The Post Weld Heat Treatment Response in the Heat Affected Zone of

2.25Cr-1Mo Steel

THESIS

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By

David K. Hodgson
Graduate Program in Welding Engineering
The Ohio State University
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Master’s Thesis Committee:
Professor John Lippold – Advisor
Professor Sudarsanam Babu
Abstract

F22 (2.25Cr-1Mo) steel is used in a variety of applications in the oil and gas industry. One of the primary uses is for subsea well equipment where exposure to elevated temperatures and sour service conditions is common. In order to be acceptable for sour service conditions, the National Association of Corrosion Engineers (NACE MR0175) stipulates maximum permissible hardness of 22 HRC (250 VHN). In welded components made of steel such as F22, this is particularly problematic due to the formation of hard martensite in the heat affected zone (HAZ). To meet these requirements a post weld heat treatment (PWHT) is used. In practice, it has been observed that materials with similar compositions and similar welding parameters will temper differently during PWHT.

To investigate the cause of this discrepancy, 16 heats of different composition within the specification limits for F22 were investigated. As a basis of comparison, each heat was subjected to an austenization treatment followed by a water quench with the goal of producing a fully hardened martensitic microstructure. When comparing the hardness of these samples with previous research it was found that the heats with higher carbon content were softer than expected. Upon further investigation with optical microscopy, it was found that second phase particles (which are presumed to be alloy carbides) are still
present in the microstructure. The presence of these carbides (along with observed autotempering) occupies carbon and contributes to a softer microstructure than as predicted from the carbon content alone.

To study the temper response, autogenous spot welds were made using parameters designed to replicate the HAZ observed in a typical weld used for cladding with a corrosion resistant layer. After welding, the welds were tempered for a range of Hollomon-Jaffe parameters which was inclusive of the post weld heat treatment (PWHT) used in practice. The average hardness in the HAZ was used to calculate the average tempering rates for each heat.

In the as-welded condition, two heats of the same composition displayed radically different behavior in the HAZ, with one being hardest in the coarse grained heat affected zone (CGHAZ) and the other being hardest in the fine grained heat affected zone (FGHAZ). In examination of these regions using scanning electron microscopy, there was a qualitative difference in the size and distribution of precipitates, but resolution using this technique was not sufficient to fully characterize the microstructure. Upon tempering, several different heats exhibited secondary hardening behavior as a result of specific heat treatments. When compared to the HAZ, the tempering response in the fusion zone typically displayed similar tempering response with the exception of the overall hardness being higher and the secondary hardening reactions were greater in the fusion zone.
To explore the impact of the welding thermal cycle on the variety of carbides found to be present in F22, thermodynamic and kinetic simulations were conducted for the temperature range found throughout the HAZ. These simulations indicated that for carbides of identical size, those typically found later in the precipitation sequence were more stable and dissolved slower.
To my wife Rachel,

your love and support provide constant encouragement to be my best
Acknowledgments

I would like to thank my advisor, Dr. John Lippold for providing a tremendous resource in both technical knowledge and professional guidance throughout the research and graduate school process.

I’d also like to thank Dr. Suresh Babu for participating on my examination committee, providing assistance in learning and troubleshooting simulation tools as well as providing a great foundation and introduction for my continued learning of steel metallurgy. Additionally, his efforts as Director of the National Science Foundation supported Center for Integrated Materials Joining for Energy Applications (CIMJSEA) allowed for a great opportunity to interact with industry members. Also, thanks to all of the other faculty and members of the welding engineering department at the Ohio State University for providing a great environment to learn.

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Vita

August 1984 .............................................. Born - Cleveland, Ohio

December 2006 ........................................ B.S. Mechanical Engineering, University of Toledo, Toledo, Ohio

March 2011 to Present ................................ Welding and Joining Metallurgy Research Group, The Ohio State University, Columbus, Ohio

Fields of Study

Major Field: Welding Engineering

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CHAPTER 1: INTRODUCTION

Grade 22 is a class of chromium (Cr) and molybdenum (Mo) alloyed heat resisting low alloy steels that is often used in the forged condition (F22) for subsea oil well components and in other grades (T22) in boiler tube applications [1]. The Cr and Mo alloying additions provide good creep strength as well as good oxidation resistance. The composition and heat treatment parameters are controlled by the American Society for Testing Materials specification A182 and are shown in Table 1.1. In some cases in order to increase the strength, the limit for the carbon content is increased to 0.20 weight percent.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>F22 Composition</td>
<td>0.05-0.15</td>
<td>0.30-0.60</td>
<td>0.04</td>
<td>0.04</td>
<td>0.5</td>
<td>2.00-2.50</td>
<td>0.87-1.13</td>
</tr>
</tbody>
</table>

Table 1.1 – Compositional Limits for F22 as Stipulated by ASTM A187 with single values representing maximums
A critical element of subsea applications is the exposure to hydrogen sulfide (H₂S) which is present in these wells. Exposure to H₂S can be lead to failure by a stress corrosion cracking failure mechanism called sulfide stress corrosion cracking (SSCC). H₂S does not directly cause SSC failures, but rather contributes by increasing the relative amount of hydrogen absorption in low alloy steels [2]. Often, a corrosion resistant clad layer is deposited via a welded overlay process which decreases the effect of the corrosive environment, however the heat affected zone of the weld is still vulnerable. Since the failure is a result of hydrogen embrittlement, material hardness plays a critical factor in susceptibility to failure [3]. Figure 1.1 shows the correlation between increasing yield strength and lower threshold concentration of H₂S for SSC. Because of this, the National Society of Corrosion Engineers (NACE) and the International Standards Organization (ISO) require that the maximum as tempered hardness of the steel not exceed 22 HRC or 250 VHN through standard NACE MR0175/ISO15156. In application, a difference in as tempered hardness has been observed in compositionally similar heats.
This was verified by unpublished research conducted in October of 2010 by Lippold and Fusner which indicated that two very similar heats yielded different as tempered hardness and tempering rates when exposed to the same austenization and tempering heat treatment [4]. The composition of these two heats, L7976 and 4891AH8, is shown in Table 1.2.
<table>
<thead>
<tr>
<th>Element</th>
<th>Heat No.</th>
<th>4891AH8</th>
<th>L7976</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.167</td>
<td>0.161</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.42</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.011</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.011</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.24</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.19</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1.01</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>2.22</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.079</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.005</td>
<td>0.023</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.015</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.011</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.0001</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.0001</td>
<td>0.0048</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.0021</td>
<td>0.0051</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.017</td>
<td>0.017</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2 – Composition of Initially Studied F22 Heats

The base metal of these two heats was subjected to solution austenitizing treatment of 954°C for one hour; water quenched and subsequently tempered using six different treatments. Throughout the tempering treatments, the two heats demonstrated a significant difference in both as tempered hardness and tempering rate. Results are summarized in Figure 1.2.
When additional solution austenization treatments of 1121°C for 1 hour and 1148°C followed by a water quench was conducted, the macrohardness in the as-quenched condition of the two heats began to converge, suggesting that there was an undissolved alloy carbide preventing carbon from being available to produce the maximum as quenched hardness.

Figure 1.2 – Tempered Hardness of F22 Heats
In order to further investigate this behavior, the study was expanded to include 15 additional heats plus one (L7976) included in the initial investigation. These heats contained examples from the range of compositions allowed by ASTM A182 as well as some examples of a “high performance” grade with a carbon content between 0.15 and 0.20 weight percent and contained forgings ranging from a approximately 5 to 240 pounds in various shapes. To account for these variations, material is specified by the end user to conform not only to chemical composition requirements but also several mechanical property limits, which are shown in Table 1.4.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>4891AH8 (HRC)</th>
<th>L7976 (HRC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>954°C-1 Hour</td>
<td>46.3</td>
<td>42.3</td>
</tr>
<tr>
<td>1121°C-1 Hour</td>
<td>44.6</td>
<td>43.2</td>
</tr>
<tr>
<td>1148°C-4 Hour</td>
<td>44.8</td>
<td>44.8</td>
</tr>
</tbody>
</table>

Table 1.3 – As-Quenched Hardness after Solution Austenization Heat Treatments
<table>
<thead>
<tr>
<th>Minimum Tensile Strength</th>
<th>95,000 PSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Yield Strength, 2% Offset</td>
<td>75,000 PSI</td>
</tr>
<tr>
<td>Minimum Elongation</td>
<td>18%</td>
</tr>
<tr>
<td>Reduction of Area</td>
<td>35%</td>
</tr>
<tr>
<td>Hardness</td>
<td>197-237HB</td>
</tr>
</tbody>
</table>

Table 1.4 – Mechanical Property Requirements for F22

To understand the underlying cause of the variation in tempering and solution austenization treatments, several approaches were taken. Base material samples were used for three different austenization treatments with the goal of achieving a homogeneous solutionized microstructure as indicated by the macrohardness in the as-quenched condition. To understand the response of the heat affected zone to welding conditions, autogenous gas tungsten arc spot welds were produced and tempered through a range of tempering conditions as characterized by Hollomon-Jaffe parameters. The response of these samples was characterized by microhardness readings of the fusion zone and heat affected zone of each sample.
Both the austenitized base material and spot welded samples were further characterized using light optical and scanning electron microscopy. Additionally, thermodynamic and diffusion simulation software were used to predict the stability of microstructural features during welding conditions.
CHAPTER 2: BACKGROUND

2.1 Heat Treatment in 2.25Cr-1Mo Steels

ASTM covers F22 under the “Standard Specification for Forged or Rolled Alloy and Stainless Steel Pipe Flanges, Forged Fittings and Valves and Parts for High-Temperature Service” under its specification A182 [5]. This specifies that F22 can be supplied in the annealed or normalized and tempered condition after a solutionizing treatment at 900°C. The annealing treatment stipulates a furnace cooling from solutionizing temperature for the annealed condition and air cooled for the normalized condition. The normalized condition then undergoes a tempering treatment at 675°C minimum. If additional strength is required, F22 can be specified in the quenched and tempered condition, which is subject to the same tempering requirements as the normalized and tempered condition [5].

2.1.1 Processing of F22

Forging

Forging is a process which uses mechanical deformation to produce a near net shape product and can be conducted throughout a range of temperatures. Typically, the forging temperature of steels is selected based on the carbon content and the maximum recommended temperature for an alloy steel containing 0.2 wt% carbon is 1275°C [6].
Based on the equilibrium iron-carbon phase diagram (Figure 2.1), this is in the austenite phase field. This is beneficial because the austenite phase is easier to deform than the ferrite phase. However, high forging temperatures can result in coarsening of the austenite grains. The deformation induced by forging can help refine the grains by the recrystallization process, but because of the inhomogeneous nature of the deformation, the austenite grain size can vary within the material [7].

Figure 2.1 – Iron-Carbon Equilibrium Phase Diagram with Typical Processing Temperatures [7]
**Normalized and Tempered Condition**

The normalizing treatment (Figure 2.2) is conducted after forging in order to create a uniform, refined structure. The steel is heated to slightly above the $A_3$ temperature into the fully austenitic region, but below the temperature in which grain coarsening occurs. This results in the nucleation of fine austenite grains, as well as dissolution of carbides that may have formed during cooling from forging. After a soak time at normalization temperature, the steel is allowed to air cool, which in 2.25Cr-1Mo steel typically results in a mixture of allotriomorphic ferrite, bainite and martensite [8]. In order to reach specific properties, a tempering process is then conducted.

