC TECHNIQUES FOR DETERMINATION OF INTERSTITIALS IN ADVANCED MATERIALS

by:

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ABSTRACT

The modern electronics industry offers new extremely sensitive electronic and magnetic property measuring systems. This investigation has applied these systems to assess and correlate electronic properties to microstructure, phase, and interstitial content in structural engineering and energy storage materials. These correlations illustrate new non-destructive methods to rapidly assess materials during manufacturing and service. The fundamental basis for these microstructural and constitutional correlations to electronic properties is presented.

Thermoelectric power measurement in conjunction with Beeghly ester-halogen digestion (nitride determination) has been successfully developed to conveniently assess and quantitatively map soluble nitrogen content in nitrogen-strengthened austenitic stainless steel weldments. The hydrogen storage capabilities of LaNi₅ intermetallic compounds were investigated utilizing the combination of thermoelectric power, Beeghly ester-halogen digestion, and Leco hydrogen determination. Thermoelectric power has demonstrated a rapid hydrogen assessment capability and can achieve the equivalent of the pressure-composition-temperature (activity) diagram. Effective use of hydrogen storage materials occurs in the alpha+beta two-phase region of the activity diagram. A thorough assessment of the content of each phase in this two-phase region can optimize the performance of hydrogen storage materials. Hydrogenation behavior of NaAlH₄ intermetallics has been investigated utilizing thermoelectric power and magnetic analyses. Using both thermoelectric power and magnetic susceptibility measurements on these intermetallics allows confirmation and further insight into
hydrogen's role in altering the material's electronic structure, which will indicate the direction for further alloy development to optimize hydrogen storage.

Through the use of a combination of electromagnetic and acoustic analysis (acoustic and electric impedance), a new non-contact sensor has been developed for in-situ determination of diffusible hydrogen content in coated steel linepipe. These techniques allow for a rapid, non-destructive assessment of hydrogen accumulation in the coated steel line pipe and thus an evaluation of the linepipe integrity.
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CHAPTER 1

INTRODUCTION

Interstitials play a crucial role in metal processing and properties. Different interstitial atoms offer unique sets of effects on metal properties and microstructure. Advancements in management of carbon have always been crucial in prior steel development, and have always necessitated improved methods to measure carbon accurately and rapidly during steel processing. Interstitial nitrogen offers an opportunity for enhancement of mechanical properties and corrosion resistance; however, the formation of nitrides can reverse the improvement in properties. Diffusible hydrogen can have detrimental effects on steel properties, but hydrogen can also be utilized for reversible energy storage materials such as metal hydrides. Boron promotes hardenability. Oxygen results in inclusion formation, which then act as nucleation sites in iron. In all of these cases, industry and government need improved abilities for rapid assessment and measurement of interstitials. Each interstitial alloying element is measurable through a large selection of traditional methods. The purpose of this research is to apply modern chemistry and solid-state physics concepts to achieve greater sensitivity in non-destructive interstitial content measurements in nitrogen-strengthened stainless steel weldments, hydrogen storage materials, and structural steel.

Chapter 2 begins with a literature review of the role of interstitials as alloying elements and their solubility and electronic signatures in ferrous alloys and hydrogen storage materials. In this research, interstitial nitrogen and hydrogen
are specifically emphasized with examples of the use of nitrogen in austenitic stainless steels and hydrogen in advanced storage materials and structural ferrous alloys.

This research demonstrates that multiple non-destructive tools can be utilized for interstitial content assessment. New advanced electronic, magnetic, and electromagnetic tools can be utilized to increase sensitivity of assessment of interstitial contents. Thermoelectric power measurement by electronic tools can be utilized for interstitial assessment because thermoelectric power is a function of electron concentration, effective mass, and scattering parameters (which are negligible with high impedance). Interstitial atoms either donate or accept electrons to/from the host metal electron conduction bands, so the addition of an interstitial atom results in a change to both electron concentration and the Fermi energy level, which change the electronic effective mass. The effective mass is a measure of the curvature of the electronic bands at the Fermi energy level, and the thermoelectric power coefficient is extremely sensitive to changes in the electron concentration and Fermi energy level (e.g. interstitial additions). Interstitial additions similarly affect magnetic properties of metals because magnetic properties are sensitive to changes in atomic volume and chemical binding (donation of electrons to the host metal electron bands) during filling of the interstitial sites. Electronic and magnetic techniques are complementary techniques for measuring interstitial contents in materials. Electromagnetic techniques such as impedance measurements can also be utilized for interstitial content assessment. Impedance measurements are very similar to thermoelectric power measurements in that impedance is also very sensitive to changes in the electron bands of the steel because the addition of hydrogen results in changes in the material resistivity. Resistivity measurements are however very sensitive to grain boundaries, unlike thermoelectric power, so it is important to utilize multiple tools to eliminate any variables. A literature review of
the electronic, magnetic, and electromagnetic tools utilized in this research is given in Chapter 3.

Thermoelectric power measurement in conjunction with Beeghly ester-halogen digestion (nitride determination) has been successfully developed to conveniently assess and quantitatively map soluble nitrogen content in nitrogen-strengthened austenitic stainless steel weldments. The hydrogen storage capabilities of LaNi\textsubscript{5} intermetallic compounds were investigated utilizing the combination of thermoelectric power, Beeghly ester-halogen digestion, and Leco hydrogen determination. Thermoelectric power has demonstrated a rapid hydrogen assessment capability and can achieve the equivalent of the pressure-composition-temperature (activity) diagram. The hydrogenation behavior of NaAlH\textsubscript{4} intermetallics has been investigated utilizing thermoelectric power and magnetic analyses. Using both thermoelectric power and magnetic susceptibility measurements on these intermetallics allows confirmation and further insight into hydrogen's role in altering the material's electronic structure and will illuminate the direction for further alloy development to optimize hydrogen storage capability. Through the use of a combination of electromagnetic and acoustic analysis (acoustic and electric impedance), a new non-contact sensor has been developed for in-situ determination of diffusible hydrogen content in coated steel linepipe. These techniques allow for a rapid, non-destructive assessment of hydrogen accumulation in the coated steel line pipe and thus an evaluation of the linepipe integrity.

Standardization and calibration of each of these new techniques is necessary to quantify the interstitial contents in advanced materials. Techniques and specimen preparation for determination of total nitrogen and hydrogen contents and interstitial nitrogen and hydrogen contents are described in Chapter 5. With the proper calibration, these electronic, magnetic, and electromagnetic
techniques successfully allow for rapid, non-destructive assessment of interstitial contents.

Chapter 6 shows prior work on determination of interstitial nitrogen content in austenitic stainless steel weldments utilizing thermoelectric power measurement. This prior work is important because it has acted as the stepping-stone for future research in utilizing advanced techniques for determination of other interstitial contents such as hydrogen determination in advanced hydrogen storage materials. The prior research also led to the development of new alternative tools for hydrogen content determination. Chapter 7 shows the results of thermoelectric power and electromagnetic techniques for determination of interstitial hydrogen content in advanced hydrogen storage materials and structural steels. To properly understand the thermoelectric power and electromagnetic results it is important to develop thermodynamic models, which are given in Chapter 8. Chapter 9 lists the final conclusions for the non-destructive thermoelectric power assessment, magnetic analyses, and electromagnetic assessment of interstitial contents in advanced materials. Chapter 10 offers suggestions of future opportunities in research and development of thermoelectric, electromagnetic, and elastic analytic sensors and practices to assess interstitial content and behavior in engineering and energy storage materials.
CHAPTER 2

LITERATURE REVIEW OF INTERSTITIALS IN ADVANCED MATERIALS

A literature review of the behavior and role of interstitial contents in advanced materials is necessary to give the reader an understanding of why it is necessary to develop advanced non-destructive techniques for rapid interstitial content quantification. This thesis will focus particularly on nitrogen and hydrogen in structural, ferrous, and energy storage materials.

2.1. Interstitial Solubility

Understanding the solubility of interstitials is key to knowing which phases are present and therefore the material properties. Wiswall [1978] indicates two definitions for “solubility”. The first definition of solubility refers to the total amount of interstitial solute contained in the solid phase at a specific pressure, which also may be called the overall solubility of a single phase. The second definition of solubility is the limiting or terminal solubility, which refers to the single-phase saturation concentration, which when exceeded a second solid phase begins to appear. Pressure-composition-temperature (activity) diagrams give insight into the solubility and phases of interstitials. A schematic pressure-composition-temperature (PCT) diagram is shown in Figure 2.1. The pressure or composition can be viewed as the independent variable. The PCT diagram (Figure A) is divided into three distinct regions: (1) $\alpha$-region, (2) $(\alpha+\beta)$-region and (3) $\beta$-region. In the $\alpha$-region, interstitials are in pure solid solution. In the $\alpha$-region
at low interstitial contents, all isotherms have a common slope (for diatomic gases) having the relationship:

\[ x \propto \sqrt{P} \quad [2.1] \]

where \( x \) is concentration and \( P \) is pressure. This relationship is called Sieverts’ law and is the region indicated in Figure 2.1. Sieverts’ law only holds true for diatomic gases, so it is necessary to understand the dissociation of the diatomic gas into interstitial hydrogen (solute atom) at equilibrium:

\[ H_2 \rightarrow 2H \quad [2.2] \]

where the equilibrium constant, \( K \), is given as:

\[ K = \frac{[H]^2}{P_{H_2}^2} \quad [2.3] \]

so that the concentration of the solute hydrogen is:

\[ [H] = [K]^{1/2} P_{H_2}^{1/2} \quad [2.4] \]

where the equilibrium constant is equivalent to:

\[ K = e^{-\Delta G^o/kT} = e^{-\Delta H^o/kT} e^{\Delta S^o/R} \quad [2.5] \]

The second region (Figure 2.1) is a two-phase region (\( \alpha+\beta \)), which is the so-called plateau region. In this second region, there is the coexistence of interstitial solid solution and formed second phase particles (e.g. nitrides, hydrides,
carbides, oxides). The third region is the single $\beta$-phase, which represents complete insolubility of the interstitial solute, so that there is only second phase precipitates (e.g. pure nitrides, hydrides, carbides, or oxides) present. Pressure-composition-temperature diagrams are also very important to understand and utilize in this research because direct correlations exist between electronic property measurements and the activity diagrams.

The positioning of the interstitial atoms in the metal lattice plays a significant role in the solubility of the interstitials atoms. The next section describes the locations of interstitial atoms in different close-packed crystal structures and discusses the resulting effects of the interstitial additions on the overall solubility.

Figure 2.1: Schematic pressure-composition-temperature diagram for nitrogen where $\alpha$-phase is interstitial solid solution, ($\alpha+\beta$)-phase is interstitial solid solution and formed precipitates, and the $\beta$-phase is pure precipitation (interstitial solid solution is completely insoluble).
2.2. *Interstitial Positioning in the Metal Lattice*

In interstitial alloys and compounds, small atoms are introduced into particular spaces in lattice positions in the metal matrix. The interstitials include hydrogen, boron, carbon, nitrogen, and oxygen. The metal matrix is densely packed, so that there are octahedral and tetrahedral spaces between the host metal atoms providing sites for interstitial atoms. When the interstitial atom is located in the tetrahedral site, the interstitial atom is surrounded by four metal atoms and when located in the octahedral site the interstitial atom is surrounded by six metal atoms. The octahedral and tetrahedral sites are shown in Figure 2.2 for face-centered cubic, body-centered cubic, and hexagonal close packed crystal structures.

![Diagram showing octahedral (O) and tetrahedral (T) sites for interstitial atoms in the fcc, hcp, and bcc crystal lattice.](image)

*Figure 2.2: Octahedral (O) and tetrahedral (T) sites for interstitial atoms in the fcc, hcp, and bcc crystal lattice [Fukai, 1993].*
The solubility of each interstitial is dependent upon the phase in which it is present because the austenitic and ferritic phases have very different octahedral and tetrahedral site sizes. In the body-centered cubic lattice there are three octahedral sites per metal atom and six tetrahedral sites per metal atom. The octahedral sites are located at the center of the cube face and at midpoint of the cube edges. Assuming the atoms are spheres, the radius can be geometrically determined in terms of the lattice parameter, \( a \), given as \( r = 0.25a\sqrt{3} \) [Pepperhoff and Acet, 2001]. Using this radius, the octahedral site has an equivalent radius of 0.154\( r \) and the tetrahedral site has an equivalent radius of 0.291\( r \) assuming the metal-atoms are close packed. The tetrahedral site offers a very large volume for interstitial occupation.

In the face-centered cubic lattice the radius of the metal atom is \( r = a/2.28284 \). The octahedral sites are situated at the center of the cube and at the cube edges. The number of octahedral sites is equivalent to the number of metal atoms. The octahedral site has a radius of 0.41\( r \) and the tetrahedral site has a radius of 0.225\( r \). The size of the octahedral and tetrahedral sites in the body-centered cubic lattice and the face-centered cubic lattice oppose one another, thus explaining the differences in the interstitial solubilities. In the hexagonal close-packed lattice, each octahedral site is neighboring six other octahedral sites. The octahedral sites are located in planes perpendicular to the c-axis with a spacing of \( c/2 \) [Pepperhoff and Acet, 2001]. The \( c/a \) ratio for the octahedral and tetrahedral sites is approximately 1.633.

The number of occupied interstitial sites in the metal lattice is much lower than the number of available interstitial sites [Pepperhoff and Acet, 2001]. When the interstitial atom occupies the interstitial site, the nearest neighbor atoms are shifted, thus causing a displacement field or lattice strain. The superposition of these long-range displacement fields leads to a strained expansion in the entire lattice making it more difficult for neighboring interstitial sites to become
occupied. This lattice strain results in a decrease in the solubility of the interstitial to a level lower than is geometrically possible [Pepperhoff and Acet, 2001] [Gavriljuk and Berns, 1999].

When considering the resulting lattice strain due to interstitial additions, it is important to consider how the electronic bands of the host metal are affected. Figure 2.3 (a) is a plot of the number of electrons as a function of energy, which shows the filling of the electronic s, p, and d bands before the addition of the interstitial atom. Once the interstitial atom has been introduced into the metal lattice (Figure 2.3 (c)), there is a resulting lattice strain, which changes the shape of the s, p, and d bands as shown in Figure 2.3 (b). Figure 2.3 (b) shows the electronic bands in reciprocal lattice space, so that the interstitial atom changes the electronic bands by causing less d-electron overlap between lattice transition atoms. Changes in the electronic overlap alters the Fermi energy and thus the effective mass. The effective mass is a measure of the curvature of the electronic bands at the Fermi energy level. Electronic, magnetic, and electromagnetic measurements are extremely sensitive to changes in lattice strain and electron concentration, therefore allowing for non-destructive interstitial content assessment.

The ratio of atomic sizes of the host and metalloid atom is however not the only factor contributing to lattice strain, but the nature of chemical binding between the host and metalloid atom is also a factor. The chemical binding occurs due to the donation of electrons from the metalloid atom to the 3d-electron band of the host metal. The interstitial solubility is therefore reliant upon the availability for their p-electrons to be donated to the 3d electron band. The solubility decreases rapidly as the d-electron band of the host metal becomes increasingly full.

Further details will be given of the solubility and electronic signatures of interstitials using nitrogen and hydrogen as specific examples. Interstitial
nitrogen and hydrogen in ferrous, structural, and advanced hydrogen storage materials has been the focus of this research.

![Graphs and Diagrams](Image)

Figure 2.3: Filling of the electronic bands showing the effect of the addition of a hydrogen atom.

2.3. **Nitrogen**

Nitrogen can be both beneficial and detrimental dependent upon the location and phase in which nitrogen is present. Nitrogen acts much like nickel in steel, however nitrogen is a much stronger austenite stabilizer, while lacking the expensive cost of nickel. Nitrogen is utilized as major alloying addition for strengthening of fully austenitic stainless steels. The interstitial nitrogen content must be known to obtain and maintain the derived mechanical properties and
corrosion resistance. High nitrogen contents in fully austenitic stainless steel partitions into interstitial nitrogen and transition metal nitrides. It is essential to quantitatively determine the nitrogen content that is in solid solution and the nitrogen content associated with various nitrides.

Austenitic stainless steel structure is face-centered cubic, so that the addition of nitrogen contributes both to chemical binding through the donation of electrons and lattice strain because the radius of nitrogen is larger than the octahedral site that it prefers to occupy. Nitrogen prefers to occupy the octahedral sites because the occupation of a tetrahedral site requires outward displacement of all four neighboring iron atoms, whereas the irregular octahedral site can be occupied with the displacement of only two iron atoms parallel to the cube edge. This displacement of the iron atoms leads to lengthening of the lattice in the direction causing lattice distortion or residual strain. Figure 2.4 shows the concentration dependence of the volume per iron atom determined from the lattice constants where the full lines show the solubility limit. These changes in the lattice strain are easily detectable using magnetic and electronic assessment.

2.3.1. **Solubility of Nitrogen in Metals**

The solubility of nitrogen is important in ferrous alloys for three reasons: (1) austenite phase stability, (2) strengthening, and (3) enhanced corrosion resistance. When the solubility of interstitial nitrogen is exceeded, nitrides begin to form changing the mechanical properties and corrosion resistance. A thorough description of nitrides is given in Appendix A.

The temperature range at which nitrogen is stable is shown in Figure 2.5 for the various phases of iron showing that nitrogen has a much higher solubility in austenite than it does in ferrite.
Figure 2.4: The metal concentration dependence of the atomic volume of iron in Fe-N and Fe-C. $V_c$ is the critical volume for the LS-HS transition in austenitic iron [Pepperhoff and Acet, 2001].
Figure 2.5: Solubility of nitrogen (wt %) at 1 atm in the various modifications of iron as a function of temperature [Darken and Gurry, 1953].
Many factors play an important role in the overall solubility of interstitial nitrogen in ferrous alloys, so that Figure 2.5 is a basis to begin understanding the solubility of nitrogen. The addition of alloying elements such as chromium, manganese, etc. can increase or decrease the solubility of interstitial nitrogen in austenitic stainless steel. The filling of the electronic bands is also important in terms of nitrogen solubility because the addition of a nitrogen atom is associated with the donating of its electrons to the host metal lattice, which must have space available to accept the electrons. The next two sections will discuss the effect of alloying elements and electronic structure on the solubility of nitrogen in austenitic stainless steel.

**Effect of Alloying Elements on Nitrogen Solubility**

Wada and Pehlke [1977] developed the activity coefficient as a function of temperature and alloy composition for nitrogen at one atmospheric pressure in liquid Fe-Cr-Ni alloys [Turkdogan, 1996]. Wada and Pehlke [1977] then established the nitrogen activity coefficient in liquid Fe-Cr-Ni-Mo-Mn alloys as a function of temperature and alloy composition given as:

\[
\log f_n = \frac{A}{T} + B + C
\]  

[2.6]

where A is:

\[
A = -164(\%Cr) + 8.33(\%Ni) - 33.2(\%Mo) - 134(\%Mn) + 1.68(\%Cr)^2
\]

\[-1.83(\%Ni)^2 - 2.78(\%Mo)^2 + 8.82(\%Mn)^2 + (1.6(\%Ni) + 1.2(\%Mo) + 2.16(\%Mn))(\%Cr)
\]

\[+(-0.26(\%Mo) + 0.09(\%Mn))(\%Ni)\]  

[2.7]
B is:

\[ B = 0.0415(\%\text{Cr}) + 0.0019(\%\text{Ni}) + 0.0064(\%\text{Mo}) + 0.035(\%\text{Mn}) - 0.0006(\%\text{Cr})^2 + 0.001(\%\text{Ni})^2 + 0.0013(\%\text{Mo})^2 - 0.0056(\%\text{Mn})^2 + (-0.0009(\%\text{Ni}) - 0.0005(\%\text{Mo})(\%\text{Cr}) + (0.0003(\%\text{Mo}) + 0.0007(\%\text{Mn})(\%\text{Ni}) \]  

and C is:

\[ C = (0.13(\%\text{C}) + 0.06(\%\text{Si}) + 0.046(\%\text{P}) + 0.007(\%\text{S}) + 0.01(\%\text{Al}) - 0.9(\%\text{Ti}) - 0.067(\%\text{Nb}) \]  

The nitrogen solubility can then be calculated for liquid Fe-Cr-Ni base multicomponent alloys at any temperature by the following equation:

\[
\log(\text{wt}\%\text{N})_T = \left(\frac{-247}{T} - 1.22\right) - \left(\frac{4780}{T} - 1.51\right)\left(\log f_{n,1873K}\right) - \left(\frac{1760}{T} - 0.91\right)\left(\log f_{n,1873K}\right)^2
\]  

Stainless steels can have a limited solubility for nitrogen in the liquid state, depending upon the alloying content. In stainless steels, elements such as chromium and manganese enhance nitrogen solubility, while elements such as nickel and carbon decrease the solubility of nitrogen. The level of solubility can be calculated from known chemical composition through the use of Figure 2.6 shown below [Peckner and Bernstein, 1977].

The nitrogen solubility index, \( S_N \), is the logarithm of the given activity coefficient of nitrogen, \( f_N \). To estimate the nitrogen solubility limit in a given steel composition, Figures 2.6 (a) and (b) are utilized to determine the nitrogen solubility index. This graph is not applicable to welded microstructures because
solidification due to welding results in coring or segregation of the alloying elements presents. Coring results in two distinct region in the weld microstructure called the dendritic and interdendritic regions. The mechanical properties and corrosion resistance are different in these two regions. More information on the solidification of weldments can be found in Appendix B.

Figure 2.6: Method for estimating limit of nitrogen solubility in stainless steels (a) Solubility index SN of nitrogen in iron at 1600°C as a function of alloying elements. (b) Chart for converting SN into percent nitrogen soluble in steel at 1600°C and 1 atm nitrogen pressure [Langenberg and Day, 1957], [Peckner and Bernstein, 1977].
Effect of Electronic Structure on Solubility

Nitrogen solubility decreases rapidly as the d-band in the host metal becomes increasingly full [Pepperhoff and Acet, 2001]. The electronic structure of a nitrogen atom is $1s^22s^22p^3$ as shown in Figure 2.7. The nitrogen atom has one excessive p-electron, which tightens the 2p electron shell of the nitrogen atom and decreases its radius. The electronic exchange between austenitic iron and nitrogen atoms amounts to an interaction between the 4s- and 3d- electrons of the steel and the s, p- electrons of the interstitials, resulting in a complicated hybridization. Theoretical calculations have been performed on the electron band structure for pure austenite iron alloyed with and without nitrogen allowing a forecast to be made of the electronic density distribution due to nitrogen [Gavriljuk and Berns, 1999].

Figure 2.7: Electron structure of a free nitrogen atom [Gavriljuk and Berns, 1999].
Nitrogen donates its free electrons just at the Fermi energy level as shown in Figure 2.8, while carbon shifts the maximum of the electron density of states just below the Fermi energy level. The electron energy bands were calculated by Shanina [1995] using the \textit{ab initio} method of norm-conserving transferable pseudopotential developed by Bachelet \textit{et al.} [1982]. It can be expected that nitrogen atoms in austenite increases the concentration of free electrons as shown in Figure 2.9, thus enhancing the metallic component of atomic interactions. The main difference between nitrogen and carbon is that nitrogen makes a significant contribution to the density of s-electrons centered at nitrogen atoms.

Calculative methods for determination of solid solubility in alloys have been determined by numerous researchers [Hume-Rothery, 1965, 1967], [Gschneidner Jr, 1979], [Miedema and Chatel, 1979], [Machlin, 1979]. For example Hume-Rothery [1969] uses atomic size ratio to determine solid solubility, while Miedema [1975] uses electronegativity for solid solubility determination. It has been accepted that an electronegativity of +/- 0.4 electronegativity units and a fifteen percent atomic size factor restricts solid solubility. This criteria is however not always valid and this situation is true for the case of transition metal alloys [Morinaga \textit{et al.}, 1984, 1985]. Gschneidner [1979] rules can be utilized to find which solute-solvent interactions of size and electronegativity can be used to make solubility modifications.

This reported electronic behavior changes with interstitial solute content, which suggests that electronic property assessment tools can be applied to determine the interstitial content if properly calibrated to a reference material.
Figure 2.8: Density of electron states for nitrogen and carbon in fcc alloys [Gavriljuk and Berns, 1999].
Figure 2.9: Effect of nitrogen (open circles) on the concentration of free electrons in austenitic Cr18Ni16Mn10 steel. The filled circles is the free electron concentration for Cr20Ni16Mn6 [Gavriljuk and Berne, 1999].
2.3.2. Nitrogen in Austenitic Stainless Steel

To show the attributes of interstitial nitrogen in austenitic stainless steel, mechanical property and corrosion resistance data are briefly discussed. Based on a detailed analysis of all published strength data for Fe-Cr-Mn-N steels, strength data (MPa) in the annealed condition as a function of composition (wt pct.) can be calculated [Balachandran et al., 2001]:

\[ YS = 3.03 \text{ (wt\% C)} + 335.60 \text{ (wt\% N)} + 5.08 \text{ (wt\% Mn)} + 8.41 \text{ (wt\% Cr)} \\
  - 9.39 \text{ (wt\% Si)} - 172.71 \text{ (wt\% P)} - 94.95 \text{ (wt\% S)} - 21.94 \text{ (wt\% Mo)} \\
  + 15.19 \text{ (wt\% Ni)} - 94.25 \text{ (wt\% Cu)} + 3188.33 \text{ (wt\% V)} + 176.62 \]

[2.11]

Notice the very large dependence of interstitial nitrogen content on the overall yield strength. It is known that carbon adds strength to steel, but notice the difference in the yield strength dependence between carbon and nitrogen. Carbon increases strength by a factor of 3.03, while nitrogen increases strength by a factor of 335.60. This yield strength data is very important because if the solubility can be controlled, much larger levels of nitrogen can be utilized to double, triple, or even quadruple the yield strength of normal austenitic stainless steels. Rawers [1999, 2000] at Albany Research Center has been working on the development of high nitrogen-carbon interstitial stainless steels with carbon and nitrogen exceeding much greater values than 0.5 wt. pct., without the formation of nitrides and carbides.

Nitrogen in austenitic stainless steel also has a very positive effect on corrosion resistance. Interstitial nitrogen is shown to shift the breakdown potential of pitting to more positive values, thus retarding the breakdown of the austenitic passive film. A comparison of pitting potential data on the influence of various alloying elements in stainless steels is shown in Figure 2.10. The beneficial effect of nitrogen is clearly shown, which also may suggest that
nitrogen compensates the detrimental influence of manganese on pitting corrosion. Chromium and molybdenum assist nitrogen in improving the resistance to the pitting attack and intergranular corrosion as reported by Mudali et al. [1996].

Figure 2.10: Shift in pitting potential by different alloying elements of austenitic stainless steel in dilute chloride solution [Speidel and Pedrazzoli, 1992].
Because nitrogen partitions into interstitial nitrogen and formed nitrides, it is necessary to monitor the interstitial nitrogen content at all times to gain these beneficial mechanical properties and corrosion resistance. Until this point, there are no available destructive or non-destructive techniques for interstitial nitrogen content determination in austenitic stainless steels. Destructive techniques such as x-ray diffraction analysis can be utilized to determine interstitial contents, however x-ray diffraction is a very time consuming practice for industrial activities. With increasing popularity of utilizing interstitial nitrogen as a strengthener and for its corrosion resistance it is essential to quantify its contents. The resulting lattice strain due to nitrogen additions and the donation of electrons allows the interstitial nitrogen content to be non-destructively assessed utilizing electronic and magnetic tools.