![Continuous Cooling Diagram](image)

Figure 2.2 – Normalizing Treatment on a Continuous Cooling Diagram [7]
**Quenched and Tempered Condition**

An alternative (or additional) processing step is to perform a water quench after an austenitizing treatment. The austenization treatment time and temperature is selected for a similar purpose as the normalizing treatment, to prevent significant austenite grain growth as well as dissolve carbides that are present from previous processing. In 2.25Cr-1Mo a temperature of 1000-1050°C is has been found to be sufficient to fully dissolve these carbides [9,10]. The faster cooling rate provided by the quenching process then produces a nearly fully martensitic microstructure which can be tempered to produce the desired properties.

**2.2 Hardenability**

When cooling from the austenite phase field, the transformation to martensite can occur, termed hardenability [11]. Continuous cooling transformation (CCT) diagrams can be a useful tool to account for phase transformations during continuous cooling from above the A₃ temperature to room temperature and gauge the impact of the hardenability of alloy and cooling rate on the final microstructure.
In steels, the highest possible hardness of a particular alloy composition results when the microstructure is 100% martensitic [13]. Alloys which have higher hardenability therefore, can typically reach a fully martensitic microstructure under slower cooling conditions. Additionally, under paraequilibrium conditions and slightly slower cooling rates, there is also a hardening effect from the formation of bainite but this phase has a lower hardness than martensite.
2.2.1 Effect of Alloying Additions On Hardenability

Grange studied the impact of individual of elements on the hardenability of a pure Fe-C steel by determining the maximum diameter which could be hardened to contain a 90% martensitic structure as a result of brine quenching [14]. He found that the most potent element for increasing the hardenability was carbon. He also found that all other alloying elements tested, Mo, Cr, Si, Mn, Cu, Ni in a 0.2 wt% C steel, all contributed to increasing hardenability to varying degrees with results summarized in Figure 2.4.

![Figure 2.4](image-url)
Previously, Grossman had concluded that these effects were multiplicative [15]. During investigation of high carbon steels, Jatczak noted that Mo had the highest impact on hardenability (besides C) regardless of carbon content, but that austenitizing treatment conditions had a large impact on the effect due to Mo being a strong carbide forming element, which if tied up in a carbide, would not be as effective [16]. Similarly, austenitizing treatment conditions affected the hardenability effect of Cr, which had a relatively weaker overall impact when compared to Mo. In studying low carbon steels, deRetana and Doane noted that the effect of both Cr and Mo were reduced with lower carbon contents at lower alloy contents [17]. However, above 1.1 wt% of Cr the effect was much greater in the low carbon steels than in the higher carbon steels tested by Jatczak.
In order to apply the effect of complex composition on the hardenability of welds, carbon equivalent equations are often used [18]. Two of the more commonly used formulas are the International Institute of Welding Carbon Equivalent (\(CE_{IIW}\)) for alloys with carbon contents above 0.18 wt% and the Ito-Besseyo (\(P_{cm}\)) formula for carbon contents below 0.18 wt%. The \(P_{cm}\) has smaller coefficients for the effects of substitutional alloying elements because the transformation kinetics are more affected by the carbon than the substitutional elements in low carbon steels [18,19].
\[ CE_{IW} = C + \frac{Mn + Si}{6} + \frac{Mo + Cr + V}{5} + \frac{Ni + Cu}{15} \]

Equation 2.1 – International Institute of Welding Carbon Equivalency Formula

\[ P_{CM} = C + \frac{Si}{30} + \frac{Mn + Cr + Cu}{20} + \frac{Ni}{60} + \frac{Mo}{15} + \frac{V}{10} + 5B \]

Equation 2.2 – Ito-Besseyo Carbon Equivalency Formula

**2.2.2 Effect of Prior Austenite Grain Size**

In addition to affecting carbide dissolution, austenitizing treatments also have an impact on hardenability by changing the austenite grain size. Because ferrite nucleates first on austenite grain boundaries, increasing the size of the grains reduces the area available for nucleation sites. This slows the transformation to ferrite and increases hardenability [18]. This results in higher hardenability in materials with larger austenite grains.

Additionally, the temperature at which the martensitic transformation starts \((M_s)\) has also been shown to increase as the austenite grain size is increased [20]. This acts to increase hardenability by reducing the cooling time required to reach the \(M_s\) temperature. This effect is illustrated in Figure 2.6, which shows the change in hardenability multiplication factors for a range of carbon content, based on grain size.
2.3 Martensite

2.3.1 Strengthening Mechanisms in Martensite

The strength of martensitic steel alloys is a product of several different mechanisms. Morito et al. summarize these mechanisms in Equation 2.3 [21]. These factors are the lattice friction from pure iron ($\sigma_0$), the precipitation strengthening ($\sigma_P$), the solid solution strengthening ($\sigma_s$), the hardening from dislocation interactions within the lath structure ($\sigma_p$) and the grain boundary strengthening effect ($K_{HP}d^{-1/2}$).
\[ \sigma_y = \sigma_0 + \sigma_p + \sigma_s + \sigma_{\rho} + k_{\mu P} d^{-1/2} \]

Equation 2.3 – Contributions to the Strength of Martensite [21]

Precipitation Strengthening

An element of strengthening can be achieved by a refined dispersion of precipitates. These second phase particles increase the strength of a material by forcing dislocations to either loop around or cut through the particle to continue moving [22]. Each of these options can lead to different behavior. In a material with a specific volume fraction of precipitates, a dispersion of small precipitates which are coherent with the matrix favor the cutting mechanism because the spacing between the particles is too small to favor the increase of dislocation line length required to loop around the precipitate. As the dislocation moves through the particle, the effective area of the particle on the slip plane is reduced. This provides less resistance to the next dislocation attempting to move past the particle and leads to a material that will work soften [22]. As the particles coarsen and the spacing between them becomes greater, it becomes easier for the dislocation to bend around the particle and form a loop as it passes. When the next dislocation approaches, it encounters the remaining loop which has a like sign. The repellent force from these like signs makes it more difficult for the dislocation to form another loop which leads to a work hardening behavior [22]. Though precipitates contribute to the mechanical properties of low alloy steels, those produced during the tempering process
most often act to reduce the overall strength and hardness by reducing the amount of available carbon to provide a solid solution strengthening effect [18].

**Solid Solution Strengthening**

Solid solution strengthening effects come from both interstitial and substitutional elements. The main interstitial effect in steel alloys comes from carbon which, when occupying interstitial sites becomes an impediment to dislocation motion. Because the presence of interstitial carbon causes an expansion of the lattice, carbon atoms are drawn to the expanded areas in an edge dislocation, which provides a pinning effect [23]. Additionally, carbon provides an added component of strengthening when present in as quenched martensite. Traditionally, martensite is thought of as having a body centered tetragonal structure (BCT) caused by the distortion of a carbon atom trapped in an interstitial location of a face center cubic (FCC) structure of austenite and the body centered cubic structure (BCC) of ferrite [24]. Because this distortion is asymmetrical, it can also allow for interactions with screw type dislocations [23]. Also, there is a component of solid solution strengthening resulting from substitutional alloying elements such as chromium, molybdenum and manganese. These elements act to strengthen the material by causing a strain in the crystal structure due to differing atomic diameters, which provides an impediment to dislocation motion [23].
Lath Boundary Strengthening

Another contribution to the strength of martensite is a result of its lath structure. There is a well known relation, the Hall-Petch relation, between grain size and material strength as a result of grain size, with smaller grains leading to higher strength [25,26]. This is the result of the restriction of dislocation motion by the grain boundaries. Martensitic microstructures can further be classified into two different morphologies, plate or lath. Plate microstructures are found in Fe-C alloys with carbon contents above 0.6 wt%, while lath microstructures are found in lower carbon alloys [27]. The lath structure is comprised of parallel long sheaths which contain a tangled network of dislocations. During transformation from austenite a complex structure incorporating several different crystallographic orientations forms. Each prior austenite grain can contain several differently orientated packets. These packets form with a relation to the crystallography of the austenite, known as the Kurdjumov-Sachs (K-S) orientation relationship, in 24 different variants [28]. Each of these packets is broken down into blocks which are groups of single crystal laths that share a crystallographic variant. These different blocks can therefore be separated by low or high angle boundaries dependant on the individual variant, with the small angle boundaries forming sub blocks [27,29]. A reduction in the length of the lath structure or the packet diameter results in an increase in yield strength and impact toughness resulting from a Hall-Petch relation [30,31]. Morito et. Al. determined that there was little effect on the block structure from the prior austenite grain size but the overall packet size had a scalar relation to the increase of the prior austenite grain size [21].
2.3.2 As Quenched Hardness

Several researchers have investigated the dependence of the hardness of as quenched martensite on carbon content, shown in Figure 2.8.
In the carbon contents up to approximately 0.5 wt%, there is a fairly linear dependence of hardness. In the higher carbon contents there is a diminishing effect of increased carbon contents. This is attributed to an increase in retained austenite as a result of the austenite
stabilizing effect of carbon which reduces the temperature at which the martensite transformation occurs [32]. Many experimenters, such as Hollomon and Jaffe, quenched samples to well below room temperature in order to achieve a complete transformation [33]. The lower hardness of austenite is a result of larger octahedral interstitial sites in the FCC crystal structure compared to BCC, which increases the solubility of carbon in the austenite phase while reducing the lattice strain [18]. Because the solubility is higher, carbon can partition to retained austenite even during the displacive martensitic transformation, resulting in the possibility of retained austenite having a higher concentration of carbon than the average alloy content [34].

Although martensite is typically characterized as BCT, evidence has been found that indicates that BCT structure is less common in low carbon martensites. Speich calculated that nearly 90% of the carbon present in Fe-C alloys below 0.2 wt% C was located in lattice defects like dislocations and lath boundaries during the quenching process [35]. In X-ray diffraction studies by Hutchinson et al., this was confirmed by showing that only 0.02 wt% C was contained in solid solution [36]. They hypothesized that even though the majority of carbon was segregated to lath boundaries and dislocations, it still acted to restrict the movement of mobile boundaries as if it were in solid solution providing the high hardness of the as quenched martensite.

It is worth noting that even in lower carbon content steels, there is still some fraction of retained austenite, as shown in Figure 2.9, which is a transmission electron microscope (TEM) micrograph showing linear retained austenite in a lath martensitic microstructure.
in 4130 steel. The lath boundaries are a common location for retained austenite, due to the segregation of carbon to these areas.

2.3.3 Autotempering

The migration of carbon during cooling can also play a significant role in the hardness of the as-quenched microstructure because of a phenomenon called autotempering. Speich found that even if the cooling rate during the quenching process is fast enough to result in martensite formation, it is not fast enough to suppress diffusion of carbon to lath
boundaries and dislocations [35]. Previously Aborn showed that even during fast quenching in an ice brine bath, samples of AISI 1013 steel showed formation of cementite plates near the center of the sample [37]. While these features were present in the center, the higher cooling rate on the surface of the samples prevented carbide formation in these areas. This demonstrates that in all but the most extreme cooling conditions, some autotempering will occur. Ruhl and Cohen investigated the carbides present in splat cooled samples of various compositions and found that they contained carbides with a stoichiometry of Fe$_{2.4}$C, ε carbide [38]. The addition of silicon as a third element significantly increased the formation of ε and the carbon content of retained austenite even during the extremely high quench rates associated with splat cooling. Because both cementite and ε carbides reduce the carbon available for solid solution strengthening, the resulting martensite will be softer than expected in the as quenched condition.

### 2.4 Tempering

Because the hardness and strength of as quenched martensite is high, it is often desirable to perform further heat treatment to regain ductility. This is true especially in the HAZ of a weld where the thermal cycle has produced an area of significantly higher hardness than the surrounding base material. By applying a tempering treatment, the elevated temperatures allow for the diffusion of substitutional and interstitial elements to form particles such as carbides and nitrides which typically results in a softer microstructure [18].
2.4.1 Time-Tempering Relations

Because the nucleation and growth of second phase particles involves both diffusional and a driving force components, both the time and temperature at which the tempering is conducted is important in determining the resulting microstructure. In order to combine these elements into one factor, Hollomon and Jaffe studied plain carbon steels in a range of carbon contents [33]. The result was Equation 2.4, used to calculate the Hollomon-Jaffe Parameter (HJP), where $T$ is the tempering temperature (Kelvin), $t$ is the tempering time (hours) and $C$ is a constant based on the steel alloy.

$$HJP = T \times (C + \log(t))$$

Equation 2.4 – Hollomon-Jaffe Time-Temperature Tempering Parameter [33]

With this relation, they determined that the hardness (HRC) decreased linearly with increasing HJP. According to their results they determined that as long as the HJP was the same, the hardness resulting from a higher temperature, short time heat treatment would be the same as that from a lower temperature, longer time tempering. The constant $(C)$ was found to decrease relatively linearly with increasing carbon content and recommended a value of 19.5-20 for regular carbon and alloy steels. Through comparison with literature existing at the time, they determined this relationship to be valid independent of the starting microstructural constituents or secondary hardening.
effects for compositions from 0.31-1.15 wt% C, 0-5 wt% Mo and up to 5 wt% Cr. The valid tempering conditions ranged from 100°C to 710°C for times from 6 seconds to 1000 hours.

2.4.2 Plain Carbon Steels

In the early stages of tempering, the elevated temperature allows for further diffusion of carbon and depending on the temperature, different microstructures can result [35]. If the temperature is below 150°C for plain carbon steels containing less than 0.2 wt% C, the carbon further segregates to dislocations and lathe boundaries, but there is no carbide precipitation. In this temperature range, Cheng et al. reported the precipitation of transition carbides (ε/η) but this was observed in 1.13 wt% C plate type martensite and it does not occur with carbon which has segregated to lattice defects [39,40]. Therefore, plain carbon steels containing 0.2 wt% C will not contain transition carbides. At 250°C and above, there is sufficient driving force for the nucleation of Fe₃C precipitates, with the morphology being dependant on the temperature range. At 250°C the Fe₃C is rod shaped while at 400°C the rod shaped carbides dissolve and spheroid precipitates replace them [35]. In this temperature regime, Cheng noted that retained austenite transforms to ferrite plus cementite [39]. Caron and Krauss report that the lath structure also coarsens in this temperature range, but retains the elongated structure until very late in the tempering process when an equiaxed structure gradually develops as a result in the reduction of low angle boundaries by a recovery mechanism [41]. They also report that Fe₃C particles are present in the laths and at the boundaries very early in the tempering
treatment and that the boundary particles coarsen quickly by Oswalt ripening, likely due to increased diffusion of solute via the grain boundaries [22]. During this coarsening, the enrichment in carbon of the carbides happens at the expense of the carbon present at lath boundaries and dislocations, resulting in a reduction of the hardness of the martensite. In plain carbon steels, these tempering reactions result in the reduction of hardness and recovery of ductility as shown in Figure 2.10.
M₃C carbides are often iron rich, or in the case of cementite almost all iron [43]. However the solubility of other elements within M₃C is quite high. Because they have the same orthorhombic structure, Mn can completely replace Fe in the carbide given sufficient available solute. Cr is also highly soluble in M₃C, and can comprise as much...
as 20% of the iron sites. When the M₂C carbides contains other elements, coarsening can be prevented and help maintain a Widmanstätten structure up to the 500-550°C range, which can slow the softening process during tempering [18].

2.4.3 Alloy Carbides/Secondary hardening

In addition to the tempering reactions that occur in plain carbon steels, low alloy steels have additional effects as a result of alloying additions. The addition of carbide forming elements such as chromium and molybdenum can result in a secondary hardening effect which in some cases can produce a microstructure nearly as strong as that in the as quenched condition with the added benefit of increase in toughness due to the refined dispersion of alloy carbides [42]. This increase in hardness is the result of the precipitation of other metastable carbides besides Fe₃C. Because the slow diffusion rates of the carbide forming alloying elements prevent the nucleation and growth of these precipitates, this type of carbide begin to form at temperatures from 500-600°C [18].

Fe-Cr-C System

In addition to being a significant substitutional solid solution strengthener, chromium is also a strong carbide former. Grange et al. investigated the effect of chromium additions of 0.10 to 0.63 wt% to a 0.19C-0.3Mn steel [44]. They concluded that the increase in hardness due to Chromium was maximum in martensite tempered at 800°F (427°C) and then decreased as tempering temperature was increased due to coalesce of the metallic carbides. However, because it substitutes for some of the iron in cementite it can prevent
the same effect in $M_3C$ type carbides. Bain determined that larger alloying additions can also help inhibit softening in medium carbon steels, with additions of 12% even resulting in an increase in hardness slightly above the 800°F tempering temperature noted by Grange et al [45].

Figure 2.11 – Effect of Chromium Content on Tempered Hardness [45]
M₇C₃

In the Fe-C-Cr system, M₇C₃ carbides follow M₃C in the precipitation sequence. Kou demonstrated that before this transformation occurs, there is an increasing concentration of Cr in the M₃C structure, and nucleation of this type of precipitate most often occurs at interfaces between M₃C and ferrite [18,43]. Baker and Nutting reached a similar conclusion by noting that in the normalized condition, this carbide only formed in areas of bainite where M₃C was previously present, even though the ferritic regions contained higher amounts of Cr [46]. This type of carbide does help in slowing down the rate of softening during tempering but does not result in a significant secondary hardening effect in alloys with less than 12% Cr because of rapid coarsening at 550°C [47]. This resistance to coarsening is improved in carbides that have a high ratio of Cr to Fe [48].
Figure 2.12 – TEM Micrograph Displaying the Morphology of M\textsubscript{7}C\textsubscript{3}, M\textsubscript{23}C\textsubscript{6}, and M\textsubscript{6}C Precipitates [49]

\textbf{M\textsubscript{23}C\textsubscript{6}}

The M\textsubscript{23}C\textsubscript{6} is an equilibrium precipitate in 2.25Cr-1Mo steels, however in samples with lower carbon contents, the equilibrium carbides shift to M\textsubscript{7}C\textsubscript{3} and M\textsubscript{3}C types based on experimental evidence [46,50]. It is Cr rich but there is significant solubility for Mo. It can exist in a wide range of compositions comprised of Cr, Mo and Fe sometimes acts as an intermediate precipitate between M\textsubscript{3}C and M\textsubscript{6}C [18,51]. Typically, these particles precipitate at prior austenite grain boundaries or other high angle boundary types at the
same time as $\text{M}_7\text{C}_3$ and grows preferentially to the point where $\text{M}_7\text{C}_3$ is completely dissolved, which corresponds to an over aged condition [18,52].

**Fe-Mo-C System**

Another significant carbide former, molybdenum has been found to have a stronger hardening effect than chromium. Bain noted a strong secondary hardening peak at tempering temperatures of approximately 1100°F (592°C) with as little as 2 wt% Mo additions [45]. Grange et al. reached the same conclusion in lower carbon (0.15C-0.3Mn) steel noting that 1000°F (538°C) and 1100°F (592°C) produced that same hardening effect, but a decrease in hardness at 1200°F (649°C) [44]. They also noted that at elevated temperatures, Mo partitions to the carbides, which contributes to maintaining a fine dispersion of particles. Thompson and Miller determined that this partitioning does not occur during tempering at 350°C for 40 hours, but does occur in 187 hour treatments at 450°C due to the increased mobility at the higher tempering temperature [53].
Figure 2.13 - Effect of Molybdenum Content on Tempered Hardness[45]

M₂C

The M₂C carbide is primarily a Mo rich precipitate although it does show some solubility for Cr [43]. It is the particle responsible for the secondary hardening behavior in alloyed steels and nucleates primarily at dislocations within the ferrite but also on prior austenite
and ferrite grain boundaries [18]. The transformation of $M_2C$ to $M_3C$ occurs as a separate nucleation event which can be suppressed in favor of a $M_3C$ to $MC$ or $M_3C$ to $M_{23}C_6$ transformation in alloys with a Mo to C ration of less than 1.5 [43]. The strong secondary hardening behavior is a result of these particles nucleating as a fine dispersion of coherent precipitates [42]. Baker and Nutting noticed that $M_2C$ was more stable in the ferritic regions of the normalized condition, which imparted better creep properties [46]. The morphology of $M_2C$ precipitates can vary depending on the area in which it nucleates, with those formed within the grains having a needle shape and those nucleated on grain boundaries and dislocations typically having a globular shape [54].
The $M_6C$ carbide was determined by Baker and Nutting to be the equilibrium Mo rich carbide in 2.25Cr-1Mo steel. This was confirmed by Abdel-Latif et al. based on extended artificial aging at 630°C to simulated service time of 100,000 hours at 540°C as well as Wada at 712°C by thermodynamic analysis [51,55]. $M_6C$ has considerable solubility for Cr, up to 0.3 of the atomic fraction of Fe present (which is up 0.5 atomic fraction) in the structure [43,56]. Baker and Nutting observed the formation of $M_6C$. 

Figure 2.14 - TEM Micrograph Displaying the Morphology of M₇C₃ and M₂C Precipitates [49]
precipitates on the grain boundaries in both bainitic and ferritic regions and also concluded that these precipitates form directly from the $M_2C$ type in the ferritic areas, transitioning from needle like to globular while growing rapidly at the expense of other carbides in the area [46].

2.5 Tempering in 2.25Cr-1Mo

2.5.1 Precipitation Sequences

Baker and Nutting extensively studied the precipitation sequence during tempering treatments of both the quenched and normalized condition of a commercial composition of 2.25Cr-1Mo [46]. The tempering treatments ranged from 400-475°C and for times up to 1000 hours. In the quenched condition, the initial microstructure consisted of martensite with small amounts of retained austenite. Within the martensite, there were lenticular cross section plates that were identified as $\varepsilon$ carbides, with some of the larger specimens likely being cementite. In contrast to low carbon plain carbon steels, the $\varepsilon$ carbide was relatively stable and did not transform to cementite until after a 5 hour, 500°C temper treatment. The normalized specimen was a mix of proeutectoid ferrite (approx. 55%) and bainite (approx. 45%). There were no carbides found in the ferrite, but the bainite contained plate and lath like carbides that were likely $\varepsilon$ and cementite. Also, lath like $M_2C$ type carbides were found on the ferrite and bainite boundaries which were likely formed on cooling from the normalization treatment. The precipitation
sequence they found is shown diagrammatically in Figure 2.15 and schematically in Figure 2.16. The results for the two different conditions are similar, likely because since both microstructures have similar amounts of features that affect the precipitation kinetics, such as dislocations, prior austenite grain boundaries, and lath boundaries [57].

Figure 2.15 - Favored Precipitates in Quenched (left) and Normalized (right) 2.25Cr-1Mo Steel as a Function of Tempering Time and Temperature [46]
Pilling and Ridley studied 2.25Cr-1Mo steels which had a significantly lower carbon content than those by Baker and Nutting (0.018, 0.06 and 0.09 vs. 0.15 wt%) and found a slightly different precipitation sequence [50]. Their samples were heat treated to result in a coarse grained bainitic/martensitic microstructure typical of a normalization treatment and noted that instead of $M_2C$ carbides transitioning into $M_{23}C_6$ precipitates, they observed $Fe_3C$ dissolve very early in the tempering treatment followed by simultaneous precipitation of $M_2C$, $M_7C_3$ and $M_{23}C_6$ variants. They also noted that a reduction in carbon from 0.09 to 0.06 wt% changes the equilibrium carbide types from $M_7C_3$ and $M_6C$ to $M_{23}C_6$ and $M_6C$ types. Also, they noted that a decrease in carbon contents sped the...
evolution between carbide types. Thompson and Miller also investigated the early stages of tempering in as quenched specimens [8]. They used atom probe field ion microscopy to observe that even during the earliest stages of tempering at 350°C, clusters of Mo and C atoms that were likely ultra fine M$_2$C carbides indicating that M$_2$C particles can be present far earlier in the tempering cycle than Baker and Nutting witnessed.