2.4. **Hydrogen**

Just like nitrogen, hydrogen can be both beneficial and detrimental dependent upon the location and phase in which hydrogen is present. In steel hydrogen can have a devastating result on properties such as hydrogen assisted cracking, so that in steel any hydrogen uptake should be closely monitored. Hydrogen, on the other hand, can be extremely beneficial in terms of energy usage. Hydrogen is combined with metals such as LaNi₅ to allow for reversible hydrogen energy storage. In both cases, it is necessary to monitor the amount and content of hydrogen at all times.

The ability of a metal alloy to absorb and desorb hydrogen depends on the interaction with the metal's electronic bands. When hydrogen enters the crystal lattice it acts as either an electron acceptor or an electron donor as seen in Figure 2.11. The elements on the left of manganese on the periodic table are
electron acceptors, having a negative heat of mixing with hydrogen, which results in the formation of hydrides. The elements to the right of manganese on the periodic table are electron donors having a positive heat of mixing so that hydrogen stays in solution.

![Figure 2.11: Electronic behavior of hydrogen in transition metal alloys.](image)

**2.4.1. Solubility of Hydrogen in Metals**

When hydrogen enters the metal lattice it dissociates into a proton and an electron. The proton occupies the interstitial site in ferrous alloys and the electron is donated to the host metal electronic d-band. The proton is very small when compared to the size of the interstitial site. The positive charge of the proton must be screened to maintain the electrical neutrality [Pepperhoff and Acet, 2001]. The electrical neutrality is preserved by the formation of an atomic sized electron cloud, however this process is not perfect so that repulsive forces occur between the proton and the neighboring positively charged metal nuclei. These repulsive forces result in a local expansion and lattice distortion. Figure 2.12 shows the change in volume of the unit cell with increasing hydrogen.
concentration due to the repulsive forces from the electron cloud. Hydrogen does not only cause large lattice distortion, but it also contributes to the chemical potential of the electron in the metal. Figure 2.13 shows the change in the chemical potential in zirconium nickel alloys due to the addition of hydrogen atoms. The chemical potential is the upper most filled electron band, otherwise known as the Fermi energy. The solubility of hydrogen in the metal lattice is affected by the electronic filling of the host metal electronic conduction bands by other metallic solutes because there must be space for hydrogen to donate its electron.

The solubility of hydrogen in iron can be described by an Arrhenius-type plot as shown in Figure 2.14 in the temperature range of 500 to 900°C. An increase in the hydrogen solubility is observed due to lattice defects (traps) at temperatures less than 500°C, so that the actual room temperature solubility can only be extrapolated. Hydrogen traps [Maroef et al., 2002] also play a role in the solubility of hydrogen because it literally traps the hydrogen atoms, no longer allowing the hydrogen to diffuse through the metal lattice. At lower temperatures, hydrogen prefers to occupy tetrahedral sites and at higher temperatures, hydrogen prefers the occupation of octahedral sites.

Sieverts' law holds true for hydrogen because hydrogen gas molecules become dissociated into atoms while being dissolved into metals in the region where hydrogen can be regarded as an ideal gas. At higher pressures and temperatures, the chemical potential and solubility of hydrogen deviates from the ideal gas behavior, thus Sieverts' law no longer applies. The chemical potential of hydrogen gas increases dramatically at even higher pressures resulting in a great solubility enhancement [Fukai, 1993]. As with nitrogen, there are many factors affecting the solubility and diffusivity of hydrogen in metals. Further details and thermodynamics of hydrogen are given in Appendix C.
Figure 2.12: Increase in volume in the unit cell with increasing hydrogen concentrations at $T=38^\circ K$ and atmospheric pressure [Pepperhoff and Acet, 2001].
Figure 2.13: Chemical potential of hydrogen in amorphous Zr<sub>y</sub>Ni<sub>1-y</sub> alloys plotted against normalized variations in hydrogen content. The upper limit corresponds to the standard state of hydrogen gas at 295°K and 1 atm [Harris et al., 1987].
Figure 2.14: Solubility of hydrogen in iron under ambient pressure [Silva et al., 1976].
2.4.2. **Advanced Hydrogen Storage Materials**

Hydrogen is a versatile fuel that can quickly be generated from and converted to other forms of energy. To store hydrogen, is to store energy [Wiswall, 1978]. Efficient hydrogen storage and transportation are major issues for hydrogen energy technology because it is not only important to store hydrogen, but release of the hydrogen at a later time and date is also necessary.

In hydrogen-fueled automobiles, if the hydrogen is stored in gas cylinders or liquid form, the automobile will never be efficient. Gas cylinders are much too large and heavy and to liquefy hydrogen requires a power input of 14,450 kJ/kg or 6.96 kcal/mol [Wiswall, 1978], so that the use of liquid hydrogen is energetically wasteful, which leads to alternative methods for hydrogen storage.

Metal hydrides can serve as hydrogen sources through either chemical reactions or thermal decomposition. If hydrogen can be obtained through a thermal decomposition reaction, normally the metallic product can be quickly and easily reconverted back to hydride very simply by direct combination with hydrogen [Wiswall, 1978].

The first reversible hydrogen storage material was palladium and was discovered by Thomas Graham over 100 years ago. In the past 100 years, hundreds of other metal-hydrogen systems have been shown to possess the same reversible properties as palladium. In some cases, large amounts of hydrogen dissolve interstitially into the metal system. The addition of hydrogen to a metal system would soon result in the metal becoming supersaturated with hydrogen to begin to form a hydrogen-rich hydride phase [Wiswall, 1978]. When choosing a hydride for hydrogen storage use, it is the amount of hydrogen stored per unit volume and per unit weight of the medium that is important to consider.

The definition of a hydride is broadly described as the case where the structure of the metal lattice is changed by the absorption of hydrogen [Fukai, 1993]. However, the definition of a hydride can be used a little more loosely so
that it includes the cases where the hydrogen atoms are distributed so that the solid solution becomes ordered as the temperature is decreased. So in general, all hydrides are designated as metal-hydrogen systems other than a random interstitial solid solution. Ordered hydride structures are stable over certain ranges around stoichiometric compounds with a larger range at higher temperatures. However, a certain degree of disorder usually exists in hydride phases [Fukai, 1993]. To determine the structure of hydrides and the location of hydrogen atoms, it is necessary to compliment x-ray diffraction studies with neutron diffraction or inelastic scattering experiments [Fukai, 1993].

Table 2.1 lists some typical densities and the number of atoms per cubic meter of hydride for numerous hydride materials. The usefulness of hydride is not only dependent on the amount of hydrogen stored per unit volume, but also on the effectiveness of the medium to release the hydrogen, which means that the heat of the requisite quality and quantity must be available to supply the enthalpy of dissociation [Wiswall, 1978]. The desired thermal quantities will be dependent upon the application of the hydride. Quite different hydrides will be selected to supply aqueous fuel cells as opposed to internal combustion engines. In most cases, it is useful to focus on the hydrides that have $\Delta H_f$ values with smaller (less negative) values than -20 kcal/mol [-83.4 kJ/mol].

The stability of a hydride is measured by its heat of formation or the change in enthalpy due to the formation of the hydride from the reaction of one mole of hydrogen (H$_2$) gas with a metal [Fukai, 1993]. The heat of formation of a hydride $MH_{x\beta}$ is defined for a hypothetical reaction as:

$$\frac{1}{x\beta} M + \frac{1}{2} H_2 \rightarrow \frac{1}{x\beta} MH_{x\beta}$$  \hspace{1cm} [2.12]
where $x_\alpha$ is a certain range of values corresponding to the stoichiometry composition. A hydride is actually formed by the hydrogenation of a solid solution ($\alpha$-phase) through a reaction of the form [Fukai, 1993]:

$$
\frac{1}{x_\beta - x_\alpha} MH_{x_\alpha} + \frac{1}{2} H_2 \rightarrow \frac{1}{x_\beta - x_\alpha} MH_{x_\beta}
$$

[2.13]

The enthalpy and entropy changes in this reaction is expressed as $\Delta H^{\alpha \rightarrow \beta}$ and $\Delta S^{\alpha \rightarrow \beta}$, so that the equilibrium condition can be expressed as:

$$
\Delta H^{\alpha \rightarrow \beta} - T \Delta S^{\alpha \rightarrow \beta} = 0
$$

[2.14]

**NaAlH$_4$ and LaNi$_5$**

For this particular research LaNi$_5$ and NaAlH$_4$ will be the hydrogen storage materials of choice. This section will describe the chemical reactions and thermodynamics for these hydrides.

Group III (A and B) metals beyond aluminum such as scandium, yttrium, and the rare earths all form extremely stable dihydrides. Aluminum is similar to beryllium in that it is very different from the heavier members of its group. Its hydride AlH$_3$ is very unstable and must be made by reactions like [Wiswall, 1978]:

$$
3LiAlH_4 + AlCl_3 \xrightarrow{(C_2H_5)_2O} 4AlH_3 + 3LiCl
$$

[2.15]

AlH$_3$ was thought to be a great candidate for rocket fuel, so that its chemistry was thoroughly investigated. AlH$_3$ contained up to ten weight percent hydrogen and decomposes on heating at just a little above 100°C deeming it a great hydrogen
storage material, however the indirect synthesis of this material is much too expensive. AlH₄ cannot be made directly from the elements even at hydrogen pressures greater than 4000 psi (28 MPa) at -196°C or at 8200 psi (57.4 MPa) at room temperature, which has also been thermodynamically verified [Wiswall, 1968].

<table>
<thead>
<tr>
<th>Medium</th>
<th>Density (g/cm³)</th>
<th>Weight Percent Hydrogen</th>
<th>N₄H₄, atoms hydrogen per cm³ *10²²</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂, gas at 100 atm</td>
<td>8.2E-5</td>
<td>100</td>
<td>0.49</td>
</tr>
<tr>
<td>H₂ liquid</td>
<td>0.071</td>
<td>100</td>
<td>4.2</td>
</tr>
<tr>
<td>Water</td>
<td>1.0</td>
<td>11.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Liquid Ammonia</td>
<td>0.6</td>
<td>17.8</td>
<td>6.5</td>
</tr>
<tr>
<td>LiH</td>
<td>0.8</td>
<td>12.7</td>
<td>5.3</td>
</tr>
<tr>
<td>NaH</td>
<td>1.4</td>
<td>4.2</td>
<td>2.3</td>
</tr>
<tr>
<td>MgH₂</td>
<td>1.4</td>
<td>7.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Mg₂NiH₄</td>
<td>2.6</td>
<td>3.8</td>
<td>5.9</td>
</tr>
<tr>
<td>CaH₂</td>
<td>1.8</td>
<td>4.8</td>
<td>5.1</td>
</tr>
<tr>
<td>CaH₂ + H₂O</td>
<td>-</td>
<td>6.7</td>
<td>-</td>
</tr>
<tr>
<td>AlH₃</td>
<td>1.48</td>
<td>10.1</td>
<td>8.9</td>
</tr>
<tr>
<td>LiAlH₄</td>
<td>0.91</td>
<td>10.6</td>
<td>5.74</td>
</tr>
<tr>
<td>CeH₃</td>
<td>5.5</td>
<td>2.1</td>
<td>7.0</td>
</tr>
<tr>
<td>TiH₂</td>
<td>3.8</td>
<td>4.0</td>
<td>9.0</td>
</tr>
<tr>
<td>TiFeH₁.₉₃</td>
<td>5.47</td>
<td>1.8</td>
<td>6.0</td>
</tr>
<tr>
<td>LaNi₆H₆.₇</td>
<td>8.25</td>
<td>1.5</td>
<td>7.58</td>
</tr>
<tr>
<td>VH₂</td>
<td>4.5</td>
<td>2.1</td>
<td>10.3</td>
</tr>
</tbody>
</table>
Aluminum hydrides can be stabilized through combinations with other hydrides, which are called aluminohydrides or alanates, which are examples of salt-like complex hydrides [Wiswall, 1978]. Some typical alanates include NaAlH₄ and Mg(AlH₄)₂. Alanates release hydrogen at readily accessible temperatures, however the reactions are very complex. For example, NaAlH₄ first decomposes to complex hydride Na₃AlH₆, which then at higher temperatures decomposes itself to NaH:

$$NaAlH₄ \rightarrow \frac{1}{3}Na₃AlH₆ + \frac{2}{3}Al + H₂$$  \hspace{1cm} [2.16]

$$Na₃AlH₆ \rightarrow 3NaH + Al + \frac{3}{2}H₂$$ \hspace{1cm} [2.17]

For the first reaction, Dymova et al. [1975] reported an equilibrium pressure of 153.5 atmospheres at 210°C and for the second reaction an equilibrium pressure of 21.4 atmospheres also at 210°C. Further work on the synthesis and decomposition needs to be performed on the alanates to produce useful hydrogen storage systems.

Because alanates are considered to be the most promising of the complex metal hydrides for hydrogen storage applications NaAlH₄ has been investigated in this research. Under moderate conditions, NaAlH₄ can generally store up to 4 weight percent hydrogen, while the temperature required to release hydrogen from NaAlH₄ is very high for practical purposes. Bogdanovic et al. [2002] has shown that new catalysts such as titanium and iron alcoholates, enhance rates of both dehydrogenation and rehydrogenation of Ti/Fe doped NaAlH within cycle tests reaching a reversible gravimetric hydrogen storage capacity of 4 weight percent. The formation of NaAlH₄ from the elements requires temperatures of
200-400°C above the melting temperature of the tetrahydride and hydrogen pressures between 100-400 atm. Introducing catalysts to this reaction can significantly improve the reversibility of the hydride making it more practical as a hydrogen storage material [Bogdanovic and Sandrock, 2002].

The kinetics and the thermodynamics of reaction in Equation 2.16 are important in optimizing the hydrogen capacity in NaAlH₄. The temperature dependence of the plateau pressures in Figure 2.15 can be related to the Van't Hoff equation allowing for a direct comparison of the thermodynamic properties of NaAlH₄ to that of other hydrogen storage materials such as LaNi₅H₆ and MgH₂ as shown in Figure 2.16. NaAlH₄ has thermodynamic properties comparable to those properties of classic low-temperature hydrides such as LaNi₅H₆ and TiFeH.

There are also a large number of other rare earth materials of great interest and these are described by the formula AB₅, where A is the rare earth material and B is the non-hydriding forming transition element such as nickel. Pressure-composition-temperature information is available for a variety of AB₅ compounds. Some examples of well-studied AB₅ compounds include: LaNi₅, (La,Ce)Ni₅, PrNi₅, NdNi₅, LaCo₅, PrCo₅, NdCo₅, CeCo₅, etc. Most of the AB₅ compounds hold less hydrogen than LaNi₅. The highest known hydrogen content is for LaCo₅ at a pressure of 137.3 MPa (1334.7 atm), however the isotherm for LaCo₅ does not have a suitable form for hydrogen storage purposes.

LaNi₅ has been such a promising material, that it has also been chosen as the candidate material for this investigation because it has been thoroughly studied as a potential material for rechargeable metal-hydride batteries and hydrogen storage devices. A LaNi₅ metal-hydride battery would operate in the two-phase, (alpha+beta)-region, as seen on the pressure-composition-temperature diagram (activity diagram) for LaNi₅ shown in Figure 2.17 [Van Vucht et al., 1970]. The two-phase region consists of both soluble (diffusible) hydrogen, a, and formed hydrides, b. Theoretically, the rule-of-mixtures can be
utilized in this two-phase region to determine the percentage of hydride and diffusible hydrogen at a given H/LaNi₅ value. The ability to quantify and characterize both the diffusible hydrogen and hydride contents in this two-phase region is critical to the performance of the reversible hydrogen storage materials.

2.4.3. **Hydrogen in Structural Steel**

High strength linepipe steels (in excess of 70 ksi (490 MPa) yield strength) are being rapidly introduced for operation and use at higher pressures and larger radii. New approaches for hydrogen management need to be addressed. With increasing steel strength there is a reduction in the allowable diffusible hydrogen content to avoid hydrogen assisted cracking. Hydrogen-assisted cracking and hydrogen embrittlement are common terms used to describe sub-critical cracking due to hydrogen in metals. Hydrogen damage refers to the action of hydrogen reducing the physical and mechanical properties of a material to a degree that renders a material dangerous (Beachem, 1977).

Hydrogen can be introduced into the linepipe steel in numerous ways; for example, through welding procedures, cathodic protection, corrosion reactions with the environment, and interactions with the contained media in the pipes. Research efforts in hydrogen damage are seriously hampered because the equipment available only measures the total effects of very large numbers of hydrogen molecules, ions, or protons, as they act on a specimen or service component [Beachem, 1977].

Due to the abundance of hydrogen sources in pipelines, it is important to quantify the amount and form of hydrogen present in the steel because there is a distinction between total, residual, and diffusible hydrogen.
Figure 2.15: Pressure-composition-temperature isotherms for NaAlH₄ and Na₄AlH₆ [Bogdanovic et al., 2000].
Figure 2.16: Van't Hoff plot comparing the dissociation pressures as a function of temperature for various hydrogen storage materials [Bogdanovic et al., 2000].
Figure 2.17: Isotherms of hydrogen gas (pressure $p_{H_2}$ atm) in equilibrium with absorbed hydrogen in LaNi5 (concentration: $H$ atoms/LaNi5) [Van Vucht et al., 1970]. Notice the alpha-region is where hydrogen is in solid solution in the alloy lattice, the (alpha+beta)-region is made-up of both solid solution hydrogen and hydrides, and the beta-region is only formed hydride.

Diffusible hydrogen is considered to be mobile at lower temperatures ($<100^\circ$C), whereas the remaining residual hydrogen is trapped in the metal at microstructural discontinuities or by the formation of hydrides with alloying elements. Total hydrogen is the combination of the two fractions. Each form of hydrogen exhibits different properties. For example, diffusible hydrogen
increases dislocation motion, whereas dislocation motion would be temporarily hindered by a formed hydride because the dislocation will have to cut or bow around it (dependent upon the shear stress). It is also well established that the formation and fracture of brittle hydrides promote hydrogen-assisted cracking.

Thomas Graham coined the term "occlusive capacity" defined as the concentration of hydrogen within a compact metal when it has established a steady state of exchange with hydrogen gas of certain temperature and pressure [Smith, 1948]. The occlusive capacity is the solubility dependent on the degree of strain or plastic deformation [Beck et al., 1965]. The occlusive capacity is important because hydrogen tends to accumulate in regions of high stress (stress-assisted hydrogen diffusion). There are many regions of high stress in pipelines. Some examples high stress regions include: (1) heat-affected zones (2) grain boundaries, (3) voids, and (4) crack tips. The most common types of cracks occurring in pipelines are hydrogen induced cracks, fatigue cracks, stress corrosion cracks, and cracks in the weld HAZ. The occlusive capacity describes the true solubility of hydrogen in the pipeline due to stress. Figure 2.18 shows the importance of the occlusive capacity because variations in hydrogen content play a vital role on the stress state for crack growth during hydrogen assisting cracking and stress corrosion cracking. The concentration of hydrogen at a crack tip will change the mode of hydrogen cracking at a particular stress intensity factor [Beachem, 1972]. The curved dashed lines indicate critical combinations of stress intensity factor and hydrogen content for the cause of crack growth by the three fracture modes. The existence and position of each of the curves are microstructure dependent, so this graph does not hold true for all materials. Below the lowest curve, no hydrogen cracking is expected. Each of the curves are drawn to meet at the critical stress intensity factor because quench and tempered steels tend to exhibit one or all of these fracture modes when failure occurs in the absence of induced hydrogen [Beachem, 1972].
Figure 2.18: Suggested interrelationships between stress intensity factor as a function of dissolved hydrogen concentration in microscopically volumes of crack tip material showing the changes in hydrogen assisted cracking fracture modes. (IG: Intergranular, QC: quasi-cleavage, MVC: micro-void coalescence) Beachem 1972.

**Hydrogen Assisted Cracking Models**

Hydrogen damage has been divided into three different forms. One form of damage results in internal pores, cracks or other flaws arising from either the
entrapment of hydrogen bubbles during solidification of the melt or diffusion of hydrogen through the metal lattice to cause flaws. At higher temperatures, hydrogen reacts predictably to alter chemical compositions to form collecting pockets of gaseous molecules that cannot escape by diffusion and remains trapped. The second form of damage results when formed hydrides assume specific lattice positions within the metal, thus lowering the mechanical properties and the toughness of the metal. The third form of hydrogen damage results despite the absence of a known chemical reaction or hydride formation; nevertheless the hydrogen causes crack formation and growth, particularly in the presence of sustained stress. This form of damage is called hydrogen-assisted cracking (otherwise known as hydrogen embrittlement) [Buzzard and Cleaves, 1951], [Johnson, 1873-1875], [Troiano et al., 1974], [Beachem, 1977]. This third type of damage has been related to localized microplasticity in the region of the triaxial stress at the crack tip.

The following conditions must be met for the occurrence of hydrogen assisted cracking: (1) sufficient atomic hydrogen in the material, (2) tensile stress, (3) susceptible material, (4) temperature range that supports very localized hydrogen transport (-50 to 150°C in steel). When these conditions are met, in non-hydride forming elements, there are three mechanisms of hydrogen embrittlement worthy of consideration [Darken and Smith, 1949], [Beck et al., 1966] [Lynch, 1991]. These mechanisms include: (1) hydrogen-enhanced localized plasticity, (2) hydrogen-enhanced de-cohesion, and (3) adsorption-induced dislocation emission. These mechanisms have been proposed for embrittlement in external (H₂, H₂S, H₂O) and internal (introduced into steel during welding, plating, etc) hydrogen environments [Lynch, 2001]. It should be recognized that the cracking mechanisms could be similar, however the rate controlling processes are very different.
Hydrogen-Enhanced Localized Plasticity (HELP)

Hydrogen-enhanced localized plasticity is based on the presence of solute hydrogen ahead of cracks, specifically in hydrogen atmospheres around both mobile dislocations and obstacles to dislocations [Paskin et al., 1983, 1984] [Thomson, et al., 1986], [Daw and Baskes, 1984], [Lynch, 1999], [Beachem, 1972]. It has been suggested that the hydrogen atmospheres distort when mobile dislocations approach obstacles, meaning that the repulsion by obstacles is decreased. Since hydrogen accumulation is localized near crack-tips, deformation is localized and facilitated near crack-tips, resulting in an overall lower strain for fracture [Lynch, 1999, 2001].

Hydrogen-Enhanced Decohesion (HEDE)

Hydrogen-enhanced decohesion is the weakening of iron-iron intermetallic bonds at or near crack tips due to high localized hydrogen concentrations in the lattice resulting in tensile separation of the atoms [Oriani, 1972, 1977], [Troiano, 1960]. The weakening of bonds may be the result of a decrease in the electronic charge density between metal-metal atoms due to the existence of hydrogen in the crystal lattice in interstitial sites [Lynch, 2001]. For hydrogen-enhanced decohesion, fracture surfaces should appear basically featureless with a few cleavage steps and tear ridges separating de-cohered regions [Lynch, 1999].

Adsorption Induced Localised Slip (AIDE)

Adsorption induced localised slip is based on hydrogen-induced weakening of interatomic bonds, but with crack growth occurring by localised slip [Birnbaum, 1994], [Lynch, 1999]. It has been proposed that adsorbed hydrogen weakens substrate interatomic bonds and thereby facilitates the emission of dislocations
from the crack tips. There is also substantial dislocation emission ahead of the crack tip, resulting in the formation of voids around particles or at slip band intersections. This behavior means that crack propagation occurs due to dislocation emission from crack tips also with a contribution from the void formation ahead of the crack tip [Birnbaum, 1994], [Lynch, 1999, 2001].

A combination of these three mechanisms occur in most cases. Figure 2.19 schematically illustrates the HELP, HEDE, and AIDE. The most dominant mechanism will be dependent upon variables such as strength, microstructure, slip-mode, stress intensity factor, and temperature, thus affecting the fracture path and appearance [Lynch, 2001].

Figure 2.19: Schematic diagrams illustrating HEDE, HELP, AIDE mechanisms of hydrogen-assisted cracking [Lynch, 2001].
CHAPTER 3

LITERATURE REVIEW OF THE TECHNIQUES FOR DETERMINATION OF INTERSTITIAL CONTENTS

To properly use interstitial additions in advanced materials it is necessary to quantify the total, interstitial, and formed precipitate contents. Non-destructive techniques are described to assist in determination of interstitial contents in advanced materials involving the development of both contact and non-contact techniques. Multiple techniques have been developed for use as hydrogen sensors. Some of these techniques include volumetric displacement, gas chromatography, laser ablation with mass spectrometry, laser ablation with gas chromatography, and opto-electronic diffusible hydrogen sensors.

Volumetric displacement is the standard AWS method for measuring hydrogen in weld specimens. In this method a sample is placed into a eudiometer and allowed to evolve hydrogen at temperatures varying from 45 to 150°C [AWS, 1993]. The evolved gas displaces the mercury in the top of the column and the amount of displacement is measured as a function of volume. The results are reported as a function of milliliter of hydrogen per 100 grams of deposited weld metal [AWS, 1993]. Due to the increased health concerns of using mercury displacement testing, gas chromatography has become another very popular method.

In gas chromatography, hydrogen specimens are placed in sealed containers and baked to release the hydrogen. The evolved gas is transferred to a gas chromatograph and then separated with a packed molecular sieve column to be
analyzed using a thermal conductivity detector. The gas chromatograph gives comparable results to mercury testing [AWS, 1993], [Quintana, 1988].

Laser ablation methods use laser energy to release diffusible hydrogen from the surface to allow for the determination of hydrogen levels in particular areas on weld surfaces. Laser energy releases very small amounts of hydrogen, thus requiring very sensitive detection methods such as mass spectrometry [Smith et al., 1999, 2001]. The presence of organic material on the surface poses problems due to decomposition and hydrogen formation from the contaminants in the laser plasma.

The opto-electronic diffusible hydrogen sensor utilizes the optoelectronic properties of hydrogen sensitive material such as tungsten oxide to generate analytical signals [Smith et al., 1997]. When hydrogen is absorbed on the surface it reacts to form an ion insertion compound. The optical properties of the compound are altered and can be detected visually or spectroscopically. The opto-electronic diffusible hydrogen sensor takes approximately one hour and can be utilized on actual welds as opposed to laboratory specimens.

3.1. Thermoelectric Power Analysis

Due to the electronic nature of nitrogen and hydrogen, it is possible to assess interstitial contents utilizing a technique based on a modern physics concept called the Seebeck effect, otherwise known as thermoelectric power. A thermoelectric phenomena occurs when two dissimilar metals are connected and the junction held at different temperatures, there are five phenomena that occur simultaneously, which are (1) the Seebeck effect, (2) the Joule effect, (3) the conduction of heat, (4) the Peltier effect, and (5) the Thomson effect [Zemansky,
1957], [Heikes and Ure, 1961]. Phenomena 2 through 4 are summarized in Appendix D.

The use of thermoelectric power for material characterization has become increasingly important due to its ease and rapidity of measurements. A brief history of thermoelectric power and the theory behind the Seebeck effect is described in the following sections.