2.5.2 Effect of Tempering On Mechanical Properties of 2.25Cr-1Mo

In the study performed by Baker and Nutting, different mechanical properties were observed depending on the tempering temperature [46]. At 400°C, the hardness increased with increased tempering times caused by the formation of M$_3$C from ε. At 600°C there was a hardness increase after 1 hour of tempering as a result of the precipitation of M$_2$C followed by a steady decrease for the longer heat treatments. Above 650°C, the hardness decreased linearly with respect to the logarithm of tempering time which corresponds with the Hollomon-Jaffe Parameter approach. As expected, as the temperature of tempering increased, the hardness for equivalent treatment times decreased. Pilling and Ridley noted similar finding tempering at 700°C, including a drastic decrease in the hardness from the as quenched condition after the first short tempering treatment with a lower rate of softening in subsequent treatments [50].

Additionally, both the as quenched and tempered hardness showed a dependence on carbon content. Tao et al. indicated that the decrease seen in hardness during the later stages of the tempering process was due to the coarsening of carbides reducing the effect of precipitation strengthening [48].
Figure 2.17 – Hardness as a Function of Tempering Time at 700°C [50]

2.6 Welding of Low Alloy Steels

In applications such as power generation and oil and gas, fusion welding is the most commonly used form of welding. A fusion weld joint is broken into several regions as identified by Savage et al.; the fusion zone (which contains both the composite region and the unmixed zone), the partially melted zone, and the true heat affected zone (HAZ) [58]. The fusion zone is the region in which the temperature has exceeded the liquidus
temperature and hence has fully melted. The partially melted zone is the region in which the temperature was between the liquidus and solidus temperature, resulting in an area that did not completely melt but had areas that formed liquid. The true HAZ is the region which temperatures do not exceed the solidus and therefore all reactions are solid state type [59].

2.6.1 Heat Affected Zone
On Heating
Since carbon and low alloy steels undergo an allotropic phase transformation, the HAZ is an area in which drastic changes occurs during the welding thermal cycle [10]. As can be seen in Figure 2.18, the regions of the HAZ can be related to the equilibrium iron-carbon phase diagram.
The HAZ can be further divided into coarse grain heat affected zone (CGHAZ), fine grain heat affected zone (FGHAZ) and the intercritical heat affected zone (ICHAZ). The CGHAZ is region in which the temperature reaches high into the austenite phase field, resulting in pronounced grain growth. This is the result of the reduction in free energy by the decreasing grain boundary area (and curvature) and the dissolution of carbides and nitrides, that act to pin boundaries and restrain growth [10,61]. The FGHAZ is the region which reached a temperature slightly above the upper critical transformation temperature ($A_3$), which allows for recrystallization and results in grain refinement. Because it is only
above this threshold for a short time, the ferrite present in this region does not completely transform to austenite and refines the grain structure on cooling [62]. In the ICHAZ, the temperatures range between the A$_3$ and lower critical (A$_1$) temperatures. Because of this, there is partial transformation to austenite during the welding thermal cycle.

**On Cooling Transformations**

During cooling from welding, phase transformations can play a large role in the properties and microstructure in the HAZ. Regions of the HAZ that were transformed to austenite will transform to a wide variety of phases based on welding parameters and material hardenability. In applications such as corrosion resistant cladding, the dilution of the weld filler metal by the base material must be controlled carefully to maintain the appropriate properties [63]. For this reason, the heat inputs used in these welding processes are typically very low, and result in extremely fast cooling rates which lead to a near completely martensitic microstructure in the HAZ. Other applications, such as joining power generation boiler tubes, call for much higher heat input conditions which result in slower cooling conditions and microstructures consisting of bainite, ferrite and possibly martensite [64].

**2.6.2 Tempering in the HAZ of 2.25Cr-1Mo**

Hippsley investigated the temper response of a commercial composition simulated weld HAZ after a stress relief treatment consisting of a 100°C per hour heating to 702°C, with specimens examined at 452°C, 567°C and 702°C [65]. The microstructures consisted of primarily lower bainite and for all but the highest temperature heat treatment, the only
carbide was $M_3C$ and was observed both inter and intragranularly. At 702°C $M_2C$, $M_7C_3$ and $M_{23}C_6$ were seen both inter and intragranularly with $M_6C$ also being observed at grain boundaries as well. This sequence is consistent with what Baker and Nutting observed in base material, with the exception of a much sooner occurrence of both $M_{23}C_6$ and $M_7C_3$ in Hippsley’s experiments.

Peddle and Pickles also investigated the precipitation in the HAZ of 2.25Cr-1Mo, but used a temperbead technique as well as a conventional weaving procedure [9]. In the as-welded condition, the maximum hardness between the temper-bead and conventional process differed by almost 100 HVN, 400 HVN and 305 HVN respectively. After welding, the samples were heat treated at 538°C for durations of 100, 1000, 2000, and 4000 hours to simulate service conditions and at 725°C for 3 hours to simulate a post weld heat treatment cycle. Prior to heat treatment the tradition weaving microstructure was mostly upper bainite with some martensite, while the faster cooling inherent to the temperbead process resulted in a fine grained, fully martensitic microstructure. As expected, the hardness of the microstructure softened much more rapidly during the PWHT cycle versus the in service tempering cycle as can be seen in the HAZ hardness traverses in Figure 2.19 and Figure 2.20.
Figure 2.19 – Heat Affected Zone Microhardness Traverses in the Root (Top) and Bay (Bottom) Regions of Conventionally Welded 2.25Cr-1Mo
Figure 2.20 - Heat Affected Zone Microhardness Traverses in the Root (top) and Bay (bottom) Regions of Temperbead Welded 2.25Cr-1Mo
However, after between 1000 and 4000 hours, the values converged, though by different mechanisms. Due to higher diffusion rates at the elevated temperature of the PWHT, the development of coarse alloy carbides was favored, while the finer precipitates dissolved or spheroidized. The service simulation temperatures still contained a high density of fine acicular $M_2C$ carbides, even after 4000 hours and the development of coarser grain boundary carbides of $M_7C_3$ and $M_6C$.

Tsai and Yang also investigated the precipitation in a simulated HAZ and found that even with heat inputs as high as 0.2KJ/mm there was still a significant amount of martensite formation [66]. During tempering at 700°C for times up to 50 hours, they found a different precipitation sequences depending on the microstructure of the area, shown in Figure 2.21.
They observed that in the intralath martensitic regions, the transformation from a predominantly $M_3C$ precipitate to the $M_7C_3$ precipitate occurred more quickly and also that after the longest tempering time, $M_2C$ carbide was observed coincidently with $M_{23}C_6$ and $M_7C_3$. However, $M_6C$ was not encountered which is in disagreement with most other researchers.

### 2.6.3 Hydrogen Induced Cracking

One of the chief weldability concerns in low alloy steels is hydrogen induced cracking (HIC). While there is no unified theory that completely explains HIC, several researchers have proposed mechanisms. The Surface Absorption Theory proposed by Petch and Stables resulted from the study of crack propagation in glass [67]. They suggested that gas covering the fracture surface could allow the crack to extend at the rate at which the gas could be supplied. Once the crack had extended to the point at which

![Figure 2.21 – Heat Affected Zone Precipitation Sequence According to Tsai [66]](image)
the stress reached the fracture value of the base material, the delayed cracking propagation would occur. The Decohesion Theory was proposed by Troiano on the basis that hydrogen at the located near a crack tip results in a weakening of the cohesive strength of the atomic lattice [68]. This theory was expanded upon by Oriani and Josephic with a study on the stress state and cohesive force near crack tips in AISI 4130 steel which were in agreement with the decohesion principles [69]. Another theory was proposed by Beachem based on the characterization of fracture surfaces in AISI 1020 and 4340 steel [70]. The results of this study indicated that the presence of hydrogen in the lattice ahead of the crack tip facilitates whatever deformation process the microstructure allows.

In order for HIC to occur, four conditions must be met which are a threshold level of hydrogen, a susceptible microstructure, high restraint levels and low temperatures [71]. If one of these conditions can be prevented, HIC can typically be avoided. In some cases, controlling the restraint level is difficult in welding due to the strain resulting from shrinkage of cooling weld metal, but often this can be minimized by joint geometry. At low temperatures (such as room temperature) the diffusion of hydrogen is slow, but the use of preheating and minimum interpass temperatures can increase the mobility of hydrogen, which slow the cooling rates from welding, allowing it to escape before it can contribute to cracking. The other two factors can be more difficult to control in low alloy weldments. The susceptibility of a microstructure to HIC is related to the hardness, with higher hardness phases such as martensite being much more susceptible than softer
phases like ferrite. Because of this, the high hardenability of low alloy steels like F22 makes the HAZ particularly susceptible to HIC. Since this alloy has applications in subsea service in the petroleum industry, it is often exposed to H₂S in service conditions which enhances iron dissolution reactions and increases the amount of hydrogen that can be absorbed by the base material [2]. Additionally, cathodic protection is often used to protect these components from corrosion. As side effect of this technique, water may undergo a reduction reaction which results in monatomic hydrogen which may be absorbed [72]. Hence, the importance of avoiding a susceptible HAZ microstructure is magnified.
CHAPTER 3: OBJECTIVES

The objective of this research was to evaluate the post weld heat treatment (PWHT) response in the heat affected zone (HAZ) of a range of commercial compositions of F22 (2.25Cr-1Mo) steel and to determine the range of hardness values that can result from standard PWHT procedures. Another objective was to validate the use of a Hollomon-Jaffe type tempering parameter approach to evaluate temper response in the HAZ. An additional objective was to develop a model based approach to evaluate the dissolution of several different types of carbides throughout the temperatures found in the HAZ.
CHAPTER 4: EXPERIMENTAL PROCEDURE

4.1 Materials

In order to expand on the preliminary study to a typical range of compositions, 16 heats of various product forms were provided by Cameron International. The compositions of these heats as determined by optical emission spectroscopy (OES) are shown in Table 4.1. The carbon content of these heats ranged from 0.108 to 0.168 weight percent with IIW carbon equivalents of 0.80 to 1.02 and $P_{CM}$ values from 0.311 to 0.410. For studies of the response to solution austenization, samples were sectioned into cubes 13mm x 13mm x 13mm (1/2” x 1/2” x 1/2”) and cleaned with ethyl alcohol to remove any cutting fluid residue. In order to prevent oxidation and decarburization, groups of 5 or 6 samples were encased in a quartz tube and sealed with 0.2 partial pressure of Argon. To investigate the response of these heats to welding, samples 10mm x 19mm x 19mm (3/8” x 3/4” x 3/4”) were also produced.
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Table 4.1 – Composition of Selected Heats of F22
4.2 Solution Austenization Heat Treatments

Samples were subject to three different heat treatments, 954°C (1750°F) for one hour, 1148°C (2100°F) for one hour and 1148°C (2100°F) for four hours. These treatments were selected based on the requirements specified by ASTM A182 and thermodynamic simulations using JMatPro®. The thermal history of each sample was not recorded, but based on thermal data collected during process development unencapsulated samples reached the furnace set point temperature in approximately 5 minutes. In each test, heat treatment time corresponds to total time in the furnace, including the heating time. Each tube was placed in a Lucifer model 7GT-K24 box furnace on a preheated nickel plate to facilitate fast removal. Once the heat treatment time was completed, the tubes were removed from the furnace and quenched in room temperature water. If the quartz tubes did not fracture due to the thermal shock, they were broken immediately to achieve the highest feasible cooling rate.