3.1.1. Free Electron Theory

The free electron model assumes valence electrons of the constituent atoms become conduction electrons and move about freely through the volume of the metal. For example, copper has a loosely bound valence electron. When copper atoms are brought together to form solid copper, these electrons become a part of a “gas” of nearly free electrons that can easily move through the metal lattice. Certain properties of metal can be determined from the electron gas properties. The properties of the metal are determined by the occupation of the valence and conduction bands, by the spacing between the valence and conduction bands, and by the relative location of the Fermi energy [Krane, 1996]. A conduction electron is scattered by perturbations of periodicity like lattice defects, impurities, phonons (quants of lattice vibration), etc. A conduction electron is scattered only infrequently by other conduction electrons, which is a consequence of the Pauli-exclusion principle, which states that no two electrons in a single atom can have the same set of quantum numbers [Kittel, 1996].

The Pauli-exclusion principle is the most important rule governing the electronic structure of atoms, and no study of the properties of atoms can be attempted without a thorough understanding of this principle [Kittel, 1996]. So, a
Fermi free electron gas is just a gas of free electrons subject to the Pauli-exclusion principle.

The available electronic states are determined from solutions to the Schrödinger equation. The highest electronic energy state assumed by an electron at absolute zero is the Fermi energy as shown in Figure 3.1. The Fermi energy is:

\[ E_F = \frac{\hbar^2 k_F^2}{2m} \]  \hspace{1cm} [3.1]

where \( \hbar \) is the Planck's constant divided by 2\( \pi \), \( m \) is the mass of an electron, \( k_F \) is the Fermi wave vector.

Figure 3.1: Half-filled band at T=0°K, showing the Fermi-Dirac distribution of on the right [Krane, 1996].

The Fermi wave vector can be determined in terms of the electronic density resulting in:

\[ k_F = \left(3\pi^2 N_e\right)^{1/3} \]  \hspace{1cm} [3.2]
where \( N_e \) is the number of electrons per volume of the crystal. Substituting the Fermi wave vector into the Fermi energy equation now becomes:

\[
E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N_e}{\nu^2} \right)^{2/3}
\]

[3.3]

It is important to notice that the Fermi energy for free electron gas is primarily a function of the electron concentration.

The kinetic energy of the electron gas increases as temperature increases. Some energy levels, which were empty at absolute zero may become occupied with a temperature increase and some energy levels, which were occupied at absolute zero may become empty as shown in Figure 3.2.

Figure 3.2: Fermi-dirac distribution function applying to an electron gas in three dimensions [Kittel, 1996].
The Fermi-Dirac distribution gives the probability that an electronic state at energy, $E$, will become occupied in an ideal electron gas in thermal equilibrium:

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1} \quad [3.4]$$

The quantity $\mu$ is the chemical potential of the free electrons, which is a function of temperature [Kittel, 1996]. The chemical potential is unique characteristic for particular systems. The chemical potential for electrons is the Fermi energy level at all temperatures. In metals the chemical potential (Fermi energy) coincides with the highest energy of a state occupied with an electron at a temperature of absolute zero.

### 3.1.2. Thermoelectric Power Theory

The thermoelectric power coefficient is a function of the electronic scattering behavior, the electron concentration, and the effective mass of the electron in this alloy, which are all influenced by solute content, lattice strain, microstructural changes, material processing, and time dependent phase changes [Caltech.edu, 2003]. The thermoelectric power coefficient is a valued property for microstructural assessment. Because alloy microstructure correlates directly to electronic properties, the thermoelectric power coefficient is a rapid and effective way to assess alloy aging and microstructural changes before significant defects arise resulting in structure failure.

In metallic alloys, the value and the sign of the thermoelectric power coefficient depends on the electronic features in the vicinity of the Fermi energy level, changes in the electronic carriers, and is also dependent on the effective mass tensor, density of electronic states, and the dominating scattering
mechanism [Park et al., 2003]. In turn, the Fermi energy value (Fermi energy surface in the k-space) changes with electronic filling in the conduction band due to the electron donation by interstitial atoms. For example, with the high degeneracy of the free electron gas, the resulting thermoelectric power coefficient, \(Z\), is related to the electron theory through the following expression, the degeneracy of the electron gas at high carrier concentrations is given as:

\[
Z = \left( \pm \frac{\kappa}{e} \right)^{(27.1)} \left( r + \frac{3}{2} \right) \left( \frac{m_e}{\hbar^2} \right) \left( \frac{2}{kTn} \right) \left( \frac{2}{3} \right) \left( \frac{2}{3} \right) \left( \frac{2}{3} \right) \quad [3.5]
\]

where \(r\) is the scattering parameter determined by the dominating scattering mechanism, and \(\hbar\) is Planck’s constant, \(\kappa\) is Boltzmann’s constant, \(n^*\) is the electron concentration, and \(m_e\) is the effective mass. From the free electron model, the electron concentration is directly related to the Fermi energy. The effective mass describes the rate of filling of the energy states in k space at the Fermi energy level with increasing electron concentration [Park et al., 2003]. The effective mass can be described as:

\[
m_e = \hbar^2 \left( \frac{d^2 E}{dk^2} \right)^{-1} \quad [3.6]
\]

where \(k\) is the wave vector. The effective mass, \(m_e\), describes the shape of the s, p, and d bands that are in contact with the Fermi energy level. The shape of the bands at the contact position offers a sensitive indication of changes in alloy composition, phase content, and lattice strain.
Use of the Effective Mass of an Electron

To understand the role of the effective mass of the electron in interpreting the electronic interactions with the lattice consider a free electron wave function in a lattice. Figure 3.3 is an illustration of the free electron wave function, described by the dashed line, with local electron interactions of the potentials associated with the lattice atoms.

![Free Electron Wave](image)

**Figure 3.3:** The (augmented plane wave) wave function produced by a combination of atomic states with a free electron wave function between the ion cores [Wilkes, 1973].

If a lattice atom is a solute atom or is situated in a strain field, the localized potential will be altered and will offer a different interaction to the nearly-free conduction electron wave function. In the free electron model, the potential is V=0, the electron’s energy is given as \( E = \frac{1}{2}mv^2 = \frac{P^2}{2m} \), where \( P \) is the electron’s momentum, the deBroglie expression is \( P = \hbar k \), and the energy is
expressed as \( E = \frac{\hbar^2 k^2}{2m} \), where \( m \) is the mass of an electron. For situations where there are localized lattice potential interactions, the conduction electron's energy could be described as \( E = \frac{\hbar^2 k^2}{2m} + V \), where \( V \) is associated with the potential energy experienced by the conduction electron in the vicinity of the lattice atom. Now, allowing the value of the mass of the electron to be altered to quantitatively incorporate the effect of \( V \), the effective mass, \( m_e \), is introduced to describe the total energy as \( E = \frac{\hbar^2 k^2}{2m_e} \). In this manner the free electron formulation can be used to derive the electron properties of an alloy, thus making the effective mass a valuable parameter to assess the microstructure and alloy stability through electron property measurements.

To gauge the magnitude of this effect, the Seebeck coefficient is introduced which is defined as the potential difference developed per unit temperature difference:

\[
Z = \frac{dV}{dT} \tag{3.7}
\]

By convention, the sign of \( Z \) represents the Seebeck coefficient. The coefficient \( Z \) is widely referred to as thermoelectric power or thermoelectricity. The Seebeck coefficient is a material property that depends on temperature \( Z = Z(T) \). Given the Seebeck coefficient for material, the voltage difference between two points where temperature are \( T_0 \) and \( T_f \) is given by:

\[
\Delta V = \int_{T_0}^{T_f} ZdT \tag{3.8}
\]

To observe thermoelectricity, it is necessary to have a circuit composed of two different materials, and the net difference between their thermoelectric
properties can be measured. The electromotive force (emf) produced under these conditions is the relative Seebeck emf. The Seebeck effect exists due to a developed potential between hot and cold ends with the hot end at the positive potential as illustrated in Figure 3.4 [Kasap, 1999].

![Diagram of Seebeck effect](image)

**Figure 3.4:** A temperature gradient ($\Delta T$) gives rise to a potential difference ($\Delta V$), which is the Seebeck effect [Kasap, 1999].

The developing voltage of each element is dependent upon the Seebeck coefficient, where the potential difference between two metals $Z_{AB} = Z_A - Z_B$. The emf between the two metals, $V_{AB} = \Delta V_A - \Delta V_B$ can be expressed by following:

$$V_{AB} = \int_{T_0}^{T} (Z_A - Z_B) dT = \int_{T_0}^{T} Z_{AB} dT$$  

[3.9]
where $Z_{AB} = Z_A - Z_B$ is defined as thermoelectric power for the thermocouple pair A-B. The absolute Seebeck coefficient (ASC) of the alloy material, $Z_a$, can be determined from measurements as:

$$Z_a = \frac{V}{\Delta T} - Z_{Cu} \quad [3.10]$$

where $V$ is the Seebeck voltage measured between alloy material and reference copper block, $\Delta T$ is the temperature difference, and $Z_{Cu}$ is the well-calibrated Seebeck coefficient for copper. One of copper probe is maintained at room temperature and the other one at a temperature higher by 10 °C. More detailed information for measuring ASC for alloy material is described in experimental procedures. With the use of a Keithley nano-voltsmeter with high impedance to measure the potential difference, the scattering factor, $r$, makes a small contribution as a dependent variable for $Z_{ab}$. These conditions allow the $Z_a$ measurement to be very sensitive to the factor of the effective mass of the electron.

3.1.3. Characteristics of Thermoelectric Power Coefficients in Transition Metals

In Russia, Vedernikov [1969] was the first to conduct and publish thermoelectric power measurements on transition metals in the temperature range of 80 to 2073°C (1800K). Vedernikov [1969] conducted experiments in this (80 to 2073°C) temperature range to determine the structural and magnetic transformations in the high temperature range for transition metals. Vedernikov's experiments provided an empirical regularity in the behavior of thermoelectric power for transition metals.
The transition metals are the 38 elements in groups 3 through 12 of the periodic table shown in Figure 3.5. As with all metals, the transition elements are both ductile and malleable, and conduct electricity and heat. The transition metals are arranged in a magnetically ordered state. The transition metal valence electrons combine are present in more than one electronic shell, which is the reason that the transition metals often exhibit several common oxidation states [Vedernikov, 1969].

Numerous attempts have been conducted for the establishment of thermoelectric power theory for real metals, however theorists do not trust the available experimental data [Ziman, 1960]. Considerable difficulties are met theoretically due to the complex behavior of the thermoelectric power coefficient of real metals. The thermoelectric power coefficient of real metals is also extremely sensitive to external factors such as micro-impurities, sample history, precipitates, and etc. This sensitivity is a fact, which is very valuable for metallurgical phase and microstructure assessment in alloys.

Similarities exist for the Seebeck coefficient as a function of temperature curves for transition metals located in the same group of the periodic table as shown in Figure 3.6. The differences between the elements in each group observed in Figure 3.6 are due mainly to differences in the elements magnetic and crystal structures. Sharp changes in the thermoelectric power coefficient develop from crystal structure transformations.

The thermoelectric power coefficient for all transition metals at high temperatures is positive for groups 3 to 5 and is negative for the three divisions of group 8. The sign of the thermoelectric power coefficient is positive when the electron d-band is almost empty while the electron d-band begins to fill the thermoelectric power coefficient becomes more negative.
Figure 3.5: Periodic table with transition metals outlined in red (www.pubs.acs.org/cen/80th/elements.html).
Figure 3.6: A summary of thermoelectric power data for all transition metals, uranium and thorium. Roman numerals indicate the periodic table column) [Vedernikov, 1969].
There are common features in the data from the three elements in each group, however there are fewer similarities between the various groups. Some common features are summarized for transition metals:

- A maximum value of the $Z$ vs. $T$ curve between 50 and 100 K due to a phonon-drag peak occurs.
- There is a region in which $Z$ varies linearly with $T$, starting between 200 and 300 K and extending upward by sometimes as much as 100 K.
- There is a further maximum value of $Z$ at high temperatures. This second peak is normally thought to be due to the temperature modification of the mean density of available $d$-states within a range $kT$ of the Fermi energy.
- A fairly sharp break in the thermoelectric power as a function of temperature curve may occur when any one element undergoes a structural or magnetic transformation.

A fairly sharp break in the thermoelectric power as a function of temperature curve may occur when one element undergoes a structural or magnetic transformation [Vedernikov, 1969].

3.1.4. Thermoelectric Power Coefficients of Pure Metals

According to the Mott formula, the thermoelectric power of metals varies with temperature, however at high temperatures the thermoelectric power coefficients of many metals follow different laws [Mott and Jones, 1958]. The behavior of thermoelectric power has generally not been theoretically explained, but it is believed that the temperature dependence of the thermoelectric power is intimately related to the structure of the electronic spectrum near the Fermi energy level. In Table 3.1 the available experimental thermoelectric power data
for pure metals is given. Most of the data are for polycrystalline samples, although in some cases data was obtained using single crystals [Rowe, 1995].

3.1.5. **New and Current Developments in Thermoelectric Power**

Thermoelectric power is a technique that has been used for decades, but with increased sensitivity in the available tools, thermoelectric power has been used for detailed material characterization. In the 1970's researchers were already utilizing thermoelectric power measurements on hydrogen storage materials to generate thermoelectric power diagrams as a function of hydrogen charging pressure to be compared to activity diagrams [Baranowski, 1975]. This section will describe the use of thermoelectric power measurements for detection of carbide precipitation, to monitor aging and low cycle fatigue, for changes in phase such as retained austenite, for determination of residual stress, and so much more. If the thermoelectric power coefficient can be standardized and calibrated, its measurement possibilities are endless.

**Use of Thermoelectric Power Measurements to Monitor Carbide Precipitation**

Thermoelectric power measurements have been utilized to monitor carbide precipitation ($M_{23}C_{6}$) in martensitic steels containing 12-17 wt. pct. chromium, 0.1-1 wt. pct. carbon. These martensitic alloys are used in high strength, corrosion resistant applications including chemical and petrochemical plants, power plants, and gas turbine engines. These alloys are commonly quenched and tempered with microstructures consisting of martensite, some retained austenite at times, and complex carbides.
Table 3.1: List of Thermoelectric Power Coefficients for Elements [Rowe, 1995].

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<th>1000K</th>
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The formation of carbides in the quenched microstructure can have decisive effects on properties, so carbide control is necessary to optimize the quenched properties. To determine the volume fraction of precipitated carbides during cooling, optical microscopy and systematic point counting was utilized. Results for thermoelectric power as a function of volume fraction of precipitated carbides during cooling can be estimated with great accuracy utilizing thermoelectric power measurements as seen in Figure 3.7. Figure 3.7 (a) shows the change in the thermoelectric power coefficient due to cooling rate in the studied steel. The observed variations in the thermoelectric power coefficient are related to the precipitation of carbides during cooling [Cabellero et al., 2005]. Figure 3.7 (b) shows the amount of carbides precipitated at the different cooling rates measured on micrographs [Cabellero et al., 2005]. Figure 3.7 (c) shows the volume fraction of retained austenite present in the microstructure as a function of quenching cooling rate, together with the corresponding hardness evolution [Cabellero et al., 2005]. Thermoelectric power was found to be extremely sensitive to very small amounts of carbide precipitation.

Tkalcac et al. [2004] has also utilized thermoelectric power to monitoring tempering effects of martensitic high carbon steels. Thermoelectric power measurements were correlated to scanning calorimetry measurements showing very good agreement with one another in determining the stages of carbon precipitation.

**Thermoelectric Power for Monitoring of Neutron Embrittlement and Low-Cycle Fatigue in Nuclear Reactor**

The monitoring of neutron embrittlement and low-cycle fatigue in nuclear reactor steel is an important topic in lifetime extension of nuclear power plants.
Figure 3.7: Results on samples austenitized at 1120°C and cooled at different cooling rates: (a) Thermoelectric power measurements, (b) volume fraction of carbides, and (c) volume fraction of retained austenite present in the microstructure and corresponding hardness values [Cabellero et al., 2005].
Among several material parameters that may change due to material degradation are the thermoelectric properties [Niffenegger et al., 2005]. The specimens underwent fluences from zero to $4.5 \times 10^{19}$ neutrons/cm$^2$ with energies greater than 1 MeV. Thermoelectric power coefficient measurements were utilized to determine the effect of neutron embrittlement and low cycle fatigue. Results showed that the thermoelectric power results were very localized as shown in Figure 3.8 (a) and (b), however the use of a scanning thermoelectric power probe proved to eliminate this problem [Niffenegger et al., 2005]. At this point, thermoelectric power shows potential for use of monitoring neutron embrittlement and low cycle fatigue, however to fully understand the measurements, it is necessary to utilize a combination of tools to eliminate additional variables.

**Thermoelectric Power for Retained Austenite Measurements**

The TEP coefficient is a valued property for microstructural assessment of retained austenite. Retained austenite is very important to detect and quantify for this constituent of steel has been related to enhanced stress corrosion and hydrogen-assisted cracking [Park et al., 2003]. The use of a surface contact probe analysis to rapidly assess the tendency for corrosion is a technological advancement. Park et al. [2003] made retained austenite measurements on TRIP steels with results shown in Figure 3.9. These results indicate that the TEP coefficient corresponds very well to volume percent of retained austenite.

**Thermoelectric Power for Residual Strain Measurements**

Further investigation of thermoelectric power assessment led to residual strain results from Sun and Northwood [1994] in Canada.
Figure 3.8: (a) Seebeck coefficient as a function of fluence of irradiated specimens measured at two different positions "notch up" and "notch behind". (b) Seebeck coefficient as a function of fluence for irradiated and irradiated with time delay specimens measured at two different positions "notch up" and "notch behind" [Niffeneger, 2005].
Figure 3.9: Thermoelectric power coefficient as a function of retained austenite content in TRIP Steels [Park et al., 2003].

Figure 3.10 shows the relationship between thermoelectric power as a function of micro-strain induced from aging specimens of pure zirconium and a zirconium-chromium-iron alloy. The results of Figure 3.10 suggest that thermoelectric power can be used for investigation of both precipitation and aging studies because precipitation is an occurrence during aging, which results in an increase
in the internal lattice strain. As the micro-strain increases, the corresponding thermoelectric power coefficient decreases, suggesting that thermoelectric power is capable of assessing residual stress induced from precipitation during aging of pure zirconium and the zirconium-chromium-iron alloy.

![Graph showing TEP vs. Microstrain for Pure Zr and Zr-Cr-Fe](image)

Figure 3.10: Dependence of thermoelectric power coefficient on the microstrain for specimens aged at 350°C [Sun and Northwood, 1994].

3.2. **Superconducting Quantum Interference Device (SQUID) Measurements to Determine Magnetic Susceptibility**

A superconducting quantum interference device is a magnetic method utilized as a complimentary tool with electronic thermoelectric power measurements. A
SQUID shown in Figure 3.11 is the most sensitive device utilized for detecting magnetic flux as compared to a vibrating sample magnetometer (VSM). SQUID devices have been used to detect small magnetic fields, current, voltage, inductance, magnetic susceptibility, etc. The SQUID induces magnetic fields in the range of 0-20 Tesla, while the VSM induces magnetic fields in the range of 0-8 Tesla. The SQUID can be utilized to detect very sensitive changes in the hydrogen content because each free hydrogen atom carries one electron, resulting in an increase or decrease of the magnetic moment of the alloy.

The strong magnetic field in the SQUID is generated by utilizing a traveling steady current (charge per unit time) through a wire. A steady current traveling through a wire produces constant magnetic fields hence the term magnetostatics. A steady current implies that the charge travels per unit time without building up at any one point. The magnetic field of a steady line current is given by the Biot-Savart law [Griffiths, 1999]:

$$B(r) = \frac{\mu_0}{4\pi} \int \frac{l \times \hat{r}}{r^2} dl' = \frac{\mu_0}{4\pi} \int \frac{dl \times \hat{r}}{r^2}$$  \hspace{1cm} [3.11]

where $B$ is the magnetic field in units of Teslas, $\mu_0$ is the permeability of free space, $l$ is the steady current, $dl'$ is the element of length along the wire, and $\hat{r}$ is the vector from the source to the point $r$. The integration is along the path of the current in the direction of the current flow. The Biot-Savart law for magnetostatics is analogous to the Coulomb's law for electrostatics. The magnetic characteristics of the material determined by SQUID magnetic measurements are discussed below.
Figure 3.11: Superconducting quantum interference device [http://www.cartage.org.lb/en/themes/Sciences/Physics/SolidStatePhysics/MagneticProperties/Squid/Configuration/Configuration.htm].
In the presence of a magnetic field, matter becomes magnetized. Matter becomes magnetized because solids have many microscopic tiny dipoles, with a net alignment along a particular direction. The magnetic properties of solids have been grouped into three primary categories: (1) diamagnetic materials, (2) paramagnetic materials, and (3) ferromagnetic materials [Dekker, 1962]. In diamagnetic materials, the orbital speed of the electrons is changed in such a way to change the orbital dipole moment in a direction opposite to the applied magnetic field. Diamagnetic materials orient themselves perpendicular to a strong magnetic field. In paramagnetic materials, the dipoles are associated with the spins of the unpaired electrons, which experience a torque lining them up with the magnetic field. Paramagnetic materials orient themselves parallel to a strong magnetic field. Ferromagnetic materials are extremely attracted to the strong magnetic field and will be further discussed below.

The magnetic induction, $B$, of material is the product of the applied magnetic field, $H$, and the relative permeability, $\mu$, given as:

$$B = \mu H$$  \[3.12\]

In a vacuum the magnetic induction is written as:

$$B = \mu_0 H$$  \[3.13\]

$\mu_0$ is called the permeability of free space because in a vacuum when there is no matter to magnetize, the magnetic susceptibility reduces to zero, hence making the permeability the permeability of free space.

In paramagnetic and diamagnetic materials, the magnetic moment, $M$, that results due to the polarization of the matter is proportional to the applied magnetic field, written as:
\[ M = \chi_m H \]  \hspace{1cm} [3.14]

where \( \chi_m \) is the magnetic susceptibility, a dimensionless quantity that is different from one material to the next. The magnetic susceptibility is positive for paramagnetic materials meaning that the magnetic moment and the applied field are in the same direction as shown in Figure 3.12. The magnetic susceptibility for diamagnetic materials is negative because the magnetic moment and the applied magnetic field are in opposite directions (Figure 3.12).

The resulting magnetic induction is equivalent to the sum of the applied induction due to material polarization:

\[ B = \mu_0 (H + M) = \mu_0 (1 + \chi_m)H \]  \hspace{1cm} [3.15]

So that the magnetic permeability can be written as:

\[ \mu = \mu_0 (1 + \chi_m) \]  \hspace{1cm} [3.16]

Figure 3.12: Relationship between B and H for paramagnetic and diamagnetic materials under an applied magnetic field [Stanley, 1963].
In paramagnetic and diamagnetic materials, magnetization is sustained by the induced magnetic field, when the magnetic field is removed the magnetization disappears [Griffiths, 1999]. Ferromagnetic materials are infinitely non-linear media, thus meaning that a ferromagnetic material does not require an external magnetic field to sustain magnetization. Figure 3.13 shows the magnetic susceptibility of a ferromagnetic material where there is no linear relationship between the magnetizing force and the magnetic flux density.

![Flux density, B-H vs. Magnetizing force, H](image)

**Figure 3.13:** Relationship between B and H in ferromagnetic materials [Stanley, 1963].

When a magnetic field is applied to a ferromagnetic material and the magnetic field is removed, the material exhibits hysteresis as shown in Figure 3.14 for a pure single crystal of silicon-iron. Only iron, nickel, cobalt, gadolinium, and
dysprosium are ferromagnetic materials, however other alloys exist that also exhibit this behavior.

Figure 3.14: Magnetization curve for a single crystal of silicon iron [Williams and Shockley, 1949].

Ferromagnetism is similar to paramagnetism in that the magnetic dipoles are associated with the spins of unpaired electrons. The difference between ferromagnetism and paramagnetism is the interaction between nearby dipoles. In ferromagnetic materials, all of the dipoles of the unpaired electron spins can
become completely aligned. The alignment of the dipoles occurs in small patches, called magnetic domains. Each domain has millions of dipoles that are visible under a microscope. The domain structure represents the minimum energy state of the material [Stanley, 1963]. Figure 3.15 shows microscopic images of magnetic domains on an iron whisker single crystal and a grain in a polycrystalline silicon steel [Stanley, 1963]. A schematic diagram of magnetic domains in single crystals is shown in Figure 3.16. Figure 3.16 (a) shows the magnetic domain in the unmagnetized condition and Figure 3.16 (b) shows the magnetic domain movement under an applied magnetic field.

Figure 3.17 shows the magnetic field of an infinite straight wire where the current is coming out of the page [Griffiths, 1999]. The magnetic field has a non-zero curl, which will never happen in an electrostatic field. The integral of the magnetic field around a circular path of radius, $s$, centered at the wire is given as:

$$\oint B \cdot dl = \oint \frac{\mu_0 I}{2\pi s} dl = \frac{\mu_0 I}{2\pi s} \oint dl = \mu_0 I$$

[3.17]

The magnetic field decreases at the same rate as the circumference increases, thus the answer is independent of the radius, which means that any loop enclosing a wire would give the same answer. If there is a bundle of straight wires pass through a loop where each wire contributes $\mu_0 I$, the line integral is:

$$\oint B \cdot dl = \mu_0 I_{enc}$$

[3.18]

where $I_{enc}$ is the total current enclosed by the path of integration. The flow of charge can be written as a volume of current density, $J$, by the enclosed current taken as the integral over the surface bounded by the loop given as:
Figure 3.15: (a) Magnetic domain structure and their movement in a single crystal iron whisker. Arrows below each figure indicate the direction of the magnetic field and its relative magnitude. Arrows drawn in the domains indicates direction of magnetization. (b) Magnetic domain structure in a 3.25 wt. pct. silicon polycrystalline steel. Courtesy of Fowkes, Crucible Steel Company of America [Stanley, 1963].
Figure 3.16: Changes in magnetic domain structure produced by applied magnetic field [Stanley, 1963].
\[ I_{enc} = \int J \cdot da \quad [3.18] \]

Then using the curl theorem, otherwise known as Stoke's law, Equation 3.18 can be re-written as:

\[ \nabla \times B = \mu_0 J \quad [3.20] \]

Equation 3.20 is called Ampere's law. The integral of Ampere's law offers a very efficient means of calculating magnetic fields [Griffiths, 1999].

Figure 3.17: Magnetostatic field of a long wire [Griffiths, 1999].

3.2.1. Comparison of Electrostatics and Magnetostatics

The Maxwell Equations describe the divergence and curl of electrostatics and magnetostatics. The divergence and curl of an electrostatic field is given as:
\[ \nabla \cdot E = \frac{1}{\varepsilon_0} \rho \quad \text{(Gauss's Law)} \quad [3.21] \]

\[ \nabla \times E = -\frac{\partial B}{\partial t} \quad [3.22] \]

Maxwell's equations for electrostatics allows for calculation of the electric field if the source charge density is known. Equation 3.21 and 3.22 provides the same information as Coulomb's law including the principle of superposition [Griffiths, 1999].

The divergence and curl of a magnetostatic field is given as:

\[ \nabla \cdot B = 0 \quad [3.23] \]

\[ \nabla \times B = \mu_0 J \quad \text{(Ampere's Law)} \quad [3.24] \]

Maxwell's equations for magnetostatics allows for calculation of the magnetic field, which is equivalent to the Biot-Savart law including superposition [Griffiths, 1999].

For the magnetic measurements, of course, the Maxwell's equations for magnetostatics are important for calculation of the induced magnetic fields. In utilizing the SQUID for magnetic measurements, it is not only important to understand how the magnetic fields are generated, but also the role of magnetism on solids.

The connection between magnetic susceptibility and the thermoelectric power coefficient can be assessed by utilizing the free electron model as discussed earlier in Section 3.1.1. The free electron model offers a simple description of the behavior of non-transition metals. This investigation does however involve
both transition and non-transition metal alloys, but the correlations between these properties are still explored.

3.2.2. Prior Research Utilizing Magnetic Susceptibility with Thermoelectric Power for Material Characterization

Both the thermoelectric power coefficient and magnetic susceptibility are properties of materials related to the d-electron band concentration and the electronic band structure. Thermoelectric power and magnetic properties can be to assess the change in the electronic level of an alloy. The thermoelectric power of a material is relatively easy to measure, but it is rather difficult to interpret without a complimenting technique because it is strongly influenced by subtle details of the electronic structure. However with the aid of the magnetic measurement, a rough understanding of the electronic behavior in the compounds under hydrogenation is possible [Niyomsoan et al., 2003].

Niyomsoan et al., [2003] performed thermoelectric power and magnetic measurements on Zr$_{0.9}$Ti$_{0.1}$Cr$_x$Fe$_{2-x}$ compounds. Magnetic measurements were performed using a magnetization hysteresis loop with a transverse-field vibrating-sample magnetometer at room temperature in maximum applied fields of 0.6 T. Magnetization was computed as magnetic moment per unit mass of metal, not including hydrogen, and expressed in units of A·m$^2$/kg (equivalent to emu/g).

The magnetic susceptibility at 600 mT and the Seebeck coefficient as a function of hydrogen content of each Zr$_{0.9}$Ti$_{0.1}$Cr$_x$Fe$_{2-x}$ compound is plotted together for $\chi = 0.8$ as shown in Figure 3.18. The variation of the magnetic susceptibility and the Seebeck coefficient as a function of hydrogen concentration exhibits the same graphical features. Both quantities gradually change with dissolved hydrogen content. In the alpha-phase region, additional electrons are donated from the soluble hydrogen to the d-band raising the Fermi
energy level. The magnetic susceptibility of paramagnetic behavior is related to
the number of electrons at and in the vicinity of the Fermi energy level. These
results show that there is a one-to-one correlation between thermoelectric power
and magnetic measurements.

Figure 3.18: Magnetic susceptibility and thermoelectric power coefficient of
Zr_{0.9}Ti_{0.1}Cr_xFe_{2-x} compound with $\chi_x = 0.8$ as a function of hydrogen content
[Niyomsoan, 2003].
3.3. Electromagnetic Analyses for Interstitial Content Determination

Advanced research has lead to the improvement and development of hydrogen determination tools, which has lead to numerous non-destructive methods capable of measuring hydrogen content in steel and weldments. These techniques are, however, all contact techniques and, since pipelines are coated, it is necessary to develop a non-contact technique that can perform measurements through the pipeline coating. When properly calibrated and standardized, electromagnetic techniques allow for non-contact, non-destructive measurements of interstitial contents.

Most non-destructive tools currently utilized in industry (ultrasonics, magnetic flux leakage, etc.) are used for determination of existing cracks, flaws, defects, etc, in other words, characterization after the fact. The development of a non-destructive diffusible hydrogen meter will allow for property prediction before significant defects or cracks occur. The non-destructive diffusible hydrogen meter can beneficially be used during production and in-service.

There are many variables associated with pipelines, such as temperature, pressure, coatings, etc. This research will apply a combination of three different complimenting, non-contact electromagnetic methods to determine the diffusible hydrogen content in coated linepipe steel. The three methods utilized in this research will include eddy current analysis for impedance measurements, magnetic Barkhausen noise analysis (MBN), and electromagnetic acoustic transducer analysis (EMAT). The MBN and EMAT techniques are necessary to correct for the temperature, microstructure, and composition to allow proper standardization for the eddy current assessment of the hydrogen content. All three of these non-destructive techniques are currently utilized for pipeline inspection, however they are used individually for crack, defect, and corrosion monitoring. These three methods will be used together to eliminate any
additional variables to rapidly generate a quantitative hydrogen content associated with the coated linepipe steel. This method is based on establishing hydrogen content calibration data for equivalent microstructure, as assessed by similar magnetic Barkhausen Noise data and temperature as assessed by speed of sound measurements in the line pipe steel.

3.3.1. **Electromagnetic Theory**

Eddy currents, magnetic Barkhausen noise, and electromagnetic acoustic transducers are based on Faraday's law. Faraday's law states that, "a changing magnetic field induces an electric field." Faraday's law really distinguishes between two types of electric fields: (1) those attributed to electric charges and (2) those associated with changing magnetic fields. The curl of an electrostatic field is given by the differential form of Faraday's law is:

$$\nabla \times E = -\frac{\partial B}{\partial t}$$  \[3.24\]

where \(\nabla\) is the del operator, \(E\) is the electrostatic field, \(B\) is the magnetic flux density, and \(t\) is time.

3.3.2. **Induced Current Resistivity (Eddy Currents) Analysis**

Eddy Current analysis is a technique generally utilized to find near surface defects in alloy parts, normally in non-ferrous alloys. The ferromagnetic behavior of steel causes a significant change in the steel's impedance, which hinders the determination of cracks, but should serve as an excellent indicator for diffusible hydrogen content in the near surface region of the steel. Since diffusible
hydrogen donates its electron to the d-band of steel, which is the same band that contributes to the ferromagnetic behavior, the induced current in the steel will experience the change in resistivity due to the hydrogen and will cause perturbation in the eddy current signal. Eddy currents units have been designed and experimentally proven for flaw, cracks, and thickness examination of large diameter pipelines through coatings and insulation [Griffith et al., 1997]. The theory of induced current resistivity measurements is described below.

Theory of Induced Current Resistivity (Eddy Currents) for Interstitial Assessment

In eddy current testing, a high or low frequency electromagnetic (EM) field is generated in a conductor by an alternating current. When placed in close proximity of a material, the generated EM field induces currents (eddy currents) within the inspected material. In response, the eddy currents induced in the inspected material generates a magnetic field. The EM fields from the induction coil and the inspected material must be detected either by electromagnetic induction in a coil, by a system of coils, or by sensors such as the Hall element. In many cases the same coil is used both to excite the eddy currents, and also to detect their fields.

A significant advantage of the eddy current technique is that it can be performed at a stand off distance and through the pipeline coating. The first step in using the eddy current testing practice is to select all of the controllable parameters in such a way as to optimally detect the desired material parameter. For the proposed hydrogen sensing investigation the initial part of the effort will be to determine the optimum set of controllable parameters.

In the magnetism of solids section above, the relationship between the current flowing through a coil and the resulting magnetic field strength, H, was
discussed. The magnetic field strength produces a magnetic flux density, B, and a flux, \( \phi \), which is defined as the integral of the magnetic flux density over a particular surface given as:

\[
\phi = \int B \cdot nda
\]  

[3.25]

During induced current resistivity (eddy current) measurements, the coil is held close to the sample, so that the flux created by the coil affects the sample. The coil parameters and primary excitation current are a function of the flux. The oscillating nature of the flux induces eddy currents in the sample beneath the coil. The eddy currents produce their own magnetic field, which opposes the field which produced them (Lenz’s law) [Bray and Stanley, 1997]. The coil then senses an equilibrium flux, which is the difference between the induced primary flux and the secondary flux due to the sample [Bray and Stanley, 1997].

When AC current is applied, the coil possess both resistance and reactance. Along with resistance, there is a changing flux in the coil, which exhibits inductance [Bray and Stanley, 1997]. The coil’s inductance is the flux linkage change per unit current and is given as:

\[
L = \frac{d(N\phi)}{dl}
\]  

[3.26]

where \( N \) is the number of turns in the coil and \( l \) is the current. The inductive reactance occurs when a coil is excited at an angular frequency, \( \omega \), creating another form of resistance due to a generated back electromotive force caused by the changing flux linkage within [Bray and Stanley, 1997]. The magnitude of the inductive reactance, \( X_L \), is given as:
\[ X_L = \omega L = 2\pi f L \]  \hspace{1cm} \text{[3.27]}

where \( f \) is the frequency, which would be zero in a direct current. The phase of the current through the coil is common to both components, so that if the phase is drawn electrically as shown in Figure 3.19 then the voltage across the resistive and inductive parts are \( IR \) and \( I\omega L \) as shown in Figure 3.20 [Bray and Stanley, 1997]. Figure 3.20 shows the right triangle created by the resistive and inductive parts so that the total circuit voltage, \( V \), becomes:

\[ V = I \sqrt{\left(\omega L\right)^2 + R^2} \]  \hspace{1cm} \text{[3.28]}

Then using Ohm's law, where \( V = IZ \), the total impedance exhibited in the coil is given as:

\[ Z = \sqrt{\left(\omega L\right)^2 + R^2} \]  \hspace{1cm} \text{[3.29]}

Figure 3.19: Generalized coil [Bray and Stanley, 1997].
The total impedance of the coil will also have an often negligible term called the capacitance [Bray and Stanley, 1997]. The capacitance reactance of the coil, $X_c$ is given by:

$$X_c = 1/(\omega C) = 1/(2\pi f C)$$  \[3.30\]

where $C$ is the capacitance in farads. Capacitance reactance may play a role when the use of coil probes are attached to the eddy current instrument by very long wires [Bray and Stanley, 1997]. When a circuit contains both inductance and reactance, the total impedance of the coil becomes:

$$Z = ((\omega L - 1/\omega C)^2 + R^2)^{1/2}$$  \[3.31\]
and the phase angle, \( \phi \), between the current in and voltage across the circuit is given by:

\[
\tan \phi = (\omega L - 1/\omega C)/R
\]

[3.32]

It can be seen that the possibility arises that, if \( \omega L = 1/\omega C \), and \( C \) and \( L \) are equal to zero then the impedance becomes a only a function of the resistance, and the phase angle becomes zero degrees [Bray and Stanley, 1997]. This condition is known as resonance, and many circuits are designed to operate at or near such a condition.

The eddy current density, and thus the strength of the response from a flaw, is greatest on the surface of the metal being tested and the strength declines with depth [Bray and Stanley, 1997]. It is mathematically possible to define the "standard depth of penetration" where the eddy current is \( 1/e \) (37 percent) of its surface value. The following expression gives the relationship of the standard depth of induced current to the applied frequency [Bray and Stanley, 1997].

\[
\delta = 50 \sqrt{\frac{\rho}{(f \cdot \mu r)}}
\]

[3.33]

where \( r \) is resistivity in \( mW.cm \) and \( f \) is frequency in \( Hz \). With charging frequency the hydrogen profile relative to the pipe surface can be assessed. Figure 3.22 illustrates the eddy current density as a function of depth. The skin depth relationship given in Equation 3.33 refers only to plane electromagnetic waves. In common eddy current testing situations, small coils or encircling tubes are utilized making Equation 3.33 invalid, but it does however provide a reasonable estimate of the skin depth [Bray and Stanley, 1997]. The skin depth relation is a solution to the Maxwell’s equations, which should be determined for each particular inspection problem [Bray and Stanley, 1997].
Figure 3.21: Schematic illustration of eddy current density declines with depth [Bray and Stanley, 1997].

Figure 3.22 shows the standard depth of penetration as a function of frequency for several different materials. Both permeability and conductivity play an important role in lowering the depth of penetration [Bray and Stanley, 1997]. The resistivity is also temperature dependent, which also changes the depth of penetration.

Through thickness hydrogen measurements in the coated pipeline will require a large coil at a very low frequency (below 10 kHz). An eddy current unit is being specially designed to achieve these necessary low frequencies. This non-contact probe approach has high potential to determine the diffusible hydrogen content in a very convenient way.
Variables do exist in induced current resistivity measurements because resistivity is a function of the conductivity of the material, the depth of the measurement, and the alloy content. The conductivity is a function of the electronic effective mass, the electron concentration, and the dominating scattering mechanisms, which is altered by inclusions, microstructure, temperature, strain, and etc.

Variables also can exist if not careful in designing and preparation of the coils. The coil must always have an exact liftoff (distance between coil and specimen) otherwise results will be erroneous. Because these variables are present it is necessary to use multiple techniques to eliminate these variables.

Figure 3.22: Standard depth of eddy current penetration versus frequency [Bray and Stanley, 1997].
New and Current Achievements in Induced Current Resistivity Measurements

Eddy current analyses have been taken beyond crack and defect detection to further monitor material properties before significant defects arise. Unfortunately, the development of eddy current analyses for characterization of material properties has started out fairly slowly, but the extreme benefits in utilizing non-contact, non-destructive tools characterization of material properties is beginning to make an impact. The next section describes a new development of using eddy current analysis for carbon content detection.

Eddy Current Analysis for Carbon Content Measurements

Klumper-Westkamp et al. [2003] have utilized eddy current with harmonic analyses for non-destructive determination of carbon content in thin foils for quality assurance of gas carburizing process. Experiments were performed utilizing a set of 71 foils carburized with different carbon potentials and then analyzed for glow discharge emission spectroscopy element profiling and newly developed distortion free harmonic analysis. The system is calibrated utilizing multi-regression analysis. The input parameters are the amplitude and the phase of the first to the fifth harmonic of different frequencies, so that 36 measurements are available. By the connection of several measurements, the precision of the calibration is enhanced up to a correlation coefficient of 97.5 percent with a standard deviation of 0.06 weight percent carbon. The results are shown in Figure 3.23 for carbon concentration utilizing eddy current harmonic analysis as a function of carbon content from glow discharge emission spectroscopy. With more precise foil extraction the standard deviation would be even better.
Figure 3.23: Calibration result for a 5-dimensional regression [Klumper-Westkamp et al., 2003].

Because of the variables associated with pipelines such as temperature, microstructure, hydrogen content, etc. it may be necessary to utilize a combination of non-destructive, non-contact techniques to eliminate the variables. Appendix E shows how magnetic Barkhausen noise analyses could potentially be utilized for microstructural characterization and the use of two electromagnetic acoustic transducers to induces shear waves to measure the speed of light through the material could give insight into the temperature of the pipeline.
CHAPTER 4

STATEMENT OF PROBLEM TO BE INVESTIGATED

The purpose of this research is to develop advanced thermoelectric power and electromagnetic techniques to quantify interstitial contents in advanced materials. Many destructive techniques are available for determination of total nitrogen and hydrogen contents, however the same non-destructive tools do not exist for total nor interstitial content assessment. It is imperative to develop these non-destructive tools to monitor interstitial contents at all times, to allow for a true prediction of properties during processing, production, and in-service.

The literature review in Chapter 2 describes not only the importance of developing tools for interstitial content assessment, but also describes through thermodynamics how electronic and magnetic tools can be utilized to determine interstitial contents. Chapter 3 discusses the electronic, magnetic, and electromagnetic tools for interstitial content determination along with practices necessary to eliminate additional variables due to microstructure variations, changes in material temperature, etc.

The largest task that must be overcome in developing the non-destructive thermoelectric and electromagnetic tools is having the proper techniques for calibration and standardization. These electronic, magnetic, and electromagnetic tools have endless possibilities for what they can measure, as long as each tool can be calibrated and standardized. To standardize thermoelectric power for interstitial nitrogen content measurements, it was necessary to have a technique to calibrate the interstitial nitrogen content. When contacting steel companies and national laboratories around the world, it was clear that interstitial nitrogen
contents were not measured thus lacking true determination of properties. In this research, it was finally found that Beeghly [1942, 1949, 1952], an analytical chemist, developed an analytical digestion method using solutions of halogens in an anhydrous aliphatic ester to obtain interstitial nitrogen, carbon, and oxygen contents in steel (through back calculation from formed precipitates). Rawers et al. [1991, 1992, 1993], from the former U.S Bureau of Mines, also reported utilizing the Beeghly method for interstitial nitrogen determination. Other than these few papers, most authors failed to distinguish between interstitial and nitride nitrogen content and normally the chemical techniques are never mentioned.

Through this research, it is hoped that in the future of metals and materials, electronic and magnetic laboratories will exist to non-destructively characterize materials. The future is coming as can be seen in the literature review in Chapter 3. Researchers around the world have discovered the benefits of utilizing non-destructive testing not only for testing for cracks and defects, but for true material characterization.

The scope of this work will be to utilize thermoelectric and electromagnetic techniques to assess interstitial content in advanced materials to guarantee and maintain properties. This research will focus particularly on the assessment of hydrogen and nitrogen contents in advanced hydrogen storage materials, structural steel, and stainless steel.
CHAPTER 5

MATERIALS AND EXPERIMENTAL PROCEDURES

The advanced materials investigated in this research include nitrogen-strengthened austenitic stainless steel, advanced hydrogen storage materials, LaNi$_5$ and NaAlH$_4$, and X80 structural linepipe steel.

Nitrogen-strengthened alloy 1.4565 (AISI 34565) has been developed for applications in high chloride environments such as seawater and has been utilized for this investigation. The chemical composition of stainless steel alloy 1.4565 (AISI 34565) is given in Table 5.1, where it is important to notice that this alloy has been strengthened with a nitrogen content of 0.458 wt. pct. that results in a yield strength of approximately 60 ksi (420 MPa).

| Table 5.1: Alloy 1.4565 (AISI 34565) Nominal Chemical Composition |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| C       | Si  | Mn  | P   | S   | Cr  | Ni  | Mo  |
| 0.028   | 0.182 | 6.080 | 0.017 | <0.001 | 23.82 | 18.83 | 5.639 |
| Ti      | Nb  | N   | Cu  | Al  | Ta  | Fe  |
| 0.017   | 0.028 | 0.458 | 0.104 | 0.015 | 0.011 | 44.78 |

The lanthanum nickel (LaNi$_5$) powder is -100 mesh, 99.5% (metals basis) commercially pure purchased from Alfa Aesar. The sodium aluminum hydride (NaAlH$_4$) hydride was made by the University of Hawaii by ball milling with a tungsten carbide. No other information was provided with the sodium aluminum hydride material.
Structural linepipe steels are strength dependent, thus meaning that there is no requirements for the composition. The chemical composition for the particular X80 linepipe steel cylindrical specimens utilized in this research is approximately 0.07 wt. pct. carbon, 1.35 wt. pct. manganese, 0.004 wt. pct. phosphorous, 0.004 wt. pct. sulfur, and 0.10 wt. pct. titanium. The microstructure of the X80 linepipe utilized in this research is ferritic as shown in Figure 5.1.

![Microstructure of X80 linepipe steel](image)

Figure 5.1: Microstructure of X80 linepipe steel with a chemical composition of 0.07 wt. pct. carbon, 1.35 wt. pct. manganese, 0.004 wt. pct. phosphorous, 0.004 wt. pct. sulfur, and 0.10 wt. pct. titanium.

5.1. **Experimental Procedures**

The experimental procedures and specimen preparation for the development of non-destructive techniques for interstitial nitrogen and hydrogen contents are described below. The techniques that must be utilized for standardization and calibration of the non-destructive tools are also proposed and discussed.
5.1.1. Development of Thermoelectric Power for Assessment of Nitrogen Content in Nitrogen Strengthened Austenitic Stainless Steel Weldments

For the determination of nitrogen content using thermoelectric power, a non-destructive Seebeck measurement device has been developed at BAM (Federal Institute of Materials Research and Testing) in Berlin, Germany. The Seebeck apparatus consists of a Keithley Nano-voltmeter 2182, two Watlow temperature controllers and read-outs, two type T and two type K thermocouples, two heating cartridges, and two copper reference probes. A schematic diagram of the thermoelectric power unit is shown in Figure 5.2 and the set-up shown in Figure 5.3. The Seebeck apparatus was designed to allow the copper probes to apply a constant pressure to a surface, while performing temperature and voltage measurements.

![Schematic diagram of thermoelectric power surface contact probe design.](image)

Figure 5.2: Schematic diagram of thermoelectric power surface contact probe design.
Figure 5.3: Thermoelectric power measurement system showing the nanovoltmeter, temperature read-out and controllers, and the data acquisition system.

The Seebeck apparatus measures the Seebeck coefficient by applying a hot copper probe in the center of the weld and the cold copper probe in the base metal as shown in Figures 5.4 (a) and (b). The hot copper probe is the location of the measurement. Seebeck measurements were performed on the unprepared weld surface then the welds were milled and the Seebeck coefficient is re-measured, which gives information on the surface preparation necessary for Seebeck measurements. The Seebeck measurements for the as-welded condition and the milled condition were identical.

The tip of the copper probe has a diameter of approximately 381 μm. The depth of the thermal gradient is on the order of the diameter of the copper probe tips. Seebeck measurements can be made on uneven surfaces, which are often exhibited in weldments. A magnified illustration of the contact copper probe on an uneven surface (weldment) and a smooth surface (base metal) is shown in Figure 5.5. On the uneven surface it is possible to see that complete contact of
the entire copper probe on the surface does not occur, but the copper contact probe does have contact at some area smaller than the diameter of the copper probe.

Figure 5.4: (a) and (b) Thermoelectric power surface contact probe where (b) is zoomed in to show further detail.
This observation is important because contact issues always arise, but with utilization of thermoelectric power, as long as there is some contact area, which can be smaller than the copper probe diameter, a Seebeck measurement can be made. The amount of contact is not an issue since the nanometer has very high impedance, which significantly reduces the current making the Seebeck measurement a potentiostatic measurement. It is also important to remember that the thermal gradient is only as deep as the diameter of the area of contact. The Seebeck measurement takes approximately thirty seconds to guarantee an accurate thermal distribution or voltage difference. Appendix F gives a calculation for the uncertainty involved in thermoelectric power measurements.

Figure 5.5: Magnification of copper contact probe on an uneven surface as compared to a smooth surface.

Autogeneous plasma arc welds in a non-keyhole mode were made on 12.5 mm thick (1/2 inch) plates of stainless steel alloy 1.4565 (AISI 34565) using a shielding gas mixture of Ar-20 percent N₂ with welding parameters given in Table
5.2. Variation in the number of weld passes (or number of weld beads) was utilized to achieve a systematic increase in total nitrogen content due to nitrogen pick-up from the nitrogen-rich argon shielding gas.

<table>
<thead>
<tr>
<th>Table 5.2: Plasma Arc Welding Parameters for Alloy 1.4565 (AISI 34565)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Weld Travel Speed</strong></td>
</tr>
<tr>
<td><strong>Current</strong></td>
</tr>
<tr>
<td><strong>Voltage</strong></td>
</tr>
<tr>
<td><strong>Nitrogen Flow Rate</strong></td>
</tr>
<tr>
<td><strong>Argon Flow Rate</strong></td>
</tr>
<tr>
<td><strong>Plasma Flow Rate</strong></td>
</tr>
<tr>
<td><strong>Arc Length</strong></td>
</tr>
<tr>
<td><strong>Electrode Diameter</strong></td>
</tr>
</tbody>
</table>

The weld specimens were analyzed for both their chemical and microstructural constitution. In this investigation, the microstructure is characterized relative to both the interstitial nitrogen and the nitride contents. The interstitial nitrogen contents are determined through combined utilization of the Beeghly ester-halogen digestion method [Beeghly, 1942, 1960], [Rawers, 1992] and the Leco Nitrogen Determinator, which are thoroughly described in the following references [Beeghly, 1942, 1960], [Rawers, 1992]. The microstructure was characterized using a JEOL JXA-840 Scanning Electron Microscope (SEM).

5.1.2. **Techniques for Total Nitrogen and Interstitial Nitrogen Content Determination**

For a complete analysis of the weld metal nitrogen content, various analytical techniques are utilized for determination of total nitrogen content and interstitial
nitrogen content [Sibilia, 1996] as described in the following sections. Table 5.3 lists the analytical techniques used in this nitrogen research for the determination of interstitial nitrogen and total nitrogen contents.

<table>
<thead>
<tr>
<th>Chemical Analysis Method</th>
<th>Total Nitrogen</th>
<th>Interstitial Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Combustion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emission Spectroscopy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro-Kjeldahl Technique</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ester-Halogen Digestion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Total Nitrogen Content Measurements**

Three different techniques from BAM were utilized for the determination of the total nitrogen content in stainless steel Alloy 1.4565 weldments. These analytical techniques include: emission spectroscopy, gas combustion (Leco Nitrogen Determinator), and micro-kjeldahl. A brief description of each technique for total nitrogen content is given.

**Leco Nitrogen Determinator**

The Leco Nitrogen Determinator is one of the most widely used analytical systems for total nitrogen content. Leco Nitrogen Determinator (TC-436) has precision less than one ppm for low nitrogen levels. Samples for the Leco Nitrogen Determinator were prepared by milling each weld, while collecting eight
grams worth of mill grindings for analysis. For each run, two grams of the weld are used and then the same measurement repeated three times for accuracy. Figure 5.6 is a photograph of the Leco Nitrogen Determinator TC-436. More detailed information on gas chromatography is reported by Niessen [2001] and Jeffrey and Kipping [1964].

![Leco Nitrogen Determinator](www.leco.com, 2004)

**Emission Spectroscopy**

A plasma emission of atoms from a material emit light at a series of narrow wavelength intervals, which are termed emission lines. The emission lines form an emission spectrum characteristic of the specific atoms. The intensities of the lines are usually proportional to the number of atoms producing them. The presence of nitrogen in a sample is indicated by the presence in light from the excitation source of one or more of its characteristic lines [Farnsworth, 1986].
The concentration of nitrogen can be determined by measuring line intensities. Thus, the characteristic emission spectrum forms from the basis of quantitative elemental analysis. More information about spark emission spectroscopy is reported by Farnsworth [1986] and Walters [1969].

For emission spectroscopy sample preparation, the surface of the welds were milled to remove any decarburization or oxidation and then the welds are cut into samples of approximately 18 mm x 13 mm x 6 mm. The emission spectrometer then analyzed the total nitrogen concentration by rastering across the surface of the weld bead.

**Micro-Kjeldhal**

Micro-kjeldahl is widely used for total nitrogen content measurements in organics, liquids, and metals. Welded plasma and GTA specimens are milled to accumulate two grams. One gram is used for each run, where the sample is completely dissolved in particular acids determined by the material being digested to what changes the pH and then titrated back to the original pH or to an original dye indicator to determine the overall nitrogen content. Two measurements were made on each sample for accuracy. A Hach micro-kjeldahl unit is shown in Figure 5.7.

**Interstitial Nitrogen Content Measurements**

For quantification of interstitial nitrogen in the austenitic matrix of Alloy 1.4565, the ester-halogen digestion method designed by Beeghly [1942] has been utilized.
Ester-Halogen Digestion for Determination of Interstitial Nitrogen Content

To perform the Ester-halogen digestion process, a modernized version of the micro-Kjeldahl has been used called the Hach Digesdahl Digestion Apparatus as shown in Figure 5.7. The experimental procedure is described in the following.
First, all welds or samples were milled into shavings to reduce the digestion time. A one-gram sample was placed into a 200 ml beaker, then 3 ml of bromine was added. After the addition of bromine the water flow through the condenser is turned on and 2 ml of methyl-acetate is added to the distilling flask. After the initial reaction between bromine and methyl-acetate occurs, which takes approximately five minutes, 13 ml of methyl-acetate are added through the condenser and heat is applied. The solvent was refluxed until the sample became completely dissolved. The resulting residue (nitrides) was then poured and filtered through a Gooch crucible with a glass filter, while slowly rinsing the residue with methyl-acetate as it filters. The filter was then removed and placed in the furnace at 105°C until the residue has completely dried into a powder. The nitride powder residue was then analyzed using the Leco Nitrogen determinator and x-ray diffraction. A second titration method by Beeghly could also be used for analysis of the nitride residue. For both methods described, the interstitial nitrogen contents were then calculated from the difference between the total nitrogen content and the nitride content (residue).