4.3 Spot Welding Procedure Development

In order to simulate in service welding conditions, autogenous gas tungsten arc spot welds were made with various heat inputs were compared to a supplied sample which was clad in nickel alloy 625, see Figure 4.1. The base metal selected for procedural development was one with close chemical composition to that of the clad sample base
material. Upon completion of welding, relative size and hardness distribution within the heat affected zones of each sample were compared as was the hardness distribution. The parameters were selected that resulted in matching widths of the hardened region in the heat affected zone and are shown in Table 4.2. Based on comparison to standard industrial cladding procedure for a thick walled structure, the approximate heat input for the spot welds was 0.20 kJ/mm. After completion of the welding cycle, the samples were allowed to free cool to room temperature.

Figure 4.1 – Heat Affected Zone Hardness in Typical Spot Weld and Sample Overlay Weld
<p>| | |</p>
<table>
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<tr>
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</thead>
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<tr>
<td><strong>Welding Current</strong></td>
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<td><strong>Arc Gap</strong></td>
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<tr>
<td><strong>Voltage (approx.)</strong></td>
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</tr>
<tr>
<td><strong>Hold Time</strong></td>
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</tr>
<tr>
<td><strong>Shielding Gas</strong></td>
<td>100% Ar</td>
</tr>
</tbody>
</table>

Table 4.2 – Autogenous Gas Tungsten Arc Spot Weld Parameters

### 4.4 Tempering Heat Treatment

To gauge the response of each heat to tempering heat treatment, each sample was divided in two pieces and subjected to one of seven heat treatments as shown in Table 4.3. These heat treatments were selected to result in Hollomon-Jaffé tempering parameters which surround a currently used post weld heat treatment procedure (HT3). These values were calculated using the equation shown in Equation 4.1. During procedure development, thermal measurement determined that tempering samples reached furnace temperature in approximately 20 minutes. This heating time was not considered in the calculation of the Hollomon-Jaffé parameters. The furnace used was a horizontal Lindberg 59544 type. Upon completion of the tempering time, samples were quenched in room temperature water.
\[ HJP = T \times (20 + \log(t)) \]

Equation 4.1 – Hollomon-Jaffe Tempering Parameter

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<th>Time (hr)</th>
<th>HJP</th>
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<td>18215</td>
</tr>
<tr>
<td>HT-2</td>
<td>647°C (1197°F)</td>
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<td>18562</td>
</tr>
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<td>18924</td>
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<td>638°C (1180°F)</td>
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<td>19084</td>
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<td>HT-7</td>
<td>677°C (1250°F)</td>
<td>11</td>
<td>19982</td>
</tr>
</tbody>
</table>

Table 4.3 – Hollomon-Jaffe Parameters for Tempering Treatments

4.5 Macrohardness Testing

The as-quenched hardness of each heat of material was measured on the Rockwell C scale using a Leco LR series hardness tester. Prior to indenting, the samples were sectioned through the midline and another parallel plane in order to ensure a flat surface.
for accurate measurements. An average hardness was calculated based on four indents near the center of the cross section.

4.6 Microhardness Testing

Vickers microhardness testing was used on test samples in various conditions. Due to low hardness that prevented the use of the Rockwell C scale, the base material was measured with 1kg microhardness indents. In the as-quenched austenization samples, two-dimensional hardness mapping with a Leco LM100AT automatic microhardness testing machine was used on select samples to ensure that the quench conditions produced a high enough cooling rate to result in through thickness hardening. This technique was also used on specimens in the as welded and tempered conditions to investigate hardness trends in the heat affected zone. For each tempering treatment of each heat, a microhardness traverse was used to measure the hardness as a function of the distance from the fusion boundary. Indents for these traverses were made with 100g load and an average spacing of 75μm. These values were also incorporated into an average hardness of the heat affected zone for each tempering treatment.
4.7 Microscopy

After hardness testing, samples were mounted in Bakelite and ground using successive steps of 320, 400, and 600 grit wet silicon carbide sand papers and polished with 9, 6, 3, and 1μm diamond polishing paste. After a suitable surface was obtained, samples were chemically etched using Villea’s etch (5cc HCL + 2g Picric Acid + 100cc Ethyl Alcohol) or 2/5% natal (2/5% nitric acid + ethyl alcohol) to increase contrast of microstructural features. Selected samples were mounted in a conductive mounting medium and investigated in a scanning electron microscope. This was used to make relative comparison of quantity and appearance of carbides in various states of the as quenched austenitized samples. SEM was also used to investigate the microstructure in the different regions of the heat affected zone for several of the welded and tempered samples.

4.8 Carbide Dissolution Simulations

Dictra™ kinetic and thermodynamic simulation software was used to simulate the dissolution of several types of carbides in a Fe-C-Cr-Mo system. To relate this behavior to the HAZ, simulation temperatures varied between the calculated A₃ and near the solidus temperature. Five different types of carbides were considered (Fe₃C, M₂C, M₇C₃, M₆C, M₂₃C₆) at six temperatures ranging from 927°C to 1427°C for 30 seconds. Each simulation was run as a moving boundary type problem with a region of 0.5 micron
width of the target carbide and an austenitic region 1.0 micron in width. The composition of each region was determined using Thermo-Calc based on the thermodynamic equilibrium composition at the minimum tempering temperature recommended by ASTM A182, 675°C. In order to simulate carbides which are not favorable under equilibrium conditions, only the target carbide was allowed to form and all others were suppressed. In order to simplify the simulations, the formation of ferrite was suppressed.
CHAPTER 5: RESULTS AND DISCUSSIONS

5.1 As-Received Base Material Properties and Structure

Because of the hardness requirement stipulated by the end user shown in Table 1.4, the majority of the individual heats display similar hardness of approximately 250 VHN as shown in Figure 5.1. Because the measured hardness values in this range of compositions were very similar, this indicates that the processing conditions for each heat varied.
In Heat 2, the lowest carbon containing heat, the microstructure consists of a mix of tempered bainite, ferrite and carbides. The post forging heat treatment of this heat was a two hour normalization treatment at 954°C (1750°F) followed by a one and a half hour tempering treatment conducted at 676°C (1250°F). Details of the cooling conditions were not included in the material test report from the supplier.
The heat containing the most carbon, Heat 13, displays a mostly tempered martensitic microstructure with a much higher density of carbides as compared to Heat 2. The post forging heat treatment was a one hour normalization at 954°C (1750°F), air cooling to 927°C (1700°F) for one hour, followed by a water quench. Tempering was conducted for four hours at 607°C (1125°F), air cooled to (1100°F) and tempered for an additional four hours before a final water quench.
Two specific heats deviate from the hardness of the others, Heat 11 and 12. Despite containing carbon contents and CE_{IIW} within the range as specified, both heats display significantly higher hardness. Both heats are round forged bars with relatively smaller cross sections than the other heats studied, with outside diameters of 38mm (1.5”) and 32mm (1.25”) respectively. Because of this, these heats would have experienced a much higher cooling rate given the same processing conditions. This likely would result in a higher fraction of martensite and less of an auto tempering effect during cooling. It is also worth noting that these two heats both feature a more refined prior austenite grain structure as compared to the others, which would also contribute to a higher hardness despite the lower hardenability resulting from the smaller prior austenite grain size.
5.2 As-Quenched Condition

5.2.1 Equilibrium Simulations

As previously described, phase equilibrium simulations were conducted for the composition of each heat to understand the phase transition temperatures and to verify that each solution heat treatment would take place in the fully austenitic phase field.

Figure 5.4 – Heat 11 (0.156 wt% C) Base Material As-Received Condition
These calculations revealed that Heat 12 possessed the highest $A_3$ temperature of 865°C. They also showed that in particular heats, certain other constituents, such as carbonitrides, may be present in the 954°C treatment. For the remaining two 1148°C treatments, each heat indicated that the equilibrium microstructure would be composition of 100% austenite at temperature. Table 5.1 summarizes the calculated transformation temperatures of all the heats based on a consistent grain size of ASTM 9.
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Table 5.1 – Calculated Austenite Transformation Temperatures using JMatPro

5.2.2 *Calculated CCT Diagrams*

In addition to the equilibrium simulations, continuous cooling transformation diagrams were also produced for the specific heat compositions. These CCT diagrams indicated that for the heat with the lowest $P_{cm}$ and CE$_{IIW}$ (Heat 2), the nose of the bainite transformation curve occurs at approximately 450°C and 10 seconds. In order to miss this curve and produce a nearly 100% martensite microstructure, the cooling rate in the water quenching process would have to exceed 70°C/s when cooling from the 1148°C
solution austenization treatment. In the critical temperature range from 800°C to 500°C ($T_8^{-3}$), the actual cooling rate was measured at 93°C/s during procedural development testing [73]. This indicates that even in the heat with the lowest hardenability, the as-quenched microstructure should be nearly all martensite. In contrast, the heat with the highest hardenability showed the nose of the bainite transformation curve at 430°C and 30 seconds, requiring a cooling rate of only 24°C/s in order to achieve the desired microstructure.

Figure 5.6 – Heat 2 (0.807 CE$_{IIW}$) Continuous Cooling Transformation Diagram Calculated with JMatPro
To determine which solution heat treatment was most effective in homogenizing the as-received microstructure, the macrohardness of each treatment was measured. Since the hardness of as-quenched martensite is based primarily on carbon content, the treatments were compared to the as-quenched hardness as a function of carbon content as determined by Jaffe and Gordon [32,74].
As can be seen in Figure 5.8, heats containing lower carbon contents correlate relatively well with the predicted hardness. Each point was based on an average of four hardness indents and the maximum standard deviation for all heats was 0.83 HRC. However, in heats containing more than approximately 0.14 wt% C the hardness of the as quenched samples is notably lower than the projected hardness. One potential explanation for this deviation is that in the experiments conducted by Jaffe the experimental procedure included quenching samples in water followed by cooling in liquid nitrogen. This would reduce the amount of retained austenite present, which is much softer than as-quenched...
martensite [34]. It is likely that there is some fraction of austenite retained in the microstructure, especially considering that decreased hardness was witness in heats with higher carbon contents, but it is likely not significant enough to result in a dramatically softer microstructure. Thompson and Miller also observed carbon enriched films with a thickness of approximately 2 nm width in as-quenched 2.25Cr-1Mo-0.15C using atom probe field ion microscopy [8].