The time and temperature necessary for solutionizing of the iron matrix in the ester-halogen reagent varied with composition and particle size of the specimens. Temperatures used during the digestion of austenitic stainless did not exceed the boiling points of bromine and methyl-acetate.

5.1.3. Development of Thermoelectric Power for Assessment of Hydrogen Content in LaNi₅

Known hydrogen storage material, LaNi₅, is utilized in this study to investigate methods to determine the total hydrogen content and formed hydride contents. An experimental matrix for the LaNi₅ research is given in Table 5.4. The
hydrogen charging time ranges from 1 hour to 2 weeks. For reproducibility purposes, three trials were made for each specific hydrogen charging time.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Hydrogen Charging Time</th>
<th>Total Hydrogen Content</th>
<th>Hydride Content (Ester Halogen)</th>
<th>Thermoelectric Power Coefficient (μV/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>1 hour</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H4</td>
<td>1 day</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H7</td>
<td>3 days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H10</td>
<td>5 days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H13</td>
<td>8 days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H16</td>
<td>10 days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H19</td>
<td>12 days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H22</td>
<td>14 days</td>
<td></td>
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</tr>
</tbody>
</table>

Thermoelectric power is utilized as a non-destructive tool to assess the hydrogen content in hydrogen-charged LaNi₅ specimens. The thermoelectric power measurements are calibrated utilizing the Leco Hydrogen Determinator. The thermoelectric power apparatus utilized for hydrogen content measurements is identical to the unit used for nitrogen content determination, however a different probe arrangement has been developed for powder measurements. A schematic diagram of the thermoelectric power probe arrangement is shown in Figure 5.8 with a picture of the actual thermoelectric power contact probes shown in Figure 5.9. The tools used for hydrogen charging and hydrogen measurements are discussed below.
Figure 5.8: Schematic picture of thermoelectric power coefficient measurement apparatus.

Figure 5.9: Thermoelectric power powder measurement system.
Hydrogen Charging and Total Hydrogen Content Measurements

The hydrogen charging system used in this investigation is shown in Figure 5.10 and 5.11. Both powder and bulk specimens can be hydrogen charged in this unit. Ultra high purity helium is used to clean the system before hydrogen charging of specimens. The system was evacuated until the pressure drops to $10^{-6}$ psi before hydrogen gas was input in the system. The hydrogen content in the metal is varied by the way of desorption and the Sieverts' law is applied to calculate the remaining hydrogen content. The equilibrium pressure of hydrogen gas is measured when the pressure remains constant at any hydrogen content during desorption for at least one minute [Termsuksawad et al., 2005]. After charging LaNi$_5$ specimen with various levels of hydrogen as a function of time the specimens are quenched in cold-water to maintain the hydrogen in the specimens. If the specimen was allowed to cool, the hydrogen will diffuse back out of the specimen. The specimens are hydrogen charged with time variations between 1 hour and 1 week. After hydrogen charging the specimens underwent Leco hydrogen analysis, thermoelectric power analysis, and ester-digestion analysis.

Techniques for Total Hydrogen and Hydride Determination

The Leco Hydrogen Determinator (gas chromatograph) has been utilized throughout this experiment. The Leco Hydrogen Determinator is first used for determination of the total hydrogen content of the hydrogen charged LaNi$_5$ specimens. The Leco Hydrogen Determinator is also used later in the experiment to determine the hydrogen content of the digested LaNi$_5$ hydride residue.
Figure 5.10: Hydrogen Charging System – A High pressure and high temperature hydrogen charging system.

Figure 5.11: High pressure and temperature hydrogen charging system.
To separate the total hydrogen content into diffusible (soluble) hydrogen content and formed hydride content, the ester-halogen digestion technique described earlier for interstitial nitrogen content determination is utilized again. The only difference in using the ester-halogen digestion technique for nitride and hydride determination is the drying process for the residue. For nitrides, the residue was baked at 105°C for a specific period of time, however due to the stability of hydrides, the baking process was eliminated. The hydride residue was allowed to air dry taking approximately one hour. It is very important to make sure that all glassware is dried in an oven between digestions. A single drop of water will result in contamination. Figure 5.12 (a) shows uncontaminated digested hydrogen charged LaNi₅ residue and Figure 5.12 (b) shows water contaminated digested hydrogen charged LaNi₅ residue. Contamination results in erroneous results. After the air-drying process, the residue was removed from the filter and the hydride hydrogen content was determined utilizing the Leco Hydrogen Determinator.

5.1.4. NaAlH₄ Thermoelectric Power and Magnetic Assessment of Hydrogen

NaAlH₄ samples were prepared under argon in an environmental protection box due to the reactivity of NaAlH₄ shown in Figure 5.13. The NaAlH₄ powder is hydrogen charged to various levels of H/Al for magnetic and electronic analyses. An experimental matrix for NaAlH₄ studies is shown in Table 5.5. For reproducibility, for each hydrogen charging time, there are three different specimen trials.
Figure 5.12: Comparison of LaNi5-hydride residues digested in the Hach Micro-Kjeldahl Digestion Apparatus. (a) Uncontaminated residue and (b) water contaminated residue.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Hydrogen Charging Time</th>
<th>Total Hydrogen Content</th>
<th>Thermoelectric Power Coefficient (µV/°C)</th>
<th>Magnetic Susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>H2</td>
<td>H3</td>
<td>1 hour</td>
<td></td>
</tr>
<tr>
<td>H4</td>
<td>H5</td>
<td>H6</td>
<td>1 day</td>
<td></td>
</tr>
<tr>
<td>H7</td>
<td>H8</td>
<td>H9</td>
<td>3 days</td>
<td></td>
</tr>
<tr>
<td>H10</td>
<td>H11</td>
<td>H12</td>
<td>5 days</td>
<td></td>
</tr>
<tr>
<td>H13</td>
<td>H14</td>
<td>H15</td>
<td>8 days</td>
<td></td>
</tr>
<tr>
<td>H16</td>
<td>H17</td>
<td>H18</td>
<td>10 days</td>
<td></td>
</tr>
<tr>
<td>H19</td>
<td>H20</td>
<td>H21</td>
<td>12 days</td>
<td></td>
</tr>
<tr>
<td>H22</td>
<td>H23</td>
<td>H24</td>
<td>14 days</td>
<td></td>
</tr>
</tbody>
</table>
A schematic diagram of the hydrogen charging system (Figure 5.10 and 5.11) used in this investigation is identical to the hydrogen charging system described for hydrogen charging of LaNi₅. The NaAlH₄ specimens were hydrogen charged at room temperature at a pressure of 1000 psig. The hydrogen charging time was the variable to achieve variations in the hydrogen content.

Figure 5.13: Glovebox under argon utilized for preparation of samples and thermoelectric power measurements for NaAlH₄.

After hydrogen charging NaAlH₄ specimens with hydrogen, powder specimens were put back into the environmental box and specimens are prepared for the Leco Hydrogen determinator, thermoelectric power, and SQUID magnetic analyses. Ester-halogen digestion was not performed on the NaAlH₄
specimens due to the extreme reactivity of NaAlH₄. The Leco Hydrogen Determinator is used for determination of the total hydrogen content of the hydrogen charged NaAlH₄ specimens. Thermoelectric power is calibrated and standardized utilizing the Leco Hydrogen Determinator for total hydrogen content measurements allowing thermoelectric power to be a non-destructive hydrogen meter. The thermoelectric power contact probes are the probes that have been designed for powder measurements as shown above. For NaAlH₄, the temperature difference, ΔT, between the probes is held at 50°C, which has been chosen from a thermoelectric power analysis as a function of temperature difference. These measurements were performed on each specimen by changing the temperature difference systematically with time to see how the thermoelectric power coefficient changed with changing temperature difference, ΔT. Magnetic analyses are then used to verify the thermoelectric power data because there has been a one-to-one relationship between thermoelectric power and magnetic measurements. Use of the SQUID for magnetic measurements is described in the next section.

For magnetic measurements, a SQUID (Superconducting Quantum Interference Device) magnetometer is used. Magnetic measurements are performed by moving a sample through superconducting coils, then the sample induces an electric current back into the detection coils. The detection coils, the connecting wires and the SQUID input coils form a closed superconducting loop, so any change produced by variations in hydrogen content are detected and is proportional to the change in magnetic flux [Yang et al., 2003]. The superconducting SQUID functions as a highly linear current-to-voltage converter, so the variations in SQUID voltage output are proportional to the magnetic moment of the sample [Yang et al., 2003]. Magnetic measurements on hydrogen charged NaAlH₄ are performed on a SQUID located at NIST (National Institute of Standards and Technology). Specimens were prepared in pill-like
containers completely filled with NaAlH₄ powder as shown in Figure 5.14. Figure 5.14 shows a filled specimen and an un-filled specimen to calibrate the magnetic measurements. Magnetic measurements were also performed on the as-received specimens as well as hydrogen charged specimens. Magnetic measurements were performed on NaAlH₄ using a high and low field magnetic moments as a function of the magnetic field strength.

![Specimens](image)

Figure 5.14: Specimens prepared for magnetic measurements in the SQUID.

### 5.2. Electromagnetic Analysis of Structural Linepipe Steel

The physical experiments for non-destructive, non-contact hydrogen determination are described in the following sections. Development of a non-destructive tool to measure diffusible hydrogen in coated linepipe steel involves extensive calibration of the electromagnetic technique. The specimen preparation and calibration techniques are discussed in the following sections.
5.2.1. **Electromagnetic Analysis for Determination of Hydrogen in Coated X80 Line Pipe Steel**

First an induced current resistance measurement, which is applied to allow for an impedance (eddy current) analysis, is described for determination of diffusible hydrogen content in coated X80 line pipe steel. An experimental matrix for induced current impedance measurements is given in Table 5.6.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Hydrogen Charging Time</th>
<th>Total Hydrogen Content After Hydrogen Charging</th>
<th>Total Hydrogen Content During Impedance Measurements</th>
<th>Impedance Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>H2 H3</td>
<td>1 hour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H4</td>
<td>H5 H6</td>
<td>1 day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H7</td>
<td>H8 H9</td>
<td>3 days</td>
<td></td>
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<tr>
<td>H10</td>
<td>H11 H12</td>
<td>5 days</td>
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<td>H13</td>
<td>H14 H15</td>
<td>8 days</td>
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<td>H16</td>
<td>H17 H18</td>
<td>10 days</td>
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<td>H19</td>
<td>H20 H21</td>
<td>12 days</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H22</td>
<td>H23 H24</td>
<td>14 days</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Induced Current Resistance (Eddy Current) Analysis**

For generation and detection of eddy currents requires an oscillator, which is a means of generating a changing magnetic field close to the part, normally in the form of a coil, and a means of measuring the voltage in a detector. A Hewlett
Packard 4275A Multi-Frequency LCR Meter (Figure 5.15) has the capabilities of inducing both the magnetic field and detection of voltage so that it can properly be utilized for electrical impedance measurements on hydrogen charged X80 linepipe steel specimens. Oscillation of the field is generally sinusoidal, with varying frequencies dependent upon the application and depth of measurement. Voltage measurements consist of amplitude and phase difference measurements from the exciter coil current. The eddy current coil sensors must be configured for the particular application.

Figure 5.15: Hewlett Packard 4275A Multi-Frequency LCR Meter utilized for electrical impedance measurements on hydrogen charged X80 linepipe steel specimens.
The first step to attaining a good electromagnetic measurement is designing the proper probes to make such an analysis and the elimination of unnecessarily long wires (to reduce noise). For the first electrical impedance measurements, a simple cell was designed (at NIST) so that the tin-coated hydrogen-charged cylinder is sandwiched between two probes, each having an electrically-insulated alligator clip, as shown in Figure 5.16. One alligator clip is used to induce the current and the alligator clip at the opposite end measures the change in the induced current after it traverses across the specimen. This arrangement shown in Figure 5.16 is only used for initial experiments while the investigators are still determining the capabilities of the equipment. A copper coil probe (solenoid) has been designed such that there is a coil encircling the sample with a specific number of turns at specific lift-off as shown in Figure 5.17. Rubber grommets are utilized to ensure a constant lift-off between the specimen and the coil.

The magnetic field of a long solenoid, consisting of \( n \) closely wound turns per unit length on a cylinder of radius \( R \) and carrying a steady current \( I \). If the turns per unit length are wound very closely, then it can be assumed that each turn is circular [Griffiths, 1999]. Ampere’s law can be applied to calculate the magnetic field. The magnetic field inside the solenoid is calculated by:

\[
\oint B \cdot dl = B_z = \mu_0 I_{enc} = \mu_0 n f \cdot \hat{z}
\]  

[5.1]

The magnetic field within the solenoid is uniform. Ampere’s law is always true for steady currents, however it is not always the most useful equation. When Ampere’s law does not work, it is necessary to fall back on the Biot-Savart law [Griffiths, 1999].

Utilizing the depth of penetration information from Figure 3.22, it is important to calculate the depth of the measurement in the cylindrical X80 linepipe steel specimens. The depth of penetration in the cylindrical X80 linepipe steel
specimen is on the order of 5 mm. A depth of penetration of 5 mm is quite good for hydrogen measurements because the measurement is not a skin affect and would be able to penetrate beneath a coating. To increase the depth of penetration, the number of windings in the copper coil can be increased.

![Figure 5.16: Schematic diagram illustrating an arrangement for inducing and measuring current. The alligator clips are connected to the insulation and make no electrical contact to the cylinder.](image)

![Figure 5.17: Photograph of the encircling coil utilized for impedance measurements. Rubber gromits are utilized to guarantee constant lift-off between the specimen and the copper coil.](image)
It is extremely important to note that all of the X80 linepipe steel specimens are machined from the same piece of linepipe steel and prepared identically to eliminate the introduction of any extra variables besides hydrogen content. In preparation for electromagnetic analyses, three large cylindrical specimens (5 mm diameter) and five small cylindrical specimens (3 mm diameter) as shown in Figure 5.18 are simultaneously hydrogen charged in a reactor at 400°C as a function of various times and pressures (100-1000 psig). The large cylindrical specimen on the left (Figure 5.18) is used for electromagnetic analyses and the smaller cylindrical specimen on the right (Figure 5.18) is used for the determination of the total hydrogen content utilizing the Leco Hydrogen Determinator. There are three large cylinders and five small cylinders hydrogen charged together in the same reactor, such that the large specimens are used for repeatability of measurements and the five small cylinders are used to monitor hydrogen concentration changes over time.

Figure 5.18: Photograph of uncoated X80 steel cylindrical specimens (large cylinder: 5 mm diameter and small cylinder: 3 mm diameter).
After hydrogen charging the specimens at 400°C, the specimens must undergo an intermediate quench (dry ice and acetone) to maintain the charged hydrogen content. If the sample was allowed to slowly cool to room temperature, most of the charged hydrogen will diffuse out of the specimen. After the intermediate quench, the specimens immediately undergo a hot tinning process. The hot tinning process is necessary to hinder the hydrogen from diffusing out of the steel specimens, so that when induced current impedance measurements were performed the hydrogen concentration was homogenous across the specimen. A schematic diagram of the hot tinning process is shown in Figure 5.19. Each cylindrical specimen is individually removed from the intermediate quench and dipped into water to bring the specimen to room temperature, then submerged into the flux (which allows the tin to adhere to the steel) and finally the specimen is dipped into the first tin bath for ten seconds. It is next allowed to cool for approximately twenty seconds and then dipped into the secondary tin bath (which has mineral oil on the surface to allow for a nice finish). Normally, after the specimen has been dipped into the second batch of molten tin, there would be one more step to the process, which is an oil quench. When the specimens were oil quenched, the surface of the coating developed numerous distortions and defects. To minimize distortions in the coatings, the oil quench process was omitted and replaced with air-drying. A photograph of hydrogen-charged tin-coated specimens is shown in Figure 5.20. After the cylindrical specimens are tin-coated, the small cylinders are used for Leco Hydrogen Determinator Analysis (to track the estimated hydrogen in the large cylinders) and the large cylinders are used for electromagnetic analysis.
Figure 5.19: Schematic diagram for hot tinning of X80 steel specimens after hydrogen charging.

Figure 5.20: Photograph of tin-coated hydrogen charged X80 steel cylindrical specimens. The specimens are coated utilizing the hot tinning process shown in Figure 5.15. (The coating on the specimen is smooth and uniform, but lighting conditions from the camera and flash created irregular reflections).

Tin coated hydrogen-charged specimens were sent to CANDET in Canada for electromagnetic sensing of hydrogen. Also electromagnetic testing equipment at NIST in Boulder, Colorado was used in parallel for these electromagnetic
sensing of hydrogen measurements. The NIST system is for precision measurements used to assess material properties.

Eddy current calibration for determination of hydrogen content involves charging the larger cylindrical specimens to various hydrogen levels and creating a map or database of the change in phase lag with hydrogen shown in Figure 5.21 (a). Calibration of the eddy current unit for determination of pipe thickness will require eddy current measurements made at various pipe thicknesses to create a map or database for the particular wall thickness at a specific phase lag as shown in Figure 5.21 (b). The phase lag is important for the determination of hydrogen and thickness, however the phase lag has a complex functionality being a function of conductivity, which directly affects the electron concentration, the effective mass, and scattering sites, but it is also a function of thickness, and alloy content. With knowledge of the presence of these variables it is necessary to employ complimenting techniques to eliminate the variables associated with the linepipe.
CHAPTER 6

PRIOR RESEARCH UTILIZING THERMOELECTRIC POWER FOR INTERSTITIAL NITROGEN CONTENT DETERMINATION

The thermoelectric power coefficient was the electronic measurement utilized to assess the nature and role of the nitrogen content in nitrogen-strengthened stainless steel weldments [Lasseigne et al., 2004, 2005]. The Seebeck apparatus was designed to allow the copper probes with tungsten contact tips to apply a constant pressure to a surface, while performing temperature and voltage measurements. The constant pressure was achieved by applying a constant load on top of the probe-spring arrangement. The 10°C temperature difference (±0.1°C) was accurately controlled by two Watlow temperature controllers and read outs along with two type K thermocouples, two type T thermocouples and the potential measurements (±10 nV) were made with a Keithley Nano-voltmeter 2182. The actual thermoelectric power measurement occurs under the hot probe tungsten contact tip. Seebeck measurements were performed on different surfaces to determine the effect of surface preparation. Seebeck measurements were performed on the as-welded fusion zone and then the weldment is milled down to remove any carburization layer and the Seebeck measurement is re-measured. The Seebeck measurements for the as-welded condition and the milled condition are identical.

The resulting autogeneously welded microstructure of alloy 1.4565 (AISI 34565) is shown in Figure 6.1 with an interstitial nitrogen content of 0.469 wt. pct (0.551 wt. pct. total nitrogen). From the scanning electron micrograph it is
observed that there is an austenite-cored dendritic microstructure. Coring also
denotes that there can be variations in mechanical properties and corrosion
resistance.

Figure 6.1: Scanning electron microscope images at 2000X for plasma-welded
stainless steel Alloy 1.4565 (AISI 34565) at an interstitial nitrogen content of
0.469 wt. pct.. Notice the dendrites with the two-phase interdendritic region.

Coring is normally caused by partitioning of solute on cooling through a two-
phase field. The nature and amount of elemental partitioning is dependent upon
the alloy solute contents, solute partitioning coefficient, $k$, and the thermal
experience during solidification [Grong, 1997]. The equilibrium partition
coefficient is:

$$ k = \frac{C_s}{C_L} \quad [6.1] $$

where $C_s$ is the solute concentration at constant temperature and pressure of the
solidus and $C_L$ is the solute concentration at the same constant temperature and
pressure of the liquidus. The equilibrium partition coefficient controls the direction and extent of segregation during solidification. Micro-segregation during solidification results in an increase in the concentration of alloying elements, precipitates (carbides, nitrides, and intermetallic phases), and possibly porosity in the interdendritic liquid. Predicting from the iron-nitrogen phase diagram in Figure 6.2 and assuming that the extended phase lines on the diagram move up and to the left, a peritectic reaction similar to the iron-carbon system is expected [Brooks and Lippold, 1993]. Hence from Figure 6.2, it can be concluded that the natural tendency is for the partition coefficient to be less than one (k<1), so that nitrogen gets rejected into the liquid interdendritic region during solidification [Grong, 1997], [Kurz and Fisher, 1986], [Olson, 1985].

Because the diffusion coefficient of nitrogen is orders of magnitude above substitutional alloying elements, nitrogen is normally not prone to significant micro-segregation due to sufficient in-process homogenization [Gavrilyuk, 1999]. However, as reported by Gavrilyuk and Berns [1999], as the substitutional alloying elements begin to partition between austenite and ferrite stabilizers, nitrogen segregates to areas with higher nitride forming elements such as: chromium, manganese, and molybdenum contents, while the nitrogen is only partially depleted from areas with higher nickel, cobalt, and carbon content. During plasma arc welding the moving solid-liquid interface may reject nitrogen and there may be insufficient time for nitrogen diffusion to achieve in-process homogenization. Due to nitrogen partitioning into the interdendritic region, it becomes supersaturated in the interdendritic region, resulting in nitride formation on cooling.
Figure 6.2: Fe-N equilibrium diagram [Brooks and Lippold, 1993].

From the scanning electron microscope image in Figure 6.1, the first weld pass shows a primary austenite dendritic solidification where there are small amounts of nitrides (=15% formed nitrides) in the interdendritic region. As subsequent weld passes are made more nitrogen is absorbed adding to the interstitial nitrogen content in the interdendritic region; the interstitial nitrogen increases in the interdendritic region resulting in super-saturated interstitial
nitrogen, thus the formation of more nitrides (~20% formed nitrides). From the combined effort of energy dispersive x-ray (EDX) analysis for elemental distribution (Figure 6.3) along with x-ray diffraction (XRD) (Figure 6.4), there is an indication that the formation of chromium nitrides in the interdendritic region may result in susceptibility for sensitization due to chromium depletion adjacent to the nitrides, thus increasing the importance of characterization of interstitial nitrogen content in nitrogen-strengthened stainless steel weldments.

The EDX line scan (Figure 6.3) shows that the solute composition across the weld metal has an approximate sinusoidal profile due to coring. One way of expressing the degree of austenite stability in cored materials such as weld metal is to assume a sinusoidal distribution function, which can be applied to each of the segregating elements as shown for iron in Figure 6.5 [Kurz and Fisher, 1986]. The positive portion of the sinusoidal curve represents the interdendritic region, while the negative portion of the sinusoidal curve represents the dendritic region as shown in Figure 6.6. It is assumed here that the average dendritic composition of solute is similar to the base metal and that all nitrogen in the dendritic region is in solid solution. The composition of nitrogen left behind the solid-liquid interface is \(C_o/k\), and is assumed to represent the minimum of the dendritic region as indicated in Figure 6.6. \(C_o/k\) is the composition of nitrogen in the core of the dendritic region assuming that \(C_o/k\) describes the amplitude of the interdendritic portion of the sinusoidal curve (Figure 6.6).
Figure 6.3: Energy dispersive x-ray analysis of plasma welded stainless steel Alloy 1.4565 (AISI 34565).
Figure 6.4: X-ray diffraction scan of plasma-welded (triple pass) stainless steel Alloy 1.4565 (AISI 34565).

Fourier cosine series can be used to determine the nitrogen composition in the dendritic region given as:

\[
C_{Dendrite} = C_o - \frac{2kC_o}{\lambda} \int_0^{\lambda/4} \cos \left( \frac{2\pi x}{\lambda} \right) dx
\]  

[6.2]

Solving and simplifying Equation 6.2 gives:
\[ C_{Dendrite} = C_0 \left( 1 - \frac{k}{\pi} \right) \]  

[6.3]

The average composition of the solute in the dendrite is just a fraction smaller than the average composition of the microstructure as shown in a section of the composition sinusoid for solute in stainless steel alloy 1.4565 (AISI 34565) (Figure 6.5).

Figure 6.5: Section of the EDX scan (Figure 5) showing the average solute composition of the transverse section across the dendrite and the interdendritic region.

Figure 6.6: Sinusoidal illustration of the microstructure composition showing the dendritic and the interdendritic region.
Thermodynamic Stability of Nitrogen in Stainless Steel Alloy 1.4565 (AISI 34565)

The solid solution solubility of nitrogen in stainless steel alloy 1.4565 (AISI 34565) has been calculated from the Wada and Pehlke [1977] equations and is shown in Figure 6.7. Unexpectedly, the solubility of nitrogen decreases with increasing temperature, which means that the solution exhibits exothermic behavior [Rosenqvist, 1974]. Exothermic behavior suggests compound formation such as nitrides. In the following, the nitrogen solubility and nitride formation is modeled based on thermodynamic predictions.

The Ellingham-Richardson diagram plots the change in standard free energy of formation as a function of temperature for carbides, oxides, nitrides, etc., giving useful information about the order of nitride formations. The nitride standard free energies given in the Ellingham-Richardson diagram are customized to take into account each alloying addition in stainless steel alloy 1.4565 (AISI 34565) through the utilization of the Wada and Pehlke equation for the activity of nitrogen, as shown in Figure 6.8 [Pankratz, 1982]. Figure 6.8 is a plot of the free energy of formation of nitrides as a function of temperature for stainless steel alloy 1.4565 (AISI 34565) base metal. All thermodynamic data came from Pankratz and Elliot [1982], [Elliot et al., 1963], [Elliot and Gleiser, 1963].

Figure 6.8 indicates that thermodynamically, the first nitrides to form are titanium nitride and aluminum nitride. The aluminum and titanium quickly become exhausted leading to the formation of chromium nitrides and iron nitrides. The nitrides are present in the interdendritic region due to the supersaturation of nitrogen in this region. Iron nitride (Fe₃N) forms in stainless steel alloy 1.4565 (AISI 34565) welds as determined by x-ray diffraction shown earlier in Figure 6.4. However, thermodynamic data was not available for the Fe₃N iron
nitride phase for thermodynamic calculations. When examining the iron-nitrogen phase diagram (Figure 6.2), the Fe₃N phase is the ε-phase.

Notice from the Ellingham-Richardson diagram the positive standard free energy of iron nitride (Fe₄N) as compared to the negative free energies of aluminum nitride and titanium nitride. It would be suspected that Fe₄N would never form due to the location on the Ellingham-Richardson diagram (positive free energy) and Fe₃N must exhibit a negative standard free energy.

![Diagram showing the relationship between nitrogen content and temperature.](image)

**Figure 6.7:** Nitrogen content as a function of temperature from Wada and Pehlke calculation for solubility of nitrogen in nitrogen-strengthened austenitic stainless free steel Alloy 1.4565 (AISI 34565) [Wada and Pehlke, 1977].
Figure 6.8: Ellingham-Richardson diagram modified to take into account alloying elements in stainless steel Alloy 1.4565 (AISI 34565) and of welded stainless steel alloy 1.4565 (AISI 34565) (dashed lines).

Thermoelectric Power and Nitrogen Correlations

The thermoelectric power coefficient was determined for all welds and correlated to total nitrogen and interstitial nitrogen content. The thermoelectric power coefficient as a function of total nitrogen is plotted in Figure 6.9. In Figure 6.10, the thermoelectric power coefficient is plotted as a function of interstitial nitrogen content revealing a linear relationship. As the interstitial nitrogen content is decreased due to the formation of nitrides, the thermoelectric power
coefficient increases. The lattice strain due to nitrogen addition causes changes in d-electron overlap between lattice transition atoms, which means a change in the extent of application of the Pauli-exclusion principle. This behavior changes the electronic effective mass and thus the thermoelectric power coefficient. In the following sections, thermodynamic models will be developed to describe the behavior shown in Figures 6.9 and 6.10.

Figure 6.12 is a schematic diagram illustrating the comparison between a pressure-composition-temperature (PCT) diagram and thermoelectric power coefficient-composition temperature diagram. In the PCT diagram the (alpha+beta)-region is isobaric because the chemical potentials of alpha and beta are equal. In the thermoelectric power coefficient diagram the (alpha+beta)-region is linear (not constant). The thermoelectric power coefficient represents the entropy of the electron in the alpha and beta phases, which can be subject to a rule-of-mixtures averaging having a slope across the two-phase (alpha + beta) region.

Thermoelectric surface contact probe has a diameter of 381 microns, which when compared to the SEM micrograph in Figure 6.1 suggests that the thermoelectric power coefficient is an average of the dendritic and interdendritic regions of the weld. So, to model the thermoelectric power coefficient of an austenitic stainless steel weld, the model needs to describe the entire weld microstructure including the dendritic region and the interdendritic region as shown in Figure 6.13. On the PCT diagram, the weld composition is shifted further to the right into the (alpha+beta)-phase region as shown in Figure 6.11.
Figure 6.9: Thermoelectric power as a function of total nitrogen content for plasma welded stainless steel alloy 1.4565 (AISI 34565) with argon-20 percent nitrogen shielding gas.
Figure 6.10: Thermoelectric power as a function of interstitial nitrogen content for plasma welded stainless steel Alloy 1.4565 (AISI 34565) with argon-20 percent nitrogen shielding gas.
Figure 6.11: Schematic pressure-composition-temperature diagram for nitrogen where α-phase is interstitial nitrogen, (α+β)-phase is interstitial nitrogen and nitrides, and β-phase is nitride phase. The blue line indicates the location of the base-metal and the red-line indicates the position of the weld metal.
The thermoelectric power coefficient in the interdendritic region can be modeled using the rule-of-mixtures for composites assuming that the dendritic region is interstitial nitrogen (alpha) and the interdendritic region is both interstitial nitrogen and formed nitrides (alpha+beta). The rule-of-mixtures for composite structures is applied first for the weld microstructure (dendritic + interdendritic) given as:

\[ Z = Z_\alpha X_\alpha + Z_{\alpha'\beta} X_{\alpha'\beta} \]  \[ 6.4 \]

where \( Z \) is the total thermoelectric power coefficient, \( Z_\alpha \) is the coefficient of the bulk interstitial nitrogen content in the dendrite, \( (Z_{\alpha'\beta}) \) is the coefficient for the two-phase interdendritic region of interdendritic nitride and alpha-phase (interstitial nitrogen). \( X_\alpha \) is the fraction of the alpha-phase in the dendrite and \( X_{\alpha'\beta} \) is the fraction of interdendritic alpha and beta phase. \( X_\alpha \) in the dendrite and \( X_{\alpha'\beta} \) in interdendritic region can be obtained from the SEM micrograph from Figure 6.1. Assuming that the sum of the interdendritic nitrogen content and nitride content is equivalent to the total nitrogen content, it follows:

\[ X_{\alpha'} + X_{\beta} = 1 \]  \[ 6.5 \]

Rearranging Equation 6.5 and inserting into Equation 6.4 gives the thermoelectric power coefficient of the microstructure as:

\[ Z = Z_{\alpha'\beta} + X_\alpha \left( Z_\alpha - Z_{\alpha'\beta} \right) \]  \[ 6.6 \]

The rule-of-mixtures is reiterated to model the interdendritic region where it is assumed that the interstitial nitrogen in the dendrite is constant and \( Z_\alpha \) should
change due to super-saturation of interstitial nitrogen in the interdendritic region, but here it is assumed to be constant $Z_{\alpha'} = Z_{\alpha}$. The rule-of-mixtures for the interdendritic region becomes:

$$Z_{\alpha' + \beta} = Z_{\beta} + (Z_{\alpha} - Z_{\beta})X_{\alpha'}$$  \[6.7\]

where $X_{\alpha'}$ is the fraction of the core region of the dendrite and is assumed to be approximately constant for the same plasma welding parameters. Substitute Equation 6.7 into $Z_{\alpha' \cdot \beta}$ from Equation 6.6 and simplifying gives the thermoelectric power coefficient as:

$$Z = \text{Const.} + \left(Z_{\alpha} - Z_{\beta}\right)(1 - X_{\alpha'})X_{\alpha'}$$  \[6.8\]

Equation 6.8 suggests that the thermoelectric power coefficient is solidification microstructure dependent and thus agrees with the linear relationship for the thermoelectric power coefficient as a function of interstitial nitrogen content in the interdendritic region as shown in Figure 6.10. Equation 6.8 is also consistent with the schematic drawing of the Seebeck coefficient as a function of the fraction of interstitial nitrogen in the interdendritic region for this system as shown in Figure 6.12.
Figure 6.12: Comparison of pressure (chemical potential) and Seebeck coefficient as a function of nitrogen for the alpha-phase, (alpha + beta)-phase, and beta-phase.
Correlation of Models To Experiments

The modification of the Ellingham-Richardson (Figure 6.8) diagram accounting for high nitrogen content and alloying elements present in stainless steel alloy 1.4565 (AISI 34565) showed the thermodynamic order of formation of nitrides and is consistent with the results presented here.

The linear correlation of the thermoelectric power coefficient for plasma welded stainless steel alloy 1.4565 (AISI 34565) as a function of interstitial nitrogen content in the interdendritic region shown in Figure 6.10 is consistent with the proposed weld metal composite model. From this model, the contribution of the thermoelectric power coefficient for the dendritic region is
approximately constant, thus making changes in the measured thermoelectric power coefficient primarily sensitive to interstitial nitrogen content changes in the interdendritic region. From the rule-of-mixtures, this interstitial nitrogen content variation in the interdendritic region results in the linear correlation shown in Figure 6.10.
CHAPTER 7
RESULTS AND DISCUSSION

The electronic property assessment of LaNi$_5$ with characterization of the two-phase (alpha+beta)-region utilizing ester-halogen digestion is presented. The electronic and magnetic property assessment of NaAlH$_4$ is given. Finally, the results are presented for electromagnetic analysis utilizing impedance measurements for hydrogen content determination in X80 linepipe steel.

7.1. Characterization of Hydrogen Charged LaNi$_5$

Hydrogen charged LaNi$_5$ has been characterized utilizing thermoelectric power and ester-halogen digestion to determine the capabilities of the two-phase (alpha+beta)-region. The results of thermoelectric power coefficient (primary ordinate axis) as a function of hydrogen content (H/LaNi$_5$) hydrogen charged at 400°C are shown in Figure 7.1. The percent hydride (residue from the hydrogen charged LaNi$_5$ sample digested by the ester-halogen method) as a function of hydrogen content (H/LaNi$_5$) is plotted on the secondary ordinate axis as shown in Figure 7.2. The experimentally determined percent hydride (black dots) is compared with the theoretical rule-of-mixtures in the two-phase (alpha+beta)-region as shown by the solid red line in Figure 7.2. The ester-halogen digested residue from the hydrogen charged LaNi$_5$ underwent x-ray diffraction to determine if the digested residue was actually hydride phase. The x-ray diffraction results are shown in Figure 7.3. Figure 7.3 (a) shows an x-ray diffraction pattern for pure (not hydrogen charged) LaNi$_5$ to compare with Figure
7.3 (b) the x-ray diffraction pattern for the digested hydrogen-charged LaNi$_5$ residue.

![Diagram showing thermoelectric power coefficient as a function of H/LaNi5.]

Figure 7.1: Thermoelectric power measurements for hydrogen charged LaNi5 as a function of H/M.
Figure 7.2: Percent hydride in hydrogen charged LaNi5 as a function of the number of hydrogen atoms per metal atoms at 400°C and 1000 psig showing the formation of hydrides in the (alpha+beta)-phase region (concentration: H atoms/LaNi5). Experimental hydrides determined by ester-halogen digestion and Leco Hydrogen Determinator.
Figure 7.3: (a) X-ray diffraction scan of LaNi$_5$ and (b) X-ray diffraction scan of LaNi$_5$-hydride residue from the ester-halogen digestion method.
7.1.1. Discussion of Results for Hydrogen-Charged LaNi$_5$

In Figure 7.1, notice the similarities of the shape of the thermoelectric power coefficient as a function of H/LaNi$_5$ curve with the pressure-composition-temperature diagram for LaNi$_5$ shown in Figure 2.17. Both plots can be divided into three distinct regions: (1) alpha-phase (soluble hydrogen), (2) (alpha+beta)-phase region (soluble hydrogen and formed hydrides), and, (3) beta-phase region (formed hydrides). With an increasing hydrogen charging temperature, the two-phase plateau region decreases, meaning that the initial hydrides to precipitate would form at a higher H/LaNi$_5$ while pure hydride (beta) can be formed at lower H/LaNi$_5$.

The LaNi$_5$ powder specimens were hydrogen charged at 400°C and then after charging for a specific time period, the specimens were cold-water quenched. If the specimens were allowed to slowly cool back to room temperature, the hydrogen would diffuse back out of the powder, hence cold-water quenching to maintain the hydrogen content in the specimen. According to the pressure-composition-temperature diagram for LaNi$_5$ (Figure 2.17), at temperatures as high as 400°C are reached, it is above the envelope of forming (alpha+beta)-phase. However because after hydrogen charging the powder specimens, the reactor was cold-water quenched to bring the specimen to equilibrium, which means that the results for thermoelectric power measurements and the appropriate formed phases are not representative of 400°C, but a lower temperature. A schematic time-temperature-transformation diagram is shown in Figure 7.4 to show the actual cooling process. At 400°C, hydride formation would never occur because all of the hydrogen would be soluble hydrogen. But after being hydrogen-charged at 400°C and then being cold-water quenched a cooling process occurs allowing the cooling curve to intersect the hydride transformation curve without fully forming all hydride phase.
So to determine the actual temperature, which corresponds to the specific alpha, alpha+beta, and beta-phase regions according to the thermoelectric power results, a temperature extrapolation (Figure 7.5) can be made from the existing LaNi$_5$ pressure-composition-temperature diagram from Figure 2.17. Utilizing the extrapolation in Figure 7.5, it would appear that the hydrogen-charged LaNi$_5$ results correspond to an actual temperature of approximately 194°C. These results are very important for accurate hydrogen sensing of hydrogen storage materials because the LaNi$_5$ specimen was hydrogen charged at 400°C, but the actual results do not correspond to the hydrogen charging temperature. To obtain accurate results for specimens hydrogen-charged at 400°C it would be necessary to perform thermoelectric power measurements at 400°C, which would require building new high-temperature thermoelectric power stage that could maintain the hydrogen charging temperature as well as the temperature difference necessary to obtain the thermoelectric power measurement.

Figure 7.4: Schematic time-temperature-transformation diagram to describe the cooling of hydrogen charged LaNi$_5$ specimens after being charged at 400°C.
Figure 7.5: Pressure-composition-temperature diagram for LaNi$_5$ with a temperature extrapolation. Red dashed line indicates the regions for the alpha-phase (soluble hydrogen), (alpha+beta)-phase (soluble hydrogen and formed hydrides), and the beta-phase (formed hydrides).

The rule-of-mixtures was utilized in this research to calculate the percentage of formed hydride (beta) phase in the two-phase (alpha+beta)-region as indicated in Figure 7.2. The percentage of hydride calculated using the rule-of-mixtures can be correlated to the percentage of formed hydrides determined
experimentally by the ester-halogen digestion technique with the Leco Hydrogen Determinator. The rule of mixtures states that the composition of a composite was proportional to the volume fractions of each phase of the two-phase region:

\[ C_{\alpha+\beta} = \left( \frac{N_{\alpha+\beta} - N_\beta}{N_\alpha - N_\beta} \right) C_\alpha + \left( \frac{N_\alpha - N_{\alpha+\beta}}{N_\alpha - N_\beta} \right) C_\beta \]  

[7.1]

where \( C_{\alpha+\beta} \) is the composition of both the formed hydrides and the diffusible hydrogen content, \( C_\alpha \) is the composition of the diffusible hydrogen content, \( C_\beta \) is the composition of formed hydrides, \( N_\alpha \) is the mole fraction of the alpha-phase, \( N_\beta \) is the mole fraction of the beta-phase, and \( N_{\alpha+\beta} \) is the mole fraction in the (alpha + beta)-phase region.

The rule of mixtures is in good agreement with the percent hydride from the hydrogen charged LaNi\(_5\) residue. The ester-halogen digestion allows for a fairly rapid technique to quantify the formed hydride content. The accuracy of the ester-halogen digestion technique can be improved by using larger specimens sizes and by performing experiments at the actual hydrogen-charging temperature.

X-ray diffraction was utilized to ensure the presence of hydrides in the digested residue. Notice that many of the x-ray diffraction peaks in the residue and the LaNi\(_5\) material match. Also notice that the (001) and (002) planes are possibly shifted, suggesting that the hydrogen in the lattice is straining the lattice. The structure of the extracted hydride (residue) appears to be a strained x-ray diffraction pattern of the pure LaNi\(_5\), but it is important to notice that only two directions were strained showing anisotropy in this strain situation. The shift in the peak for the (001) plane suggests that this shift may be used as a quantitative analytical method, if calibrated, to quantify the hydride content in LaNi\(_5\) material. The similarity in the two x-ray diffraction patterns suggests the
hydride phase sits in the lattice in a manner similar to an ordered structure. This observation suggests the ordered hydride structure did not dissolve during the ester-halogen digestion process. It is obvious that further x-ray diffraction work comparing the ester-halogen digested residue with the original material (LaNi₅) will give important information on the behavior of hydrogen in the crystal lattice.

7.1.2. Summary for Hydrogen Charged LaNi₅

In summary, this research on hydrogen charged LaNi₅ was very important for numerous reasons. First of all, the concept of cooling of specimens made an important impact on the final results, but also taught importance of understanding the role of the thermoelectric power measurements to determine particular phases. The second important aspect of this research found through x-ray diffraction studies, is that x-ray diffraction shows that hydrogen in the lattice induces strain, which has been supported by Park et al. [2005], where differential thermal analysis was utilized to show that hydrogen causes strain in the crystal lattice. The final and most important aspect of the LaNi₅ research is that the rule-of-mixtures has never been verified in the two-phase (alpha+beta) region and this research developed a digestion technique to experimentally verify and confirm the use of the rule-of-mixtures in the two-phase region.

7.2. Characterization of Hydrogen Charged NaAlH₄

The electronic and magnetic properties of hydrogen charged NaAlH₄ have been characterized utilizing thermoelectric power measurements and magnetic measurements utilizing a superconducting quantum interference device. Before utilizing thermoelectric power experiments as a means to monitor phase
changes, as a function of hydrogen content, an experiment was performed to
determine the most optimum temperature difference, $\Delta T$, ($Z = \Delta V/\Delta T$) to be held
constant during thermoelectric power experiments as shown in Figure 7.6. The
thermoelectric power coefficient is plotted as function of H/Al for hydrogen
charged NaAlH$_4$ as shown in Figure 7.7.

![Graph showing thermoelectric power coefficient as a function of temperature difference](image)

**Figure 7.6:** Thermoelectric power coefficient as a function of temperature
difference (held constant for thermoelectric power measurements) to determine
the most optimum temperature difference.
High-field magnetic sweeps were performed on hydrogen charged NaAlH$_4$ with various hydrogen contents. The high-field magnetic sweep for H/M = 0.30 is shown in Figure 7.8, H/M = 0.39 is shown in Figure 7.9, H/M = 0.939 is shown in Figure 7.10, and H/M = 2.86 is shown in Figure 7.11. The horizontal red lines across Figure 7.8-7.11 shows the magnetic saturation, while the red line across the slope indicates the magnetic susceptibility. To get a closer view of the magnetic properties of hydrogen charged NaAlH$_4$, a low-field magnetic sweep was run on the sample with H/M = 0.30 and is shown in Figure 7.12.

![Graph](image)

**Figure 7.7**: Thermoelectric power coefficient as a function of H/Al for hydrogen charged NaAlH$_4$. 
Figure 7.8: High magnetic field scan of hydrogen charged NaAlH$_4$ with H/M = 0.30.

Figure 7.9: High magnetic field scan of hydrogen charged NaAlH$_4$ with H/M = 0.39.
Figure 7.10: High magnetic field scan of hydrogen charged NaAlH4 with H/M = 0.939.

Figure 7.11: High magnetic field scan of hydrogen charged NaAlH4 with H/M = 2.86.
Figure 7.12: Low magnetic field scan of hydrogen charged NaAlH$_4$ with H/M = 0.30.

7.2.1. Discussion of Results for Hydrogen Charged NaAlH$_4$

The thermoelectric power coefficient as a function of temperature difference (Figure 7.6) indicates that there is an optimum temperature difference where the thermoelectric power coefficient becomes constant. Notice that above a temperature difference of 40°C the thermoelectric power coefficients begin to reach a constant value for all three hydrogen concentrations.

The plot of thermoelectric power coefficient as function of H/Al (Figure 7.7) has many distinct features. First it is important to notice the scale of the thermoelectric power coefficient. Compare the scale of the thermoelectric power coefficient for LaNi$_5$ in Figure 7.1 with that of NaAlH$_4$ in Figure 7.7. The scale of the thermoelectric power coefficient for normal hydrogen storage materials such
as LaNi5 has the scale of µV/°C, while the scale of the thermoelectric power coefficient in Figure 7.7 is mV/°C. There are three orders of magnitude difference between the thermoelectric power coefficient of NaAlH4 and LaNi5. To guarantee the accuracy in the thermoelectric power coefficients, the nano-voltmeter was taken to the National Institute of Standards and Technology to guarantee that the nano-voltmeter was properly calibrated.

Electronically, NaAlH4 is unlike most hydrogen storage materials previously measured, in that the thermoelectric power coefficient measures changes in the s and p electron bands, instead of the s, p, and d-electron bands as in most intermetallic transition metals and hydrogen storage materials, LaNi5. When NaAlH4 is held at a temperature difference, ΔT, of 50°C, the potential created between the copper probes is in the range of 10 to 800 mV dependent upon the hydrogen content.

The pressure-composition-temperature (PCT) diagram for NaAlH4 (Figure 2.15) is very interesting in that a primary reaction occurs from approximately 0 to 1.0 H/Al and a secondary reaction occurs from approximately 1.0 to 2.5 H/Al. Thermoelectric power as function of H/Al (Figure 7.7) also exhibits the same two-reaction behavior as indicated in Figure 2.15. The dual two-phase plateau regions, primary (α+β)-region and the secondary (β + βα')-region, are the most important regions in terms of reversible hydrogen storage materials. Since NaAlH4 exhibits dual two-phase regions, then the rule-of-mixtures can be applied twice to each two-phase region to determine the percentage of formed hydride. The ester-halogen digestion technique for hydride content quantification was not performed on this material because of its extreme reactivity.

Using the thermoelectric power coefficient results from Figure 7.7, the primary two-phase plateau region ranges from ~0.03 to 0.75 H/Al (room temperature) as compared to the PCT with a primary two-phase plateau region ranging from ~0.01 to 0.9 H/Al (150°C). The thermoelectric power measurements for the
secondary two-phase plateau region ranges from ~1.0 to 2.7 H/Al (room temperature) compared to the PCT with a secondary two-phase plateau region ranging from ~1.0 to 2.5 H/Al (150°C). In the primary two-phase region, the thermoelectric power coefficient is extremely sensitive to changes in the hydrogen content (Figure 7.7), as compared to the primary two-phase region in the PCT diagram (Figure 2.15). The thermoelectric power technique allows for a non-destructive, direct assessment of the hydride content evolution in the two-phase plateau region because the thermoelectric power coefficient is a measure of the electronic entropy of the structure resulting in a curve that is not constant in the two-phase region, as seen by the chemical potential in the plateau region of the PCT diagram.

Figure 7.7 is also very interesting in that the value of the thermoelectric power coefficient changes from a positive coefficient to a very negative coefficient and then returns back to a positive coefficient. A change in sign in the thermoelectric power coefficient normally indicates a change in the effective mass or filling of the s, p, and d electronic bands. The change in sign in the thermoelectric power coefficient may be explained by examining the electronic density of states for NaAlH₄ in Figure 7.13 [Aguyor and Singh, 2004]. The band structure in Figure 7.13 indicates two band gaps in NaAlH₄. The first band gap is ~0.5 eV, while the second band gap is approximately ~4 eV. The thermoelectric power coefficient is extremely sensitive to changes in electronic filling, so that when a band gap is reached, there is a change in sign in the thermoelectric power coefficient. The change in sign in the thermoelectric power coefficient at approximately ~0.3 H/Al most likely occurs due to the crossing of the electronic band gap shown in Figure 7.13.
Figure 7.13: Electronic density of states and projection onto the H LAPW spheres for NaAlH₄, on a per formula unit basis [Aguy and Singh, 2004].

The magnetic results shown in Figures 7.8 through 7.11 are very interesting as can be seen more clearly in the low field magnetic scan shown in Figure 7.12. The magnetic results for hydrogen charged NaAlH₄ exhibit hysteresis, a phenomenon of ferromagnetic materials. Normally it would be expected that NaAlH₄ be paramagnetic, which indicates that the ferromagnetic signature is most likely caused due to contamination. The as-received material was then
further investigated to determine if the samples were contaminated during processing or during the hydrogen-charging process. The as-received material also exhibited hysteresis, indicating contamination during processing. When discussing this issue with the material supplier, it was found that the NaAlH₄ is ball milled utilizing a tungsten carbide ball. The tungsten carbide has cobalt in it, which due to the extreme reactivity of NaAlH₄, the cobalt contaminated the NaAlH₄ during processing resulting in a ferromagnetic signature.

Figure 7.14 compares the electronic (thermoelectric power) and magnetic results. This final comparison is very important because when plotting the magnetic data alone there is no correlation between magnetic susceptibility as a function of hydrogen content. When plotting the thermoelectric power coefficient and magnetic results together (Figure 7.14) it is clear that the magnetic results are being measured across different phases. If more magnetic data is collected across one particular phase region then there would most likely be a clear correlation between thermoelectric power coefficient and magnetic data as found by previous researchers [Niyomsoan, 2003].

Another interesting fact about both the thermoelectric power and magnetic data, is that even though the NaAlH₄ specimens are contaminated, both methods are measuring a deviation from the original material, which is only variations in hydrogen content. So whether the material is contaminated or not, it was still possible to collect meaningful thermoelectric power and magnetic data as a function of hydrogen content.
Figure 7.14: Comparison of thermoelectric power data as a function of H/M with magnetic susceptibility as a function of H/M for hydrogen charged NaAlH₄.
7.2.2. **Summary of Results for Hydrogen-Charged NaAlH₄**

The results for NaAlH₄ are very important for a variety of reasons. The most important finding in this NaAlH₄ investigation is the sensitivity of thermoelectric power to sense phase transformation in a material with dual two-phase (alpha+beta)-regions. The distinctions between each phase can clearly be seen. The phase changes also corresponded to the Fermi energy level at the band gap from the research of Aguyo and Singh [2004] on NaAlH₄. The magnetic results allowed for a technique to determine the contamination in the material and also a method to be correlated with thermoelectric power.

7.3. **Assessment of Hydrogen Content in Coated Line Pipe Steel**

Electromagnetic analysis has been developed and utilized for determination of hydrogen content in coated X80 linepipe steel specimens. Electromagnetic analyses have been utilized to guarantee a non-destructive, non-contact means for hydrogen content determination.

A frequency sweep was performed on cylindrical steel specimens that were hydrogen charged to different levels of hydrogen by varying the charging time at a pressure of 1000 psig and a temperature of 400°C (hydrogen content being the sole variable) content to determine if there were any measurable changes in impedance as a function of the hydrogen content. The cylindrical X80 steel linepipe specimens, which underwent the electromagnetic analyses, had total hydrogen contents ranging from 0.78 to 23.1 ppm of hydrogen determined by the Leco Hydrogen Determinator.

The initial results for the change in impedance due to changes in hydrogen content as a function of frequency is given in Figure 7.15. The impedance is
then plotted as a function of hydrogen content at approximately 100 Hz (depth of 5 mm). The results are most important at lower frequencies (Log Frequency = 2 Hz) to guarantee a maximum penetration depth of 5 mm beneath the surface. At frequencies beyond 100 Hz (> Log Frequency = 2 Hz) only skin effects (the specimens are coated with tin barrier) are being monitored, which cannot be attributed to variations in hydrogen content but variations in the coating, etc.

7.3.1. Discussion of Results for Electromagnetic Analysis of X80 Coated Linepipe Steel Specimens

In Figure 7.15, notice how the impedance as a function of frequency increases with increasing hydrogen content. Not only are there measurable changes in impedance, but the sensitivity of the impedance measurements is exceptional. It cannot only measure hydrogen below 1.0 ppm, but it can also distinguish between 0.76 and 0.90 ppm of hydrogen. As the steel strength increases, the tolerance for hydrogen approaches these small hydrogen contents. These low levels of hydrogen detection are within the uncertainty of chemical methods, but appear to be clearly measurable with physical electromagnetic tools. These preliminary results utilizing induced current impedance measurements demonstrates that it is feasible to develop electromagnetic (eddy current) measurements to assess hydrogen in line pipe steel. The impedance results in Figure 7.16 show the increasing trend of impedance as a function of hydrogen content.
Figure 7.15: Frequency sweep of impedance with change in hydrogen content in tin coated hydrogen charged X80 steel specimens. Impedance measurements were performed utilizing the Hewlett Packard 4275A Multi-Frequency LCR Meter.
Figure 7.16: Impedance as a function of hydrogen concentration for hydrogen charged X80 linepipe cylindrical steel specimens at a frequency of 100 Hz.

The impedance results are a function of both the resistance and reactance, so that the impedance is given as:

$$Z = \sqrt{(\omega L^2 + R^2)}$$ \[7.1\]

Capacitance does not play a significant role in the impedance measurements because very short wires (2.5 inches) were used in the measurements. To develop an understanding of how impedance measurements can detect changes
in hydrogen content it is necessary to closely look at each term in the impedance. The inductive reactance is a form of resistance that occurs when the coil is excited at an angular frequency creating another form of resistance due to a back electromotive force caused by the changing flux. From Chapter 3, the inductive reactance is given as:

\[ X_L = \omega L = 2\pi fL \]  \hspace{1cm} [7.2]

where \( L \) is the inductance which is the flux linkage per unit current and the angular frequency \( \omega \). Inductive reactance has a small contribution to the impedance at low frequencies used in these experiments. The lowest frequency was utilized in this experiment to gain the maximum depth of measurement, which in this research a frequency of 100 Hz is preferred to reach depth of 5 mm into the cylindrical specimen. At 100 Hz with a specimen radius of 2.5 mm, the full in-depth hydrogen content of the specimen is assessed. The contribution of inductive reactance increases with increasing frequencies, thus the inductive reactance plays a larger role (but not a very large role relative to the resistance) in the overall impedance at higher frequencies as shown in Figure 7.15.