Optical microscopy revealed another, more likely reason for this lower than expected hardness. In each of these heats, particles which are believed to be carbides are still present after the solution austenization treatments. Figure 5.9 shows a comparison between Heat 14 (0.111 wt% C), Heat 7 (0.153 wt% C) and Heat 13 (0.168 wt% C) after the 954°C-1 hour treatment. In all three materials, darker etching particles can be seen but as with the base material, there is a higher fraction of particles present with increasing carbon contents.
As expected, in the higher temperature heat treatments there are fewer particles present. In the Heat 14 samples, there were no visible particles for either one hour or four hour treatments at 1148°C. In the higher carbon Heat 13, there were particles visible for both of these treatments, but decreased in both size and frequency for the four hour treatment. Because these particles are large enough to be visible at relatively low magnification, it is unlikely that they were able to nucleate and grow to this size as a result of autotempering during the fast cooling from austenization temperatures. Because these particles are likely carbides, there is less carbon present in the matrix to contribute to the hardness of the as quenched martensite.
Under examination at higher magnification using scanning electron microscopy, these particles are visible as lighter regions in backscatter electron imaging (indicated by A labels in Figure 5.12) of Heat 13. Attempts to determine the composition of these areas by energy dispersive X-ray spectroscopy (EDS) were unsuccessful, likely due to the
relatively small size of these particles. The structure in the as-quenched condition is also visible. While this magnification is still not high enough to definitively identify the phases present, the microstructure displays a lath martensite like appearance with boundaries between packets and blocks within each prior austenite grain visible. Also, several areas have fine lenticular precipitates which is similar to findings by Baker and Nutting [46]. They identified this microstructure as \(\varepsilon\) carbide by X-ray fluorescence, which likely formed as a result of autotempering during the on cooling martensitic phase transformations. While this microstructure also has characteristics of lower bainite (i.e. intralath carbides), a martensitic microstructure is more likely based on the calculated CCT diagram.

Figure 5.12 – SEM Image of Heat 13 After 954°C-1 Hour Austenization Heat Treatment
5.2.4 Grain Growth in Treatments

Another indicator of the lower temperature and time heat treatments not being effective in solutionizing the pre-existing microstructure is the lack of significant grain growth [10]. Even in Heat 14, no significant change in the prior austenite grain size for the 954°C-1 hour heat treatment was observed. In the two higher temperature treatments, prior austenite grain growth become more prevalent. In the 1148°C-4 hour treatment, the growth is extreme, resulting in prior austenite grain sizes of over 200 microns. This illustrates that while the selected solution austenization treatments were not effective in completely dissolving all precipitates, the two higher temperature treatments did solutionize a high enough fraction to allow for a significant amount of grain growth.

Figure 5.13 – Austenite Grain Growth Resulting from 954°C-1 Hour (Left), 1148°C-1 Hour (Middle) and 1148°C-4 Hour (Right) Austenization Heat Treatment of Heat 7
5.3 Spot Welds

Although the solution austenization heat treatments gave insight into the dissolution of the carbides available in the base material, the welding process produces a different set of conditions due to its transient nature as well as a much higher peak temperature in the CGHAZ.

5.3.1 As-Welded Condition

Due to the rapid heating and cooling in the HAZ, the microstructure in this region is expected to resemble an as-quenched region. In fact, the average hardness of both the HAZ and the fusion zone exceed that which is projected by Jaffe and Gordon as shown in Figure 5.14 [74]. Since these are average values as determined by hardness traverses spanning the entire HAZ, several different mechanisms have an effect on the hardness. In the CGHAZ, the peak temperature reaches much higher values, which contributes to the faster and more complete solutionization of the carbide precipitates that are present in the base material which will contribute to a higher hardness. However in the same region, the dissolution of these precipitates and high temperatures allow for growth of the prior austenite grains, resulting in a diminished effect of packet and block boundary strengthening effects. Additionally, the larger prior austenite grain size results in higher hardenability. In the FGHAZ, these mechanisms also compete, but in opposite manners. The refined prior austenite grain size in this region contributes to higher hardness (but
lower hardenability), while the lower peak temperatures result in a less complete dissolution of precipitates. When compared to the solution austenitized heat treatments, the welding process resulted in a higher hardness in all of the tested heats. Also worth noting is that in nearly all of the heats, the weld metal region was harder than the HAZ. Since this region was heated to above the liquidus temperature, it’s expected that all the carbide precipitates in this region will be fully dissolved, resulting in the highest possible amount of carbon present for strengthening and thus the highest hardness despite the relatively coarse microstructure. Since there is a variation to the degree which the fusion zone is harder than the HAZ, it’s likely that the welding thermal cycle had a different effect on the different heats.
To better gauge the hardness in the individual regions of the HAZ, the values of the individual points can be compared. In Figure 5.15, the hardness traverses conducted in the welded condition are shown for two heats (9 and 11). Both of these heats have very similar carbon contents (0.157 and 0.156 respectively) and carbon equivalents (0.933 and 0.883 respectively) but radically different hardness profiles. Heat 9 shows peak hardness in the CGHAZ which is consistent with the idea that higher peak temperatures in this region have solutionized more of the carbide precipitates. Heat 11 however exhibits the highest hardness in the FGHAZ relative to the CGHAZ.
This trend becomes more apparent when hardness measurements are extended to two dimension maps. Figure 5.16 shows that in Heat 9, there is significant variation in the hardness of the coarse grained and fine grained regions of the HAZ with areas of maximum hardness in both. Further from the fusion boundary in the FGHAZ there is a significantly softer microstructure. In heat 11, the areas of maximum hardness occur in the FGHAZ with a relatively uniform hardness through the CGHAZ and most of the FGHAZ.
While not as pronounced as the difference between heat 9 and 11, there is a similar discrepancy between heat 6 and 7. These two heats are of particular interest because they share nearly identical compositions according to the OES chemistry results shown in Table 4.1. In Figure 5.17, it can be seen that the hardest regions of the heat 6 HAZ are
much further from the fusion boundary than those in heat 7 as well as the average hardness of heat 6 is higher than that of heat 7.

Figure 5.17 - As Welded Heat Affected Zone Hardness Maps for Heat 6 (Top) and 7 (Bottom)

The areas which displayed discrepancies between Heat 6 and 7 were selected for further investigation using backscatter electron imaging SEM. In the CGHAZ, heat 7 shows an
area of higher hardness than that same area in heat 6. In the Figure 5.18, the CGHAZ of heat 6 and heat 7 show martensitic microstructures with relatively similar block and lath sizes, suggesting that the impact of lath boundary strengthening on the hardness should be roughly equal in these two heats. Using this technique at this magnification, it is difficult to quantify the size and total area fraction of the carbides but qualitatively there appears to be a slight difference between the two heats. In heat 6 there does appear to be a higher number of precipitates that look to be smaller in size than those seen in heat 7. Based on the hardness measurements in this region, heat 6 is softer than heat 7 which indicates that the increased number of precipitates or their size is not appropriate to result in a significant precipitation hardening effect. Additionally, if there is in fact a higher volume fraction of carbides, than the amount of carbon available for solid solution strengthening would be lower, contributing to a lower hardness.

Figure 5.18 – CGHAZ of Heat 6 (Left) and Heat 7 (Right) in the As-Welded Condition
In the FGHAZ, as with the CGHAZ, the microstructural features are of roughly the same scale. In heat 6, the dispersion of precipitates seems to be relatively similar to that in the CGHAZ, despite the slightly higher hardness as indicated by the hardness map. Because the difference in hardness between these two regions is relatively small (10-20HVN), it is possible that this is a result of difference in the prior austenite grain size refinement resulting from the welding process and not due to a difference in precipitation distribution. In heat 7, the morphology of the precipitates is significantly different in the FGHAZ than in the CGHAZ. While those in the CGHAZ were located on the lath boundaries, the FGHAZ displays a much higher density of significantly larger precipitates at the block boundaries. These precipitates appear with two different morphologies in the image shown in Figure 5.19. Some of these appear as spherical and globular, while other are elongated.
Figure 5.19 – FGHAZ of Heat 6 (Left) and Heat 7 (Right) in the As-Welded Condition

5.3.2 Tempering Treatment

As expected, the tempering treatments shown in Table 4.3 resulted in extensive softening. The average HAZ hardness for each heat and treatment is listed below in Table 5.2 as well as the parameters resulting from best fit linear regression analysis for each heat. Consistent with Speich, the shortest tempering treatment resulted in the greatest rate of decrease of the average HAZ and fusion zone hardness, even though it was for the shortest time [42]. This was likely the result of the formation of new M₃C carbides, as well as potentially the coarsening of those that were already formed as a result of autotempering.
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Table 5.2 – Average Heat Affected Zone Hardness and Best Fit Regression Parameters
Figure 5.20 shows the response of the average HAZ hardness for six selected heats through the range of Hollomon-Jaffe tempering parameters tested. These six heats contained the heat that had the highest carbon content (heat 13), the lowest carbon content (heat 2), the two previously mentioned heats that showed anomalous behavior in the as-welded condition (heats 6 and 7), and the heats displaying the highest and lowest tempered hardness (heat 5 and 10, respectively).

Figure 5.20 – Average Heat Affected Zone Temper Response
The average of the HAZ hardness for Heat 5 is consistently the highest for each tempering treatment, despite carbon content lower than the next hardest heat (0.153 vs. 0.168). The composition of this heat results in the highest hardenability of those tested. Considering the rapid cooling due to the relatively low heat input used to make these spot welds, it was expected that even the heat with the lowest hardenability (heat 2) would result in a primarily martensitic HAZ microstructure in the as-welded condition.

Comparing the hardness results from these two heats to the expected values based on carbon content in Figure 5.14, they are both approximately the same amount harder than the predicted values indicating that they both met the threshold cooling rate to result in a nearly complete martensitic microstructure. Based on this, the additional hardenability should not contribute to the higher hardness in the tempered condition of heat 5. However, several of the elements which are considered in the hardenability calculations can affect tempering behavior, primarily the higher concentrations of both chromium (2.54 wt%) and molybdenum (1.19 wt%). Because of the slower rates of diffusion of both molybdenum and chromium, both of these elements retard the tempering process [44]. Molybdenum is also known to strongly partition to the carbide during tempering helping to maintain a fine dispersion of particles, which can cause an increase in the secondary hardening behavior.

In hardness traverses of heat 5 and heat 7 (which have the same carbon content) in Figure 5.21 and Figure 5.22, the difference in tempering rate can be seen in both the HAZ and the fusion zone. In the fusion zone of heat 5 after the shortest tempering treatment (HT-
1), the average hardness was 51 HVN higher than that in heat 7 despite it being 12 HVN softer in the as-welded condition. Further tempering in HT-3 and HT-4 does not result in much additional softening when compared to HT-1. During longer tempering treatments, the hardness does continue to decrease, but still maintains a hardness significantly higher than other heats.

Figure 5.21 – Heat 5 Hardness Traverses in the As-Welded and Tempered Condition
A similar trend is also found in the HAZ. In all heat treatments, the hardness in the CGHAZ of heat 5 is significantly higher than those in heat 7. Another noticeable trend in the HAZ of heat 5 is that there is relatively large difference between the hardness values in the CGHAZ and the FGHAZ. In the tempering treatments of heat 7, the values in the HAZ are relatively consistent throughout when compared to heat 5.

Figure 5.22 – Heat 7 Hardness Traverses in the As-Welded and Tempered Condition
Additionally, heat 5 also differs from the remaining heats of material because it contains niobium in a 0.021 wt% concentration. Niobium is a commonly used alloying addition in high strength low alloy (HSLA) steels because it forms carbides (NbC), nitrides (NbN) or complex carbonitrides (Nb(C,N)) which provide a grain boundary pinning effect in alloying additions as low as 0.02 wt% [75]. This principle is often applied to control grain size in hot forged components as well the traditionally controlled rolled low carbon HSLA steels [6]. Figure 5.23 shows the HAZ near the fusion boundary of both heat 5 and heat 7, which have a significantly different tempering response. In the CGHAZ area near the fusion boundary (red dashed line), there is a similar amount of grain growth for both heats, but as the distance from the fusion boundary changes differences in the prior austenite grain size appear. When compared to heat 7, the prior austenite grain size in heat 5 is smaller at an equivalent distance from the fusion boundary, likely due to the pinning effect of niobium rich precipitates. Spanos et. al investigated a HSLA-100 steel with a similar niobium concentration (0.028 wt%) determined that in the CGHAZ area (above 1400°C) Nb(C,N) particles fully dissolved, which allowed for unrestricted grain growth in the region [76]. In the FGHAZ (above 900°C), these precipitates remained stable and did not dissolve. The presence of these undissolved niobium rich precipitates can possibly explain the grain refinement effect seen in heat 5 but considering this region does not significantly harder when compared to heat 7, it is unlikely that this refined grain size has a large contribution to the higher average hardness of heat 5.
5.3.3 Secondary Hardening

Another trend apparent from the tempering treatment results displayed in Figure 5.20 is that there are several heat treatments which result in a secondary hardening response from many of the heats. In the HAZ, 8 of the 16 heats show a decrease in tempering rate (hardness decrease from as-welded condition per HJP) and an increase in hardness resulting from HT-2 when compared to HT-1. This trend is also present but more
widespread in HT-3 and HT-4 when 12 out of 16 heats show a decrease in tempering rate between these two treatments. This effect can be seen in the hardness traverses for heats 5 and 7 shown in Figure 5.21 and Figure 5.22. In heat 5, the higher average hardness is noticeable, mainly in the CGHAZ region. In heat 7, there isn’t a drastic hardness increase noticeable throughout the HAZ, but the resulting average hardness is higher by just over 3 HVN points. Of the four heats that did display a lower average hardness for the HT-4 tempering treatment, two of them saw a reduction in tempering rate when compared to HT-3.

This difference can be seen in the hardness distribution in the HAZ of heat 6 in Figure 5.24. In HT-4, there is a gradual increase in hardness throughout the HAZ. This is particularly noticeable in the coarse grained region where there are significantly more hardness indents which are above 280 HVN, as indicated by yellow coloring, in the longer tempering treatment.
In Figure 5.25 showing the hardness distribution in heat 7, the secondary hardening trend is not as clear as with heat 6. This correlates well with the trends observed in the hardness traverses shown in Figure 5.22. Since the resolution of the hardness map scale is only 10 HVN, it’s very difficult to see which regions contribute to the increase in average hardness of 3 HVN. While this is a relatively minor increase in hardness, both HT-3 and HT-4 were conducted at the same temperature (638°C) but for different times, 6 hours for HT-3 and 9 hours for HT-4. In this case, it would be expected that continued tempering would result in a relatively linear decrease in hardness. Considering the temper rate measured from the as-welded condition to the HT-3 condition, the average HAZ hardness of heat 7 for HT-4 should be approximately 260 HVN, a difference of 5 VHN from the measured value. Similarly, for heat 6 if the rate of tempering observed in
HT-3 was applied to estimate the expected hardness in HT-4 would be over 14 HVN less than the measured value.

![Heat Affected Zone Hardness Distribution for Heat Treatments 3 638°C-6hr and 4 638°C-9hr of Heat 7](image)

Figure 5.25 – Heat Affected Zone Hardness Distribution for Heat Treatments 3 638°C-6hr and 4 638°C-9hr of Heat 7

In examination of the HAZ of heat 7 using SEM, there are some differences between HT-3 and HT-4. In the CGHAZ of HT-3, there is a fine dispersion of intralath precipitates throughout the microstructure. Also, there is a smaller amount of larger precipitates which are situated at lath/block boundaries. In HT-4, there are still small precipitates visible throughout the microstructure, but there appear to be fewer precipitates present. In addition to the large precipitates present at lath/block boundaries in HT-3, there are also several smaller boundary precipitates which are visible.
In the FGHAZ shown in Figure 5.27, the carbide distribution in HT-3 consists mainly of intermediate size precipitates with some areas showing a refined dispersion of smaller precipitates similar to that in CGHAZ. In HT-4, there is a large increase in the number of precipitates located at lath/block boundaries, when compared to the FGHAZ in HT-3 as well as the CGHAZ in HT-4. Also, several regions show the refined dispersion of intralath precipitates observed in both regions from the HT-3 treatment.
Based on previous researchers work, there is an explanation for the secondary hardening effect seen between these two treatments. In Figure 5.28, the time-temperature precipitation diagram developed by Baker and Nutting for the quenched condition has been modified to include the tempering treatments used in this study. Due to the relatively short time, HT-1 remains in the regime in which Baker and Nutting did not observe any alloy carbides, only $M_3C$. HT-2 is the first treatment which enters into the $M_2C$ region, and the average HAZ hardness values plotted in Figure 5.19 show that in some heats, a secondary hardening behavior occurs here. This type of carbide is often associated with the peak hardness condition if it is present in a refined, coherent dispersion and also is a contributor to the strong creep strength of 2.25Cr-1Mo used in boiler tubes. If in fact this carbide was contributing the secondary hardening, it would likely not be visible with the techniques used in this investigation due to its size and aspect ratio. HT-3 and HT-4 were conducted at the same temperature as HT-1, but the
longer tempering time pushed these treatments into the regime in which M₂C carbides were observed. Since the tempering temperature of HT-3 and HT-4 is relatively low, continued aging from 6 to 9 hours results in an increased hardening effect for most heats, either from an increased volume fraction of precipitates or from the coarsening of precipitates below the critical size for the maximum hardness condition. In heats where there was a strong secondary hardening reaction seen in HT-2, the secondary hardening behavior is diminished. The longer remaining heat treatments were conducted at a higher temperature, therefore allowing for faster diffusion of Cr and Mo and progressing into the region in which M₇C₃ begins to appear. Because the diffusion of Cr in ferrite is faster than that of Mo, the M₇C₃ carbide coarsens rapidly which results in a higher rate of softening between HT-6 and HT-7 for most heats. In heats 7 and 10, there is a strong secondary hardening response between HT-6 and HT-7 as well as a weaker hardness increase between HT-3 and HT-4.
5.3.4 Fusion Zone Tempering Response

Considering the results for the solution austenization heat treatments discussed in Section 5.2, it is likely that even in the CGHAZ there is not complete dissolution of the precipitates present from prior processing. This is corroborated by the hardness traverses shown in Figure 5.21 and Figure 5.22 where the hardness of the fusion zone is slightly higher than that in the CGHAZ of the as-welded condition. To investigate the effect of these undissolved precipitates on the tempering response, the average hardness of the fusion zone after undergoing the same tempering treatments as the HAZ is shown in Figure 5.29.
The hardest heat in nearly all the tempered heats remains, as with the HAZ, heat 5 but the hardness heat 13 exceeds that of heat 5 in HT-7. The secondary hardening peaks observed in the HAZ are also present in the tempered weld metal however some heats do not have the same patterns. Heat 13 does not display a hardening reaction from HT-2, but does still exhibit a hardness peak in HT-4. In the case of heats 2 and 6, the secondary hardening peak of HT-2 exceeds that seen in the HAZ likely due a greater degree of dissolution of precipitates resulting in more solute available to form M$_2$C. In heat 7, the hardness peak from HT-4 is similar to that in the HAZ; however there is no increase in
hardness resulting from HT-7. Instead, there is a small increase after HT-6, but of a much smaller magnitude than that in the HAZ which coincides with possible formation of M$_7$C$_3$ carbides. In direct comparison between the average HAZ and fusion zone responses of heat 6, the difference in the magnitude of the secondary hardening peaks can be seen in Figure 5.30. In both HT-2 and HT-4, the same peaks that were present in the HAZ are seen in the fusion zone, but of higher magnitude.

![Figure 5.30 – Heat 6 Average Tempered Fusion Zone and Heat Affected Zone Hardness](image-url)
5.3.5 Effect of Precipitate Dissolution During Welding

Examining the individual hardness traverses for the HAZ explains why the average hardness in the fusion zone is higher. In HT-2 of heat 6, there is a spike in hardness in the FGHAZ while the CGHAZ is much closer in hardness to the same area in HT-1. By including the FGHAZ in the average value, the overall hardness value is increased. This gives further evidence that the secondary hardening peaks seen in HT-2 and HT-4 are the result of the formation of \( \text{M}_2\text{C} \) carbides as described in the beginning of the precipitation sequence as determined by Baker and Nutting. Based on this region having nearly the same peak hardness as the fusion zone, this suggests that the secondary hardening reaction is related to the dissolution of carbides in this region.

![Figure 5.31 – Heat 6 Secondary Hardening in HT-2](image-url)
Heat 7, as mentioned previously, features an almost identical composition to that of heat 6 but it did not exhibit as strong as a secondary hardening behavior in either the HAZ or the fusion zone. Because this secondary hardening reaction is the result of available solute from precipitates dissolved during the welding process, this suggests that the precipitates present in the starting microstructure are more resistant to welding in heat 7 than that in heat 6. In the fusion zone, the average as-welded hardness is almost identical between the two heats 425 HVN for heat 6 and 427 HVN for heat 7, which is expected because the heats have equivalent carbon contents. But heat 7 does not undergo any secondary hardening during HT-2 and much less as a result of HT-4 when compared to heat 6. The hardening that occurs in heat 7 HT-7 displays a different pattern than those occurring in other heats after shorter heat treatments. As opposed to seeing an increase in the CGHAZ such as that in Figure 5.31, Figure 5.32 shows that the higher average hardness after this treatment was a result of a smaller increase in both the coarse grained and fine grained HAZ. This pattern did not occur in the fusion zone of heat 7 which in conjunction with the increased hardness in the FGHAZ, indicates that this hardening behavior is the result of a different mechanism.
5.4 Carbide Dissolution Simulations

The difference in the behavior in the HAZ of the two heats of nearly identical condition indicates that the precipitates in the HAZ are not affected in the same way by the welding cycle. To investigate the dissolution rate at the elevated temperatures experienced in the HAZ, isothermal dissolution studies were performed using Dictra™.

5.4.1 Carbide Compositions

The composition of carbides determined based on equilibrium condition of a Fe-C-Cr-Mo system based on the composition of heat 7 are shown below in Table 5.3. As discussed previously, each of these types of carbides has significant solubility for other substitutional elements. However, because these were calculated at equilibrium
conditions, it is likely that these are not an exact representation of those present in the base material. Also, these calculations were conducted by suppressing the formation of all types besides the target type of carbide. This was another result of operating under equilibrium conditions. Based on the research conducted by the Baker and Nutting, M₆C and M₇C₃ were the equilibrium carbide types, however the thermodynamic software (ThermoCalc™) calculated M₂₃C₆ to be the equilibrium type which agreed more closely with results found by Tsai [46,66]. Another limitation of this approach was that because of limitations on available data, the databases used for these simulations have not been validated with the addition of other carbide forming elements such as Nb and V to the Fe-Cr-Mo-C system.