Now the resistance term from Equation 7.1 is more closely examined. The resistance is given as:

\[ R = \frac{\rho l}{A} \]  \hspace{1cm} [7.3]

where \( \rho \) is resistivity, \( l \) is the length of the specimen, and \( A \) is the area of the specimen. For a cylinder being induced with a current, the resistance is not only inversely proportional to the area of the specimen, but the frequency must be accounted for in the area term. As discussed earlier, at low frequencies, flux is
being generated into a greater specimen area as opposed to higher frequencies where the flux is generated only at the surface of the specimen. So accounting for the depth of measurement as a function of frequency, the area is proportional to:

$$A \propto \frac{A_o}{(\omega + 1)^{1/2}} \tag{7.4}$$

where $A_o$ is the cross-sectional area of the specimen. Then the resistance can be written as:

$$R = \frac{\rho l(\omega + 1)^{1/2}}{A_o} \tag{7.5}$$

The net resistivity must also be considered when determining the change in resistance due to the addition of hydrogen atoms. The resistivity arises from independent scattering processes which according to Matthieson’s rule are additive. For dilute solutions, Matthieson’s rule is in excellent agreement with experiments as shown for copper in Figure 7.17. Not only does Figure 7.17 show the effect of temperature on resistivity, but it also shows the effect of alloying elements on resistivity. The net resistivity is then given as:

$$\rho_{net} = \rho_{lattice} + \rho_{thermal} + \rho_{Hydrogen}[H] \tag{7.6}$$

where $\rho_{lattice}$ is scattering due to grain boundaries, defects, etc. in the lattice, $\rho_{thermal}$ is thermal scattering due temperature, and $\rho_{hydrogen}$ is the change in resistivity due to the addition of hydrogen atoms. When a hydrogen atom in
solution is entered into the metal, it also acts as a source of scattering because the scattering arises from a departure from regularity in the ion lattice. The scattering due to the hydrogen atoms also scatter independently of thermal scattering. In these experiments, the thermal resistivity can be neglected because the temperature is held constant.

![Graph showing temperature variation of resistivity for copper and copper alloys](image)

Figure 7.17: Temperature variation of resistivity for copper and copper alloys [Linde, 1932], [Wilkes, 1973].

Accounting for the net resistivity and the angular frequency, the resistance can now be re-written as:
\[ R = \frac{\left( \rho_i + \rho_t + \rho_H[H] \right) l (\omega + 1)^{1/2}}{A_o} \] \hspace{1cm} [7.7]

When measuring the flux at full depth, the area is the cross-sectional area of the specimen. When the angular frequency goes to zero (the point where ac goes to dc), the resistance is given as:

\[ R = \frac{\left( \rho_i + \rho_t + \rho_H[H] \right) l}{A_o} \] \hspace{1cm} [7.8]

Notice this relationship between resistivity and hydrogen as shown in Figure 7.15 by recognizing the systematic increase of the intercept of the various hydrogen content lines. With all things being held constant within the specimens as shown in Figure 7.16, the variations in hydrogen content are monitored due to the change in scattering or resistivity due to the departure from regularity in the crystal lattice.

When considering the effects of the resistivities due to the lattice, temperature, and hydrogen, notice in Figure 7.17 how the resistivity due to hydrogen content is a function of the slope of the line and the resistivity due to temperature and lattice variables is accounted for in the y-intercept. Using this information, it may be possible to calibrate specimens with temperature and lattice as variables utilizing the same induced current impedance measurements used for hydrogen content determination. This finding is important because it would be more efficient to be able to eliminate the variables in the pipelines by utilizing one single technique. To calibrate induced current impedance measurements for temperature and lattice variations, cylindrical specimens
would be made and impedance measurements would be performed at various temperatures and on numerous microstructures (various X80 microstructures). Then the same specimens would be charged with hydrogen to then see how the impedance changes with temperature as a function of hydrogen content and microstructure as a function of hydrogen content. Then it would be possible to determine the proper intercept as a function of temperature and microstructure, which will then be correlated to a specific slope.

Figure 7.18: Induced current measurements as a function of hydrogen content at a frequency of 100 Hz showing where the resistivity of hydrogen is the slope of the line and the y-intercept is the resistivity of temperature and lattice.
7.3.2. Summary of Results for Electromagnetic Analysis of Coated X80 Steel Linepipe Specimens

The results for electromagnetic analysis of coated X80 steel linepipe cylindrical specimens show that there is another non-destructive technique available for hydrogen content assessment. This electromagnetic technique is especially unique due to its ability to be a non-contact hydrogen sensor. The results also indicate that the same induced current impedance measurements may also be utilized for temperature and microstructure corrections.
CHAPTER 8
THERMODYNAMIC MODELING

The auxiliary work functions (Gibbs free energy and Helmholtz free energy) have allowed for establishing an analytical approach using chemical thermodynamics to guide experimental design and give insight to interstitial solute content in alloys. The Gibbs free energy has been the major function to allow for assessment and insight into electrochemical reactions through the Nernst Equation. The Gibbs free energy is an effective auxiliary function for systems experiencing external work. This function has been used to correlate thermoelectric power (Seebeck) coefficient to nitrogen content in austenitic stainless steel weldments and hydrogen content in hydrogen storage and structural materials. The analytical approach will be described and examples given of application to hydrogen storage and structural alloys.

8.1. Thermodynamics of Thermoelectric Power for Interstitial Content Determination

A thermodynamic expression of equilibrium can be utilized to derive the relationship between the thermoelectric power coefficient and the activity of interstitials. Beginning with the first law of thermodynamics and assuming a reversible process:
\[ dE = TdS - PdV - \delta w_{ext} \]  \[ 8.1 \]

where \( E \) is the internal energy, \( S \) is the entropy, \( T \) is the temperature, \( P \) is the pressure, \( V \) is the volume, and \( w_{ext} \) is the external work done by the system.

At constant pressure (\( dP=0 \)), enthalpy is introduced as the sum of the internal energy and the product of pressure and volume (\( H=E+PV \)). Differentiating enthalpy and incorporating into Equation 7 gives:

\[ dH = TdS - \delta w_{ext} \]  \[ 8.2 \]

Equation 8 is inserted into the differential Gibb's free energy (\( dG=dH-SdT-TdS \)) and is given as:

\[ dG = -\delta w_{ext} - SdT + \sum \mu_i n_i \]  \[ 8.3 \]

where the \( \sum \mu_i n_i \) is additional free energy accounting for the addition of alloying elements to the solution and \( \mu_i \) is the chemical potential of species \( i \).

The external work term is the product of the number of moles of transported electrons, Faraday's constant (96,487 Coulombs per electron equivalent), and electric potential. The thermoelectric power coefficient involves the generation of an electric potential difference, \( \Delta V \), under an applied temperature difference, \( \Delta T \) given as:

\[ \Delta V = Z\Delta T \]  \[ 8.4 \]

Under the assumption that the external work is electric work by analogy to the thermodynamics of a reversible cell, the external work term becomes:

\[ \delta w_{ext} = -nF (Z\Delta T) \]  \[ 8.5 \]
and then Equation 8.3 can be rearranged:

$$dG = -nF(Z\Delta T) - SdT + \sum \mu_i n_i$$  \[8.6\]

where $\mu_i = \mu_{i}^{0} + RT \ln a$. The external work has been considered, but the lattice strain due to the interstitial addition into the host metal lattice must also be accounted for because the amount of strain due to the addition of interstitial atoms is very significant. To emphasize the amount of lattice strain consider the case of hydrogen as an interstitial solute in iron (BCC, d-band metal), the hydrogen atom gives its electron to the d-band and behaves as a localized proton between the iron atoms. The coulombic interaction of the proton with the positive core of the iron atom causes localized repulsion. The radius of the interstitial hole in BCC iron is 0.36 Å for tetrahedral sites and 0.19 Å for octahedral sites. Hydrogen atoms lead to an effective volume increase of 2.8 ± 0.2 Å in BCC tetrahedral sites and 2.1 ± 0.2 Å in BCC octahedral sites [Fukai, 1993], which translates to an increased radius of 0.87 Å in tetrahedral sites and 0.66 Å in octahedral sites. So to account for the lattice strain due to interstitial additions, Helmholtz free energy, dA, is used and given as:

$$dA = dw_{\text{int(solute-strain)}} + dw_{\text{ext}}$$  \[8.7\]

where $dw_{\text{int(solute-strain)}}$ is the internal work due to solute lattice strain and the external work is Gibb’s free energy (Equation 8.6), which can be substituted back in to Equation 8.7 to give:

$$dA = -nF(Z\Delta T) - SdT + \sum \mu_i n_i + dw_{\text{int(solute-strain)}}$$  \[8.8\]
Then at equilibrium \( dA = 0 \), and solving for the thermoelectric power coefficient, \( Z \):

\[
Z = -\frac{S}{nF} + \sum \frac{\mu_i n_i}{nF \Delta T} + \frac{\Delta w_{\text{int(solute-strain)}}}{nF \Delta T} \tag{8.9}
\]

Because the thermoelectric power coefficient measures a change, it is important to note that the reference state thermoelectric power coefficient is a function of entropy before the addition of an interstitial atom, given as:

\[
Z = -\frac{S}{nF} \tag{8.10}
\]

Then when the interstitial atom is added to the metal lattice, the thermoelectric power technique measures a change in the thermoelectric power coefficient, which is \( \Delta Z = Z - Z^0 \), so that the actual thermoelectric power coefficient measurement gives:

\[
\Delta Z = \sum \frac{\mu_i n_i}{nF \Delta T} + \frac{\Delta w_{\text{int(solute-strain)}}}{nF \Delta T} \tag{8.11}
\]

The elastic strain energy is given in a simple form by Eshelby [1957, 1959, 1961] for an ellipsoidal inclusion with uniform eigenstrain as:

\[
E_{\text{strain}}(c) = -\frac{2}{3} \mu \frac{1}{\Omega} \left( \frac{d\Omega}{dc} \right) f(c) \tag{8.12}
\]

where \( c \) is the composition, \( \mu \) is the shear modulus, \( \Omega \) is the mean volume per atom of the alloy, and \( f(c) \) is usually a linear function. Inserting Equation 8.12 into Equation 8.11 gives:

\[
\Delta Z = \sum \frac{\mu_i n_i}{nF \Delta T} + \frac{-\frac{2}{3} \mu \frac{1}{\Omega} \left( \frac{d\Omega}{dc} \right) f(c)}{nF \Delta T} \tag{8.13}
\]
Equation 8.13 is then considered for each region of the pressure-composition-temperature diagram (PCT). There are three different regions making up the PCT diagram: (1) the alpha-phase region, which is interstitial solute, (2) the (alpha+beta)-phase region, which is composed of interstitial solute and formed precipitates, and (3) the beta-phase region, which is formed precipitates. It is important to determine the thermodynamic relationship between the thermoelectric power coefficient and the interstitial content in the alpha-phase region and the beta-phase region. With knowledge of these two regions and the use of the rule-of-mixtures, the thermoelectric power coefficient for the (alpha+beta) two-phase region can be determined.

**Alpha-Phase Region**

First the alpha-phase region is considered using hydrogen as an example, where the appropriate reaction is given as:

\[ H_2(g) \rightarrow 2H \]  \[8.14\]

\( H(M) \) is a hydrogen atom in solid solution in the metal matrix, M. The thermoelectric power coefficient for the alpha-phase region derived from Equation 8.13 where \( pH=-\log [H] \) becomes:

\[ \Delta Z_{\alpha} = \frac{1}{nF\Delta T} \left( \Delta G^* + \left( -\frac{2}{3} \mu \frac{d\Omega}{dc} f(c) \right) + RT \left( \ln[H] + 2.3pH \right) \right) \]  \[8.15\]

**Beta-Phase Region**

The thermoelectric power coefficient must be determined in the beta-phase region to develop an expression for the thermoelectric power coefficient for the
The reaction for the beta-phase region (hydride formation) is:

\[
\frac{2}{x} M + H_2(g) \rightarrow \frac{2}{x} MH_x
\]

[8.16]

The thermoelectric power coefficient, assuming the activity of the metal nitride and metal is equivalent to one \((a_M = 1, a_{MH} = 1)\), is derived from Equation 8.13 and is given as:

\[
\Delta Z_\beta = \frac{1}{nF\Delta T} \left( -\Delta G^\circ - \frac{2}{3} \mu \frac{1}{\Omega} \left( \frac{d\Omega}{dc} \right) f(c) - RT \left( \ln \left[ p_{H_2} \right] \right)^{-1} \right)
\]

[8.17]

**Alpha+Beta-Phase Region**

In the (alpha + beta) two-phase region, there is the mixture between the alpha-phase of saturated hydrogen \(X_{\Omega(sat)}\) and the beta-phase at a fixed composition \(X_b\), which forms a metal hydride \(MH_b\). In this case, the rule-of-mixtures is used to give the thermoelectric power coefficient in the (alpha+beta) two-phase region as:

\[
\Delta Z_{\alpha+\beta} = (1-Y) \left( \frac{1}{nF\Delta T} \left( -\Delta G^\circ + \left( -\frac{2}{3} \mu \frac{1}{\Omega} \left( \frac{d\Omega}{dc} \right) f(c) \right) + RT \left( \ln \left[ H \right] + 2.3pH \right) \right) \right) + \\
+ Y \left( \frac{1}{nF\Delta T} \left( -\Delta G^\circ - \frac{2}{3} \mu \frac{1}{\Omega} \left( \frac{d\Omega}{dc} \right) f(c) \right) - RT \left( \ln \left[ p_{H_2} \right] \right)^{-1} \right)
\]

[8.18]

where \(Y\) is the fraction of beta-phase. Equation 8.18 can be simplified by using constant \(A\), which is given as:

\[
A = \frac{1}{nF\Delta T} \left( -\Delta G^\circ + \left( -\frac{2}{3} \mu \frac{1}{\Omega} \left( \frac{d\Omega}{dc} \right) f(c) \right) + RT \left( \ln \left[ H \right] + 2.3pH \right) \right)
\]

[8.19]
and constant $B$:

$$B = \frac{1}{nF\Delta T} \left( -\Delta G^* - \frac{2}{3} \mu \frac{1}{\Omega} \left( \frac{d\Omega}{dc} f(c) \right) - RT \ln \left[ \frac{p_{\text{H}_2}}{p_{\text{H}_2}} \right]^{-1} \right) \tag{8.20}$$

So that the simplified version of Equation 8.20 becomes:

$$\Delta Z_{\alpha*\beta} = A + Y(B - A) \tag{8.21}$$

The relationship between the thermoelectric power coefficient and the activity of hydrogen in three regions is supported by similar experimental results for hydrogen solubility behavior in hydrogen storage material and structural steel from Niyomsoan [2003] and Termsuksawad [2004].

Figure 8.1 is a schematic illustrating the comparison between a pressure-composition-temperature (PCT) diagram and thermoelectric power coefficient-composition temperature diagram. In the PCT diagram the (alpha+beta)-region is isobaric because the chemical potentials of alpha and beta are equal. In the thermoelectric power coefficient diagram the (alpha+beta)-region is linear (not constant), which is consistent with Equation 8.21. The thermoelectric power coefficient represents the entropy of the electron in the alpha and beta phases, which can be subject to a rule-of-mixtures averaging having a slope across the two-phase (alpha + beta) region.
Figure 8.1: Schematic diagram comparing the pressure-composition-temperature diagram with the thermoelectric power coefficient as a function of hydrogen diagram. Notice the difference in slope of the two-phase regions.
CHAPTER 9

CONCLUSIONS

9.1. \textit{Nitrogen-Strengthened Stainless Steels}

- The nitrogen-strengthened austenitic stainless steel Alloy 1.4565 weld metal microstructure was characterized for its microstructure and alloy content by using SEM line analysis and X-ray diffraction and correlated to electronic property measurements.
- The determination of interstitial nitrogen content in nitrogen strengthened austenitic stainless steel welds utilizing a non-destructive thermoelectric power surface contact probe has been demonstrated.
- The use of an ester-halogen digestion technique to determine the nitrogen associated with nitrides in super austenitic stainless steel weld metal was developed and demonstrated.
- The thermoelectric power coefficient is very sensitive to microstructural changes and with careful correlation to standards, it can be used as a rapid non-destructive technique to assess alloy composition, phase, and microstructure variations.
9.2. \textit{LaNi}_{5}

- The use of the Beeghly ester-halogen digestion method with the Leco Hydrogen Determinator for determination of hydride content in LaNi$_5$ has been demonstrated.
- The use of thermoelectric power to assess total hydrogen content in LaNi$_5$ has been demonstrated.
- The use of the rule-of-mixtures for theoretical determination of hydride phase has been demonstrated and compared to the experimental ester-halogen digestion technique.
- The combination of the Beeghly ester-halogen digestion, Leco Hydrogen Determinator, and thermoelectric power offers a fairly rapid method to assess reversible hydrogen capabilities of an alloy.
- The comparison of x-ray diffraction data and the Beeghly ester halogen residue for pure LaNi$_5$ and hydrogen charged LaNi$_5$ gives insight into the nature of the two-phase region, which is so important for the performance of reversible hydrogen storage materials.

9.3. \textit{NaAlH}_4

- The use of thermoelectric power to assess the role of hydrogen in NaAlH$_4$ has been demonstrated.
- The effectiveness of NaAlH$_4$ as a thermoelectric power has been demonstrated.
- The thermoelectric power coefficient as a function of hydrogen per metal atom has been correlated to the pressure-composition-temperature diagram and density of electronic states.
9.4. **Structural Steel Line Pipe**

- The use of induced current resistivity (eddy current) measurements for determination of hydrogen content in X80 line pipe steel specimens has been demonstrated.

9.5. **Engineering Significance**

The thermoelectric power and electromagnetic assessment can be applied in the laboratory, but also in the future will be applied to large steel and stainless steel technical assemblies as well as hydrogen storage applications i.e. hydrogen fuel gauge. The thermoelectric power and electromagnetic procedures can be applied to as-fabricated material as well as on weldments to verify proper post-weld heat treatment procedures, which can also be used for selection of welding consumables. These practices can be applied to steels, stainless steels, and hydrogen storage materials as long as proper calibration and standardization has been established. The thermoelectric power and electromagnetic practices do not replace existing technology for there is no present method to non-destructively measure interstitial contents, especially if the interstitial contents are high enough to form precipitation phases.
CHAPTER 10

FUTURE WORK

Thermoelectric power has been utilized to assess hydrogen storage materials. Future work for hydrogen storage materials will be to add dopants to the NaAlH₄ to determine the change in the band gap and also in the efficiency of NaAlH₄ as a reversible hydrogen storage material. Further magnetic analyses will be performed and correlated with thermoelectric power in the different phases of the NaAlH₄ decomposition processes.

There are numerous opportunities available in the development of electromagnetic techniques for hydrogen content assessment in linepipe steel specimens and in in-service pipelines. Impedance measurements as a function of hydrogen have been achieved, however there is much more information still available within the signal such as phase angle, reactance, etc, that needs to be further studied and understood. Tools such as magnetic Barkhausen noise and electromagnetic acoustic transducers for the assessment of variations in microstructure and temperature still need to be assessed. Also the coatings utilized to protect pipelines from corrosion environments need to be studied because the coatings may contain magnetite, which will alter the magnetic signals generated by the electromagnetic measurements. It will also be important to determine whether these electromagnetic techniques could be similarly applied to stainless steel pipelines.
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APPENDIX A: PRECIPITATION IN NITROGEN STRENGTHENED AUSTENITIC STAINLESS STEEL

Ternary phase diagrams provide the beginning of an understanding of the complex metallurgy involved in these multi-component alloys. It is important to know when and which secondary phases form under particular conditions, because formation of secondary phases can have profound effects on the mechanical properties and corrosion resistance. There are two types of precipitates (secondary phases) that have been found in austenitic stainless steel: intermetallic phases and nitrides/carbides. Some of the secondary phases (intermetallics, carbides, and nitrides) that have been found in austenitic stainless steel are given in Table A.1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Symbol</th>
<th>Type</th>
<th>Formula</th>
<th>Temperature Range</th>
<th>Structure</th>
<th>Lattice Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium Carbide</td>
<td>-</td>
<td>M\textsubscript{23}C\textsubscript{6}</td>
<td>(Cr,Fe,Mo)\textsubscript{23}C\textsubscript{6}</td>
<td>600-950°C</td>
<td>Cubic</td>
<td>A=10.57 – 10.68</td>
</tr>
<tr>
<td>Chromium Carbide</td>
<td>-</td>
<td>M\textsubscript{6}C</td>
<td>(Cr,Fe,Mo, Cb)\textsubscript{6}C</td>
<td>700-950°C</td>
<td>Cubic</td>
<td>A=10.93 – 11.28</td>
</tr>
<tr>
<td>Nb-Cr Nitride</td>
<td>Z</td>
<td>MN</td>
<td>(NbCr)\textsubscript{N}</td>
<td>700-1000°C</td>
<td>Tetragonal</td>
<td>a =3.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 7.37</td>
</tr>
<tr>
<td>Sigma</td>
<td>(\sigma)</td>
<td>AB</td>
<td>(Fe,Cr, Mo, Ni)</td>
<td>550-1050°C</td>
<td>Tetragonal</td>
<td>a=8.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c=4.54</td>
</tr>
<tr>
<td>Chi</td>
<td>(\chi)</td>
<td>A\textsubscript{4}B\textsubscript{10}</td>
<td>Fe\textsubscript{36}Cr\textsubscript{12}Mo\textsubscript{10} (FeNi)\textsubscript{36}Cr\textsubscript{18} (TiMo)\textsubscript{4}</td>
<td>600-900°C</td>
<td>Cubic</td>
<td>a=8.86 – 8.92</td>
</tr>
<tr>
<td>Laves</td>
<td>(\eta)</td>
<td>A\textsubscript{2}B</td>
<td>(FeCr)\textsubscript{2}(Mo, Nb, Ti, Si)</td>
<td>550-900°C</td>
<td>Hexagonal</td>
<td>A=4.73-4.82, c=7.26-7.85</td>
</tr>
</tbody>
</table>
A.1 Carbides

The presence of carbides is normally confined to intergranular precipitates formed at intermediate temperatures upon cooling after welding. The $M_{23}C_6$ carbide is the most common type. Intergranular precipitated carbides can reduce the pitting resistance and produce intergranular corrosion as a result of chromium depletion adjacent to the carbide, but is dependent upon the morphology of the carbide and the time available to redistribute chromium depletion during cooling. The addition of nitrogen to the steel shifts the precipitation of $M_{23}C_6$ carbide to longer times as shown in Figure 2.4. At temperatures above 600°C, the stabilization of austenite with nitrogen becomes notable. Below this temperature the opposite effect can occur leading back to shorter precipitation times. Nitrogen has a strong inhibiting effect on the precipitation of all phases except $M_{23}C_6$, which is capable of dissolving nitrogen [Folkhard, 1988].

A.2 Nitrides

High nitrogen content in austenitic stainless steel favors the occurrence of various nitrides, of which $Cr_2N$ is the most common. Nitrogen is quite soluble at hot working temperatures and annealing temperatures, so if nitrides form, they most often form upon solidification. Nitrides precipitate in the sensitization temperature range and usually appear as fine intergranular particles that are difficult to distinguish from carbides and sigma phase. According to Grutzner [1971], with proper solution annealing and rapid cooling the typical 40-60 percent austenite phase balance is adequate to solutionize all available nitrogen. Due to rapid cooling, welding, however, reduces the amount of austenite available to solutionize nitrogen, thus resulting in nitride precipitation.
Like chromium carbide, either slow cooling or heating within an intermediate temperature range (1200-1740°F) will produce intergranular nitrides that can be detrimental to corrosion resistance [Nickel Development Institute, 2003]. Turkdogan [1996] reassessed the values of the solubility products of nitrides in austenite and the temperature dependence of the nitride solubility is shown in Figure 2.5. From this diagram it is obvious that the solubility products of nitrogen increase with increasing temperature [Turkdogan, 1996].

According to Gavriljuk and Berns [1999], tempering martensitic nitrogen steels at 300°C causes an increase in the contrast of fine precipitates. Diffraction patterns show that hexagonal phase ε-nitride (FeCr)$_2$N in nitrogen martensite transformed into orthorhombic ζ-nitride (FeCr)$_2$N. As the temperature increases up to 500°C, the precipitates coarsen as shown in Figure 2.6 (a). The structure of nitrogen martensite tempered at 600 - 650°C is precipitates formed as thin plates as in Figure 2.6 (b). At the same time, the stable hexagonal close-packed nitride (CrFe)$_2$N is precipitated and coarse particles are seen along with the plates of the ζ-nitrides as shown in Figure 2.6 (c) [Gavriljuk and Berns, 1999].

Rawers and Petty [1993] utilized scanning electron microscopy to show several different forms of chromium nitrides found in iron-chromium-nickel alloys which include: (1) equiaxed, primary dendrites, (2) eutectic, secondary dendrites, (3) "false" pearlite (laminar austenite and CrN), and (4) submicron-sized precipitates as shown in Figure 2.7. The form of chromium nitride (CrN) is strongly dependent upon alloy composition. For body-centered cubic alloys without nickel additions, the dominant form of chromium nitride structure is pearlite. For primarily austenitic Fe-Ni-Cr alloys, chromium nitride is present as primary and secondary (eutectic) dendrites [Rawers and Petty, 1993].
Figure A.1: Effect of nitrogen on the precipitation of M23C6 (solid lines) and M6C (dotted lines) carbides in steel Cr17Ni13Mo5 [Thier, 1967].
Figure A.2: Solubility product as a function of temperature for six different compounds in austenitic stainless steel [Turkdogan, 1996].
Figure A.3: (a) \((\text{Fe},\text{Cr})_2\text{N}\) particles in steel Cr15Mo1N0.62 after tempering at 550°C for two hours. (b) Precipitates of orthorhombic \(\varepsilon\)-(\text{CrFe})\(_2\)N (thin plates) and hexagonal \(\varepsilon\)-(\text{CrFe})\(_2\)N (round particles) nitrides in steel Cr15Mo1N0.62 after tempering at 650°C for two hours. (c) Globules of (\text{CrFe})\(_3\)C carbide and \(\theta\)-(FeCr)\(_3\)C cementite plates in the structure of steel Cr15Mo1C0.6 after tempering at 600°C for two hours [Gavriljuk and Berms, 1999].
Figure A.4: Chromium nitride precipitates showing different morphologies. (a) Three dimensional features of chromium nitrides after removal of the austenitic matrix. (b) Three different microconstituents are shown: (1) upper left are primary dendrites formed upon cooling (2) larger linear precipitates are chromium nitride-austenite eutectic phase formed during final solidification and (3) fine laminar precipitates are Cr2N-austenite "false pearlite" formed from solid-solid transformations [Rawers and Petty, 1993].
APPENDIX B: SOLIDIFICATION OF WELDMENTS

Solidification behavior of stainless steel weld metal can be classified into four different modes: (1) A – Primary Austenite, (2) AF- Austenite to Ferrite, (3) F – Primary Ferrite, and (4) FA – Ferrite to Austenite as shown in Figure B.1. These modes are dependent upon the general microstructure. Suutala and Moisio [1980] developed a relationship between weld solidification behavior and composition using the following coefficients:

\[ Ni_{eq} = Ni + 0.3Mn + 22C + 14.2N + Cu \]  \hspace{1cm} \text{[B.1]} \\

\[ C_{eq} = Cr + 1.37Mo + 1.5Si + 2Nb + 3Ti \]  \hspace{1cm} \text{[B.2]} \\

\[ F \ mode : 1.95 \leq \frac{C_{eq}}{Ni_{eq}} \]  \hspace{1cm} \text{[B.3]} \\

\[ FA \ mode : 1.48 \leq \frac{C_{eq}}{Ni_{eq}} \leq 1.95 \]  \hspace{1cm} \text{[B.4]} \\

\[ A,AF \ mode : \frac{C_{eq}}{Ni_{eq}} \leq 1.14 \]  \hspace{1cm} \text{[B.5]}
Using the nickel and chromium equivalents from Equations B.1 and B.2, a diagram can be developed that deciphers between the solidification modes for individual alloys as shown in Figure B.2.

During the cooling of primary austenite welds as shown in Figure B.2, some of the eutectic ferrite may transform to austenite (AF-type). During cooling through the austenite-ferrite region, most of the ferrite transforms to austenite, with chromium partitioning to the austenite, thus leaving ferrite only within the cores of the original dendrites. The location of ferrite is different for each solidification mode and its location is dependent upon the equilibrium partition coefficient.

The equilibrium partition coefficient plays an important role during solidification because whether the equilibrium partition coefficient is less than one or greater than one will delineate whether solute is pushed or rejected into the interdendritic region as illustrated in Figure B.3. Schobbert *et al.* [2003] and Okagawa *et al.* [1983] discuss the effects of nitrogen on the primary solidification mode in duplex stainless steel and austenitic stainless steel and the resulting solidified microstructure.

Figure B.4 is a modification of the Schaeffler/DeLong diagram, which is used to assist in the proper selection and use of austenitic filler materials and to predict weld metal microstructures and properties [Olson, 1985]. Olson [1985] summarized all of the models that have been developed to predict the weld solidification microstructure. The effect of the welding heat input must also be taken into account [Olson, 1985]. Coring results from segregation during solidification as observed in weld metal. The non-homogenous distribution of alloying elements associated with segregation reveals a corrugated microstructure. The nature and amount of sequential transformation occurring upon cooling is dependent upon the stability of the regions and the thermal stability. One way of expressing the austenite stability in cored materials such as
weld metal is to assume a sinusoidal distribution function can be applied to each of the segregating elements [Olson, 1985].

Neglecting solid diffusion, the composition in the liquid at the solid/liquid interface has been modeled by Frost et al. [1992] for the non-equilibrium Scheil equation:

\[ C_L = C_0 J_L^{k-1} \]  \hspace{1cm} [B.6]

where \( C_0 \) is the bulk concentration in the weld pool, \( C_L \) is the concentration in the liquid at the interface, and \( k \) is the equilibrium partition coefficient [Flemings, 1970]. The Scheil equation was derived for a binary alloy, but here Frost et al. [1992] used the Scheil equation to approximate a multi-component alloy. The equilibrium partition coefficient is:

\[ k = \frac{C_s}{C_L} \]  \hspace{1cm} [2.8]

where \( C_s \) is the concentration at constant temperature and pressure of the solidus and \( C_L \) is the concentration at the same constant temperature and pressure of the liquidus. The equilibrium partition coefficient can directly be calculated from the Fe-N phase diagram in Figure B.5.

The equilibrium partition coefficient controls the direction and extent of segregation during solidification. Micro-segregation during solidification results in an increase in the concentration of alloying elements and precipitates (carbides, nitrides, and intermetallic phases) and possibly porosity in the interdendritic liquid. From Figure B.5 it can be seen that the natural tendency is for the partition coefficient to be less than one \((k<1)\) where nitrogen gets rejected into the liquid interdendritic region during solidification [Kurz and Fisher, 1986]. Olson
et al. [1990] describes the role of solidification on the metal chemistry and microstructure.

Micro-segregation is normally caused due to insufficient diffusion in the solid state adjacent to the interdendritic liquid. The diffusion coefficient of nitrogen is orders of magnitude above substitutional alloying elements, so that nitrogen is normally not prone to generate segregation [Gavriljuk and Berns, 1999]. However, as the substitutional alloying elements begin to segregate, nitrogen becomes attracted to areas with higher chromium, manganese, and molybdenum contents and the nitrogen is repelled by areas with higher nickel, cobalt, and carbon content, which can be accounted for from the sign of the interaction parameter.

![Figure B.1: Ternary Fe-Cr-Ni diagram at 1173K. The dashed-dotted curve is the Md value, which is critical for the stability of austenite. The dashed line is the electron vacancy concentration, Nv (PhaComp) [Morinaga et al., 1985).](image-url)
Figure B.2: Schematic illustration of solidification models for austenitic-ferritic weld metals [Mudali and Raj, 2004].

Figure B.3: Dendritic solidification showing the effect of solute partitioning when the equilibrium partition coefficient is less than one. The solute is pushed into the interdendritic region or rejected out from the interdendritic region [Olson et al., 1990].
Figure B.4: Solidification mode for a variety of compositions compared on the basis of Creq/Nieq ratio [Brooks and Lippold, 1993].
Figure B.5: Fe-N equilibrium diagram [Brooks and Lippold, 1993].
APPENDIX C: THERMODYNAMICS OF HYDROGEN IN METALS

The solubility and diffusivity of hydrogen differ greatly between iron phases. For example, the solubility of hydrogen in austenite is very large, while very small in ferrite. The diffusivity of hydrogen in austenite is very slow, but much quicker in ferrite. Austenite is a diffusion barrier for hydrogen transport, while ferrite facilitates hydrogen transport. At a given temperature, the solubility of hydrogen in a metal increases with increasing $\text{H}_2$ gas pressure. Table C.1 lists entropy and enthalpy of solutions at low hydrogen concentrations determined by solubility data [Mueller et al., 1968], [Fromm and Gebhardt, 1976]. A much more extensive table is given in Mueller [1968].

To determine the thermodynamic quantities for hydrogen, consider the thermal equilibrium between a solid solution and hydrogen gas (H$_2$) [Fukai, 1993]:

$$M + \frac{1}{2}xH_2 \rightarrow MH_x$$  \hspace{1cm} [C.1]

So that the chemical potential of hydrogen in two-phases is given by the equality:

$$\frac{1}{2} \mu^g = \mu^a$$  \hspace{1cm} [C.2]

where $\mu^g$ is the chemical potential of gaseous hydrogen and $\mu^a$ is the chemical potential of hydrogen in solid solution.
Table C.1: Enthalpy and entropy of solution of low concentration hydrogen in metals [Fukai, 1993].

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H'$ [ev/atom]</th>
<th>$\Delta S'/k$</th>
<th>$T$ [°C]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>-0.54</td>
<td>-7</td>
<td>200-700</td>
<td>Wenzl, 1982</td>
</tr>
<tr>
<td>Mg</td>
<td>0.22</td>
<td>-4</td>
<td>500</td>
<td>Fromm and Gebhardt, 1976,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fromm and Horz, 1980</td>
</tr>
<tr>
<td>Al</td>
<td>0.70</td>
<td>-6</td>
<td>500</td>
<td>Wenzl, 1982</td>
</tr>
<tr>
<td>La</td>
<td>-0.83</td>
<td>-8</td>
<td>-</td>
<td>Fromm and Gebhardt, 1976,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>Fromm and Horz, 1980</td>
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<tr>
<td>V</td>
<td>-0.28</td>
<td>-8</td>
<td>150-500</td>
<td>Fromm and Gebhardt, 1976,</td>
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<td>Fromm and Horz, 1980, Wenzl,</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1982</td>
</tr>
<tr>
<td>Cr</td>
<td>0.60</td>
<td>-5</td>
<td>730-1130</td>
<td>Fromm and Gebhardt, 1976,</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Fromm and Horz, 1980</td>
</tr>
<tr>
<td>Mo</td>
<td>0.54</td>
<td>-5</td>
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<td></td>
<td></td>
<td></td>
<td>Fromm and Horz, 1980</td>
</tr>
<tr>
<td>W</td>
<td>1.1</td>
<td>-5</td>
<td>900-1750</td>
<td>Fromm and Gebhardt, 1976,</td>
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<td>Fromm and Horz, 1980</td>
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<tr>
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<td>-6</td>
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<td>Fromm and Horz, 1980</td>
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<td>(bcc)</td>
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<tr>
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<td>Fromm and Horz, 1980</td>
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<tr>
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<td>Fromm and Horz, 1980</td>
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</table>
From statistical thermodynamics $\mu^g$ is given as [Fukai, 1993]:

$$\mu^g = kT \ln \frac{P}{P_o(T)} - E_D$$  \hspace{1cm} [C.3]

where $E_D$ is the heat of dissociation of a hydrogen molecule, which is 4.74 eV.

$$P_o(T) = \frac{(4\pi MkT)^{3/2} kT (8\pi^2 I, kT)}{h^5}$$  \hspace{1cm} [C.4]

where $M$ is the mass of a hydrogen atom and $I_r$ is the moment of inertia. For this situation, a classical high temperature approximation has been assumed for the rotational motion and thermal excitation of the stretching vibration has been ignored. The enthalpy and entropy of gaseous hydrogen can then be obtained as [Fukai, 1993]:

$$H^g = \frac{7}{2} kT - E_D$$  \hspace{1cm} [C.5]

and:

$$\frac{S^g}{k} = \frac{7}{2} - \ln \frac{P}{P_o(T)}$$  \hspace{1cm} [C.6]

For a solid solution, the Gibb’s free energy of a crystal containing $n$ hydrogen atoms can be expressed as [Fukai, 1993]:

$$G^\alpha = H^\alpha - TS^\alpha$$  \hspace{1cm} [C.7]
where the entropy term consists of a configurational term for distributing n atoms over N interstitial sites and a non-configurational term, which is composed of a vibrational and electronic contribution. The configurational entropy is given as:

\[ S_c = k \ln \frac{N!}{n!(N-n)!} \]  \[ \text{[C.8]} \]

Then including only the configurational term of the entropy into the Gibb’s free energy gives:

\[ G^\alpha = G^{anc} - TS^\alpha \]  \[ \text{[C.9]} \]

The chemical potential of a dissolved hydrogen atom can then be written as [Fukai, 1993]:

\[ \mu^\alpha = \frac{\partial G^\alpha}{\partial n} = \frac{\partial G^{anc}}{\partial n} - T \frac{\partial S^c}{\partial n} \]  \[ \text{[C.10]} \]

Equation 2.16 can then be reduced to:

\[ \mu^\alpha = H^\alpha - TS^{anc} + kT \ln \frac{x}{r-x} \]  \[ \text{[C.11]} \]

where \( H^\alpha \) is the partial enthalpy, \( S^{anc} \) is the non-configurational part of the partial entropy of hydrogen in solid solution, and \( r \) is the number of interstitial sites per metal atom M, \( r = N/N_0 \).

The enthalpy change when one hydrogen atom is dissolved from the gas phase into metal would be:
\[ \Delta H_s = H^\alpha - \frac{1}{2} H^G \]  

\text{[C.12]}

On the other hand, the entropy of the solution is normally defined as:

\[ \Delta S_s = S^{unc} + k \ln r - \frac{1}{2} S^G \]  

\text{[C.13]}

for \( x \) much less than \( r \). These thermodynamic quantities can also be obtained from the pressure and temperature dependence of the solubilities. The temperature dependent solubilities are useful in that at a specific temperature, the enthalpy and entropy of solutions can be determined from the slope and intercept of the Arrhenius plot of the solubility [Fukai, 1993].

An example of an Arrhenius plot of the solubility data of hydrogen and deuterium in palladium is shown in Figure C.1. The enthalpy and entropy are largely temperature dependent as can be seen from the curvature existing at higher temperatures on the Arrhenius plot [Fukai, 1993]. The origin of the temperature dependence of the enthalpy of solution can be explained by differentiating the enthalpy of solution as a function of temperature, which is equivalent to the difference in specific heat per hydrogen atom under constant pressure:

\[ \Delta c_p = \left( \frac{\partial \Delta H_s}{\partial T} \right)_p \]  

\text{[C.14]}

\[ \Delta c_p = c_p^\alpha - \frac{1}{2} c_p^G \]  

\text{[C.15]}

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The specific heat per hydrogen atom in the solid solution is made up of three terms: (1) optic mode vibrations of a hydrogen atom, (2) acoustic mode vibrations, and (3) changes in the electronic specific heat shown in Equation C.16:

\[ c_P^\alpha = c_{op} + \Delta c_{ac} + \Delta c_{el} \]  

[C.16]

where the optical mode vibration of a hydrogen atom is given as:

\[ c_{op} = k \sum_{i=1}^{3} \left( \frac{\theta_{E,i}}{T} \right)^2 \frac{e^{\theta_{E,i}/T}}{e^{\theta_{E,i}/T} - 1} \]  

[C.17]

the acoustic mode vibration is:

\[ \Delta c_{ac} = \frac{\partial c}{\partial \theta_D} \frac{\partial \theta_D}{\partial x} \]  

[C.18]

and the electronic specific heat is:

\[ \Delta c_{el} = \frac{\partial \gamma_e}{\partial x} T \]  

[C.19]

where \( \theta_{E,i} \) is the Einstein temperature for the vibration mode \( i \), \( c \) is the specific heat, \( \theta_D \) is the Debye temperature, and \( \gamma_e \) the coefficient of the electronic specific heat of the host metal. From experimental values of interstitial hydrogen in palladium, it has been found that the major source of the temperature dependence of the enthalpy of solution is mainly due to the optic-mode vibration.
of the hydrogen atom, \( c_{oo} \). The sum of the electronic and acoustic specific heat is close in magnitude to one-half of the specific heat of gas over the interested temperature range, which allows these two terms to be cancelled in terms of their contribution to the heat of solution. Because of these cancellations leaving only the opical-mode vibrations, the temperature dependence of the enthalpy of solution is small, which allows the enthalpy of solution to be approximated to a single value over the whole temperature range [Fukai, 1993].

Figure C.1: Arrhenius plots for hydrogen and deuterium in palladium [Fukai, 1993]. Circles from Clewley et al., [1973], Triangles from Sieverts and Zapf [1935].
APPENDIX D: THERMOELECTRIC PHENOMENA

D.1 Joule Effect

If the thermal electromotive force (emf) is not balanced by an external emf, a current exists, whose value can be changed by adjusting the external emf. If there is no external circuit, all the electrical energy developed by the thermocouple is dissipated into internal energy, which is known as the Joule effect, under the conditions:

\[ \varepsilon I = I^2 R \]  

[D.1]

where \( R \) is the resistance of the thermocouple, \( \varepsilon \) is the electromotive force, and \( I \) is the current [Zemansky, 1957].

D.2 Conduction of Heat

If the junctions of a thermocouple are at temperatures \( T_1 \) and \( T_2 \) (where \( T_1 > T_2 \)) and are broken at one point, the two ends are maintained at some intermediate temperature \( T \) by means of an insulating reservoir. Thermoelectric current or joule effect do not occur, but heat is lost by the reservoir at \( T_1 \) and gained at the reservoir by \( T_2 \) resulting in zero net gain or loss to the reservoir \( T \). The conducted heat can be measured at various values of the temperature difference \( T_1 - T_2 \). The wires are assumed to be suitably lagged, so that there is no appreciable lateral transfer of heat across the wire surface.
D.3 Peltier Effect

For the Peltier effect, a thermocouple with junctions are held at the same temperature. If a current is produced (an outside battery) in the thermocouple, the temperatures of the junctions are changed by an amount not entirely due to the Joule effect, but also due to the Peltier effect. Taking into account the Joule effect, the heat that is either supplied or removed to restore a junction to its initial temperature is the Peltier heat. The Peltier effect occurs whether the current is provided by an outside source or is generated by the thermocouple itself. The Peltier effect is defined as the change in heat content when one coulomb of electricity crosses a junction of two dissimilar conductors. Peltier heating must be distinguished from the irreversible (Joule) heating which occurs in all conductors, excluding semi-conductors, when an electric current flows through them. Joule heating is directly related to the electrical resistivity of the substance and is entirely an irreversible effect, which depends only on the square of the current density. The Peltier heat ($P_{12}$) is directly proportional to magnitude of current flow. From experiments it has been shown that [Zemansky, 1957]:

(a) The rate at which the Peltier heat is transferred is proportional to the first power of the current.

(b) The Peltier heat is reversible. When the direction of the current is reversed, the magnitude remaining the same, the Peltier heat remains the same, but in the opposite direction

(c) The Peltier coefficient is dependent upon the temperature and the material of the junction and is independent of the temperature of the other junction.
D.4 Thomson Effect

Thomson was able to show that heat is liberated or absorbed within a single conductor when an electric current flows in the same or opposite to the direction of the heat flow carrying no current. If a current exists, the temperature distribution is altered by an amount that is not entirely due to the Joule effect. The additional change in the temperature distribution is due to the Thompson effect. Allowing for the Joule effect, the heat that must be supplied or removed at all places along the wires to restore the initial temperature distribution is the Thomson heat. From experimental observations it has been found that:

(a) The rate at which Thomson heat is transferred into a small region of a wire carrying a current, I, and supporting a temperature gradient, dT, is equivalent to the product of the Thomson coefficient, the current, and the temperature gradient.

(b) Thomson heat is reversible

The Thomson coefficient is dependent upon the material of the wire and the mean temperature of the small region under consideration.
APPENDIX E: TECHNIQUES TO ELIMINATE VARIABLES FOR INTERSTITIAL CONTENT DETERMINATION

Because of the variables associated with linepipe steel such as microstructure, inclusions, temperature, etc., it is necessary to use multiple non-destructive, non-contact techniques to eliminate these variables. Magnetic Barkhausen Noise is a technique that could be utilized to characterize microstructure and the use of electromagnetic acoustic transducers for temperature characterization can also be utilized for temperature corrections as described below.

E.1 Magnetic Barkhausen Noise Analysis

Magnetic barkhausen noise (MBN) is applicable to ferromagnetic metals and alloys and is dependent on the Barkhausen effect, which takes place when a magnetic field is swept in a ferromagnetic specimen along a hysteresis loop. Two types of high frequency signals are generated: (1) the Magnetic Barkhausen Noise (MBN) due to irreversible changes in magnetic moments during the hysteresis and (2) Magnetomechanical acoustic emission (MAE) due to elastic deformations associated with magnetic domain activities during irreversible changes in magnetization. MBN signals are acquired by a sensor coil, while an MAE signal is acquired through a piezoelectric transducer. Both MBN and MAE are sensitive to microstructure and stress conditions [Raj et al., 2000].
At temperatures below the Curie temperature, the magnetic moments of different atoms are parallel within a certain restricted area called a magnetic domain. In the de-magnetic state, the domains of the structure are arranged in such a way that the sum of the magnetic moments, the net magnetization, is zero. In single crystals and poly-crystals the arrangement of domains are different as shown in Chapter 3 in Figures 3.15 and 3.16.

The domain wall is the transition region between two domains. The domain walls move due to applied external magnetic field. In an ideal case, the domain wall movement can be quite continuous, while in the case of a single crystal or polycrystal, the movement of the domain walls can be discontinuous. Lattice discontinuities such as grain boundaries, precipitates, etc. tend to hinder the motion of the domain walls. With increasing magnetic field strength, local segments of domain walls abruptly break free from the pinning sites and move forward until they encounter the next pinning site. The abrupt microscopic changes in flux due to discontinuous wall motion are referred to as the Barkhausen effect. As a result, the hysteresis loop is not smooth and continuous, but discontinuous as shown in the magnified onset of Figure E.1 (a). The local and abrupt changes in magnetic flux within the material also gives rise to a spectrum of voltage pulses of varying heights. A typical Barkhausen spectrum for an ultra-low carbon steel sample for one complete hysteresis loop is shown as a function of time in Figure E.1 (b) [Chopra et al., 2001].

Qiang et al., [2000] performed a theoretical analysis on magnetic Barkhausen pulses due to determine the differences in Barkhausen noise as a function of microstructure. Barkhausen noise is produced when a 180° domain wall has suddenly departed from a pinning site, such as an inclusion or is nearing another pinning site.
Figure E.1: (a) The hysteresis loop of a ferromagnetic material, when magnified, shows that the magnetization increases are abrupt due to the Barkhausen jumps. (b) A typical Barkhausen spectrum for one complete hysteresis loop plotted as a function of time. [Chopra et al., 2001].

When the outer magnetic field strength reaches a critical value i.e. the strength of the domain wall can be departed from the pinning site and will arrive at the next pinning site without resistance [Qiang et al., 2000]. When the domain wall departs from one pinning site to the next, the displacement of the domain wall, L, is the mean free distance of the domain wall. When the domain wall moves from one pinning site to the next a Gauss pulse is created and the Barkhausen jump appears during a time duration, $t_0$, which is $t_0 = L/V$, where $v$ is the mean speed of the domain wall movement. The mean speed, $V$, of the domain wall is proportional to the outer magnetic field strength:

$$V = C_v H_p$$  \[E.1\]
Where \( C_v \) is a constant of proportionality and \( H_p \) is the minimum strength of the outer magnetic field to unpin the domain wall from the pinning site to produce non-reversible motion.

Because pinning sites are variable, the distribution density is also a variable. The space of a pinning site is identical to the displacement of the domain wall, \( D \), so that the time duration of a Gauss pulse, \( t_s \), is:

\[
 t_s = \frac{D}{C_v H_p} = \left( \frac{\pi}{6} \right)^{1/3} \frac{\mu_o I_s}{C_v H_p} \beta^{-1/3} W^2
\]

where \( \mu_o \) is the initial permeability, \( I_s \) is the saturated magnetization strength, \( \beta \) is the largest strength of the outer magnetic field, and \( W \) is the weight ratio from one pinning site to the next [Qiang et al., 2000]. When the magnetization period of the outer magnetic field is held at a constant value, then time for producing a Barkhausen noise is also a fixed value, i.e. \( t_{\text{total}} = \) constant. The total number of Barkhausen jumps in the magnetization process is equal to the total number of pinning sites being swept by the domain walls. The output signal from the electromagnetic instrument is the magnetization period, M.P., which is important because it is proportional to the displacement of the domain wall motion, \( L \) given as:

\[
 M.P. = C_d D
\]

where \( C_d \) is a ratio coefficient. The magnetization period can be related to changes in microstructure as shown in Figure E.2.
Figure E.2: Magnetization parameter as a function of tempering temperature for super-saturated ferritic iron measuring the changes in carbide formation [Qiang et al., 2000].

Magnetic Barkhausen noise is most often used for detection of microstructural changes such as carburized case depth, pearlite lamellar spacing, and texture. In this investigation, MBN will be used to classify the steel being measured as having specific combinations of chemical composition and microstructural features. Since each still will have its own impedance signature it is important to classify these features to use for a specific set of standards in order that the hydrogen signal can be assessed without interference. Also magnetic Barkhausen noise can be utilized for testing of surface defects that may involve changes in both stress and microstructure [Chopra et al., 2001]. Eddy currents are used to perturb the material and the electromagnetic acoustic transducers
measure the magnetic Barkhausen noise. For each different linepipe steel there is a specific microstructure and a specific source of acoustic emission at which the pinning of the magnetic domains will be released [Blitz, 1991]. A frequency sweep will be performed on every microstructure to determine at which specific frequency is there a source of acoustic emission. Each material should likely have its own particular frequency for acoustic emission, which will be used to classify each microstructure. MBN has been used in the industry and by researchers for classification and characterization of microstructures [Pumarega et al., 2005], [Qiang et al., 2000], [BRITE EURAM, 2006].

E.2 EMAT (Electromagnetic Acoustic Transducers) Analysis

Electromagnetic acoustic transducers are used for a means of temperature correction for the hydrogen measurements. EMAT’s are however among many other techniques such as optical sensors that can be used for temperature measurements. EMAT’s are devices that essentially consist of a stack of wires and magnets to excite and detect ultrasonic waves in electrically conductive material (magnetic or non-magnetic). When the EMAT transmitter is placed near an electrically conducting specimen, ultrasonic waves are launched into the material through the reaction of induced eddy currents and static magnetic fields. EMAT’s allow examination of properties without contact at elevated temperatures and in remote locations. EMAT’s can also generate and detect ultrasound through coated materials.

EMAT’s can be used to assess the temperature of the steel in the line pipe being assessed. The use of EMAT produces an elastic wave pulse, which can travel through the steel. Its velocity can be determined by pulse echo or
transducer to transducer measurements. The speed of sound depends upon the type of medium and its state given as:

\[ V_s = \frac{\sqrt{E}}{\sqrt[3]{\rho}} = f(T) \quad [E.4] \]

where \( V_s \) is the speed of sound, \( E \) is the elastic modulus, \( \rho \) is the density, and \( T \) is temperature.

Each specific temperature will have it's own unique speed of sound. The elastic modulus and density are both a function of temperature, thus the speed of sound accounts for variations in the pipeline temperature. If the affect of temperature in the pipeline is not accounted for, the eddy current analysis for hydrogen content could be erroneous.
APPENDIX F: UNCERTAINTY ASSOCIATED WITH THERMOELECTRIC POWER MEASUREMENTS

The thermoelectric power coefficient is given as:

\[ Z = \frac{\Delta V}{\Delta T} \]  \[\text{[F.1]}\]

The uncertainty associated with the thermoelectric power coefficient, \( \Lambda_Z \), can be calculated using:

\[ \Lambda_Z = \left[ \left( \frac{\partial Z}{\partial \Delta T} \right) \Lambda_T \right]^2 + \left[ \left( \frac{\partial Z}{\partial \Delta V} \right) \Lambda_V \right]^2 \]^{1/2}  \[\text{[F.2]}\]

where \( \Lambda_T \) and \( \Lambda_V \) are the uncertainty in the temperature measurement (2.2 °C) and the nano-voltmeter (10 nV). The voltage and temperature measurements are taken from plasma-welded Seebeck coefficient data. Taking the partial differential of the Seebeck coefficient with respect to temperature and voltage gives:

\[ \left( \frac{\partial Z}{\partial \Delta T} \right) = \frac{-\Delta V}{\Delta T^2} = \frac{-0.066}{18.274^2} = -0.198 \times 10^{-3} \]  \[\text{[F.3]}\]

\[ \left( \frac{\partial Z}{\partial \Delta V} \right) = \frac{1}{\Delta T} = \frac{1}{18.274} = 0.055 \]  \[\text{[F.4]}\]

Plugging Equation F.3 and F.4 into Equation F.1 gives the uncertainty associated with the Seebeck coefficient as:
\[ \Lambda_Z = \left[ \left( -0.198 \times 10^{-3} \right)^2 + 0.055(0.1)^2 \right]^{1/2} = 7.01 \times 10^{-4} \, \mu V/\circ C \] 

[\text{F.5}]

So taking into account uncertainty, the Seebeck coefficient becomes:

\[ Z = 5.63 \pm 7.01 \times 10^{-4} \, \mu V/\circ C \] 

[\text{F.6}]