<table>
<thead>
<tr>
<th>Carbide Type</th>
<th>Fe</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₃C</td>
<td>40.98%</td>
<td>36.59%</td>
<td>17.00%</td>
<td>5.07%</td>
</tr>
<tr>
<td>M₂C</td>
<td>2.00%</td>
<td>49.98%</td>
<td>39.55%</td>
<td>8.46%</td>
</tr>
<tr>
<td>M₇C₃</td>
<td>28.18%</td>
<td>4.70%</td>
<td>64.58%</td>
<td>2.54%</td>
</tr>
<tr>
<td>M₂₃C₆</td>
<td>24.91%</td>
<td>52.70%</td>
<td>14.11%</td>
<td>8.27%</td>
</tr>
<tr>
<td>M₆C</td>
<td>47.09%</td>
<td>44.62%</td>
<td>6.87%</td>
<td>1.42%</td>
</tr>
</tbody>
</table>

Table 5.3 – Equilibrium Compositions of Carbide Types Present in 2.25Cr-1Mo Steels (in wt%)
5.4.2 Carbide Dissolution Behavior

Figure 5.33 shows the dissolution behavior of the different carbides. The group of curves in the left side of the figure show the time to 25% dissolution based on carbide mass. As expected there is a strong dependence on temperature and carbide type with a nearly logarithmic relation of decreasing dissolution time with increasing temperature. While this method considered the effect of the different carbide structure, the size and shape distribution was not considered. Because of this, the relative ranking of dissolution between the different types are for an equivalent size which was selected based on the carbides present after the solution heat treatment experiments in Section 5.2. In practice, the scale of the different types of precipitates can be vastly different, as seen in Figure 2.14, which could have a large impact on dissolution behavior. This effect is seen based on the solution austenization treatments discussed in Section 5.2 which are overlaid on Figure 5.33. Based on the model, at both heat treatments at 1148°C (2100°F) all types of carbides would be fully dissolved but there were still precipitates present in these samples. This is likely the result of precipitates of larger scale taking longer to dissolve.

\( \text{M}_3\text{C} \)

The carbide with the fastest dissolution at all temperatures was the \( \text{M}_3\text{C} \) type. Note that this is also true for the time to complete dissolution which is shown in the group of curves located on the right side of the figure. This matches well with experimental findings based on the precipitation sequence in these alloys. In actual practice, the composition of this type of carbide would likely vary significantly from the equilibrium
value. In carbides formed as a result of autotempering or shorter times at lower tempering temperatures, the diffusion of Mo and Cr would be reduced and therefore the carbide would contain much less of these elements than 17% and 36% as indicated by the equilibrium calculations. The result of this higher concentration of extra slow diffusing solute would retard dissolution when compared to carbides with higher fraction of Fe present.

Figure 5.33 – Time to 25% and 100% Dissolution of Different Types of Carbides

$M_2C$
The next fastest dissolving carbide is $M_2C$. During the earlier stages of dissolution, there is an increased rate of dissolution at $1227^\circ C$ and $1327^\circ C$ data points, but this effect is not as noticeable in the time to 100% dissolution curve. The time to completely dissolve the $M_2C$ type exceeds that of the $M_{23}C_6$ type despite the faster initial rate of dissolution. As with the $M_3C$ carbide, the composition of the $M_2C$ carbide calculated at thermodynamic equilibrium may not be representative of tempered samples. Pilling and Ridley found the composition of the $M_2C$ carbide to be richer (> 50%) in Mo after tempering at $700^\circ C$ with an increasing fraction with longer tempering times [50]. They also found an increasing fraction of Cr present in the carbide structure with increasing carbon content. However, in that study the highest carbon content composition that they studied was 0.09 wt%. At the higher carbon content of the composition simulated, this makes it reasonable to project a higher Cr concentration in the carbide phase.

$M_{23}C_6$

In the initial stages of carbide dissolution, the $M_{23}C_6$ type is the next type to dissolve. Below $1100^\circ C$ the time to 25% dissolution almost matches that of $M_2C$ and at $1400^\circ C$ it actually dissolves faster. $M_{23}C_6$ is faster to completely dissolve than all other types except for $M_3C$. At temperatures below $1100^\circ C$, the relative difference between dissolution time for $M_{23}C_6$ and $M_3C$ decreases.

$M_7C_3$

The $M_7C_3$ is the next fastest dissolving type. At most temperatures it lags slightly behind $M_{23}C_6$ at both dissolution levels investigated, but it the time to reach 25% at $927^\circ C$ is less
than that of $M_{23}C_6$. For the time to complete dissolution $M_7C_3$ is always slower than $M_{23}C_6$ but at below 1100°C it is faster to dissolve than $M_2C$.

$M_6C$

The slowest dissolving precipitate is $M_6C$. It takes a longer time to dissolve 25% and 100% than any other carbide investigated except at 927°C where it nearly matched the dissolution rate of $M_3C$.

**5.5 Impact of Welding on Carbide Dissolution**

5.5.1 **Effect of Carbide Dissolution on the As-Welded Microstructure**

Based on the results of Section 5.4.2, the differing rate of dissolution for the different carbide types will have an impact on the microstructure in the HAZ. Although all carbide types dissolve a significant amount near the fusion boundary, the more complex alloy carbides will undergo significantly less dissolution than the $M_3C$ type, especially the $M_6C$ type. In Figure 5.33, the time at temperature of an example welding thermal cycle is shown in conjunction with the dissolution curves. In the region corresponding the CGHAZ (peak temperature of 1400°C), there is well over 25% dissolution of all types of carbides simulated. Although not all researchers have found evidence of this carbide in the HAZ region, it is commonly listed as an equilibrium precipitate in conjunction with either $M_{23}C_6$ or $M_7C_3$, which gives empirical confirmation of the resistance to dissolution [46,51,77].
Further from the fusion boundary, where peak temperatures are lower, the difference in the dissolution rates would result in different amounts of solute being solutionized by the welding process. In particular, the increased dissolution rate of M$_2$C in the 1227°C to 1327°C range correlates reasonably well to that secondary hardening peak illustrated in Figure 5.31. If as a result of prior heat treatment there was M$_2$C present in this region, it had likely coarsened to beyond the effective size and distribution for a strong increase in hardness. Due to the higher dissolution rate, the precipitate undergoes further dissolution than that at any other distance from the fusion boundary. In heats that had been subjected to different preprocessing conditions that resulted in a microstructure with a higher fraction of M$_7$C$_3$, M$_{23}$C$_6$ and M$_6$C (versus the faster dissolving M$_3$C and M$_2$C) the resulting average HAZ will have lower hardness in the as-welded condition. In areas further away from the fusion boundary (peak temperature of 1100°C), there is still dissolution, but less than 25% weight fraction for all carbide types.

5.5.2 Effect of Carbide Dissolution on the Post Weld Heat Treated Microstructure

Upon tempering during the post weld heat treatment (PWHT) cycle, M$_2$C can precipitate leading to the secondary hardening effect. The location of the secondary hardening peak at between HT-3 and HT-4 can be particularly problematic because HT-3 was selected to match a currently used practice for PWHT. In practical application, because of the size of the subject components, the relatively slow heat and cooling rates can increase the effective tempering time which could lead to some secondary hardening behavior as compared to considering only the time at prescribed temperature during heat treatment.
5.5.3 Prevention of Heat Affected Zone Hardening

Based on the TTP diagrams presented in Figure 5.28, it can be seen that different tempering temperatures can result in different precipitate morphology and distribution. In order to slow the dissolution of carbides from the welding cycle, it would be preferable to have a higher fraction of the coarse complex alloy carbides. This could be achieved by increasing the temperature (and possibly time) of the preprocessing tempering treatments into the range which results in the formation of $M_7C_3$, $M_{23}C_6$ and $M_6C$. While this may help to decrease the HAZ hardness in the as-welded condition and reduce PWHT times to meet the desired 250 VHN hardness level, it may be detrimental to the resistance of the structures to sulfide stress corrosion cracking. Nickel clad low alloy steel weldments are especially susceptible to hydrogen embrittlement in the region of planer growth in the partially melted zone [78]. In AISI 8630-625 overlay welds, there is a significant increase in the concentration of carbon resulting from diffusion of carbon to the interface between the base material and fusion zone after a PWHT of 677°C for 8 hours. This results in an area of hardness significantly higher than the bulk HAZ hardness, however 8630 has a significantly higher carbon content. Additionally, the beginning stages of $M_7C_3$ carbide precipitation has been observed in this area after a PWHT of 15 hours at 649°C which can provide a trapping site for hydrogen leading to potential embrittlement [79].

Regardless of the initial microstructure, the carbides in the region very near to the fusion boundary will fully dissolve resulting in carbon which is available to diffuse to the
interface. However, reducing the tempering time to decrease the average HAZ hardness to acceptable levels may reduce the build-up of carbon in the PMZ by limiting the time at increased temperatures which facilitate diffusion. However, in this scenario the CGHAZ may have an increased sensitivity to hydrogen embrittlement as a result of larger and more numerous carbides to trap hydrogen.

5.5.4 Post Weld Heat Treatment Recommendations

The average hardness values shown in Table 5.2 – Average Heat Affected Zone Hardness and Best Fit Regression Parameters indicate that even in the longest tempering treatment at the highest temperature, not all heats reached the prescribed maximum hardness of 250VHN. One possible solution to this issue would be to increase the amount of tempering time at the currently used 638°C tempering temperature. However, one problem with this approach is that based on the Baker and Nutting diagram (Figure 5.28), times up to 50 hours at this temperature still result in $\text{M}_2\text{C}$ carbides. While at this long of time, there will be some coarsening of these precipitates, it is probable that there will still be some secondary hardening effect, resulting in a higher than expected hardness.

Another potential solution would be to increase the tempering temperature. This could potentially result in a reduction in tempering time depending on the temperature. At 700°C, a tempering time of approximately 3 hours would result in a microstructure containing $\text{M}_7\text{C}_3$ in addition to $\text{M}_2\text{C}$ and $\text{M}_3\text{C}$. At 750°C tempering times as short as 1 hour can result in $\text{M}_{23}\text{C}_6$ and $\text{M}_7\text{C}_3$ carbides. In these cases, the additional complex carbide types would speed the tempering process due to their tendency to coarsen rapidly.
while the higher temperatures used would help avoid the precipitation of M$_2$C carbides and thus avoid the secondary hardening behavior. This also could result in the reduction of the strength of the tempered structure to below that which is acceptable.

A third possible approach would be to decrease the tempering temperature, but increase the tempering time. By selecting a lower temperature, the tempering process would take place in a paraequilibrium condition. While the substitutional alloying elements cannot diffuse quickly enough to result in the formation of alloy carbides, the carbon is still sufficiently mobile to form Fe$_3$C type carbides. At 550°C, the tempering times can reach up to approximately 30 hours without producing M$_2$C carbides. This would serve to avoid the secondary hardening effect associated with its precipitation and also contribute to maintaining a higher strength because the substitutional alloying elements (Cr and Mo specifically) are not contained in the carbide structure, but rather free to have a solid solution strengthening effect.
CHAPTER 6: CONCLUSIONS

1) Austenization treatments of 954°C for one hour and 1148°C for one and four hours were not sufficient to result in the total dissolution of preexisting precipitates formed from prior processing.

2) Grain growth and carbide dissolution have competing roles in the as-quenched hardness of F22 steels.

3) The average as-welded hardness of the HAZ and fusion zone exceed that in the as-quenched base materials.

4) The initial material condition effects hardness distribution in the HAZ in the as-welded and tempered conditions of low heat input welding.

5) Many of the individual heats did not reach 250VHN in even the longest tempering treatments studied.

6) The secondary hardening response in individual regions of the HAZ effects the average tempering rate.

7) Developed a model based approach to simulate carbide dissolution in the HAZ.

8) Based on the model, different types carbides in the HAZ experience differing amounts of dissolution.
CHAPTER 7: FUTURE WORK

1) Base material carbide characterization
   a. TEM or matrix dissolution and XRD
      i. Similar compositions with variable known heat treatment history
      ii. Size, composition and distribution can be used to improve dissolution model

2) Gleeble™ Simulations of HAZ
   a. Gauge the impact of different heat inputs and to simulate a multipass cladding procedure
   b. Characterize carbide evolution in the PWHT process based on specific peak temperatures
   c. Expand tempering treatments to gauge impact of tempering temperature on temper rate
      i. Higher temperature effect on mechanical strength
      ii. Same Temperature, longer time effect on secondary hardening behavior
      iii. Paraequilibrium tempering time to required hardness
REFERENCES


