Multi-Scale Characterization of Heat-Affected Zone in Martensitic Steels

DISSERTATION

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By

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Abstract

Due to the heat induced by welding process, Heat-affected zone (HAZ) microstructure and properties may significantly differ from base metal in steels. Careful designed integrity of original microstructure and composition may not exist in HAZ after welding. As a result, there is need to understand HAZ microstructure from macro scale to nano scale. In current study, various characterization tools will be applied to understand microstructure at different scale. Two steels are studied.

The first steel studied is BlastAlloy 160 (BA-160). BA-160 is a low-carbon martensitic steel strengthened by copper and M₃C precipitates. Heat-affected zone (HAZ) microstructure evaluation of BA-160 exhibited softening in samples subjected to the coarse-grained HAZ thermal simulations. This softening is partially attributed to dissolution of copper precipitates and metal carbides. After subjecting these coarse-grained HAZs to a second weld thermal cycle below the Ac1 temperature (at which austenite begins to form on heating), recovery of strength was observed. Atom-probe tomography and microhardness analyses correlated this strength recovery to re-precipitation of copper precipitates and metal carbides. A continuum model is proposed to rationalize strengthening and softening in the HAZ regions of BlastAlloy 160. A hybrid in-situ characterization system, which couples the laser scanning confocal microscopy (LSCM) with the time-resolved X-ray diffraction (TRXRD) measurement with synchrotron radiation, was used to characterize the microstructure evolution during heat-
affected zone (HAZ) thermal cycling of high-strength and blast-resistant steel. The combined technique has a time resolution of 0.3 seconds that allows for high-fidelity measurements of transformation kinetics, lattice parameters, and morphological features. The measurements showed a significant reduction in the martensite start transformation temperature with a decrease in the prior austenite grain size. In addition, the LSCM images confirmed the concurrent refinement of martensite packet size with smaller austenite grain sizes. This is consistent with dilatometric observations. The austenite grain size also influenced the rate of martensitic transformation ($\frac{df_m}{dT}$); however, the measurements from the hybrid (surface) and dilatometric (volume) measurements were inconsistent. Challenges and future directions of adopting this technique for comprehensive tracking of microstructure evolution in steels are discussed.

Similar characterization techniques were used to investigate the HAZ of Grade 91 steels. Current research suggest that modification of the ASME A387 Code-specified tempering of Grade 91 [i.e. reducing pre-weld tempering temperature from 760°C to 650°C] has the potential to increase creep life in the welded plate. To understand this improvement, weld samples were made with standard condition [normalizing (1080°C), tempering (760°C), welding and post-weld heat treatment (760°C)], as well as, samples with pre-weld tempering temperature at 650°C. Creep life of welds made with modified tempering was almost 5 times longer than that of standard welds (2414 hours vs. 518 hours). Optical and electron microscopy characterization exhibited higher volume fraction of $\text{M}_2\text{C}_6$ carbides in standard pre-welding tempered condition (1.8 vol.%) than that of the
modified pre-welding tempered condition. In the samples subjected to standard pre-weld tempering and welding, carbides at martensite lath and prior austenite grain boundaries did not dissolve completely in the FGHAZ region. During PWHT, growth and coarsening of pre-existing carbides hinders the formation of carbides on prior austenite grain and martensite block boundaries. Since carbides on the boundaries provide creep resistance, this condition has poor creep strength. In contrast, the samples subjected to modified tempering; nearly 100% dissolution of small M$_{23}$C$_6$ carbides was observed in FGHAZ. During PWHT, new and fine carbides re-precipitated on grain boundaries in the FGHAZ and thereby providing good creep strength.
Dedication

To my beloved wife, Xiaodong Guo,

who has shown unimaginable love and encouragement during my PhD study
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List of Acronyms

BA-160  Blast Alloy 160
CBED  converge beam electron diffraction
CGHAZ  coarse grain heat affected zone
CSEF  creep strength enhanced ferritic
DSC  differential scanning calorimetry
EBSD  electron backscatter diffraction
FGHAZ  fine grain heat affected zone
FIB  focus ion beam
HAZ  heat affected zone
HRTEM  high resolution transmission electron microscopy
ICHAZ  inter critical heat affected zone
IVAS  Imago Visualization and Analysis
KS  Kurdjumov-Sachs
LEAP  local electron atom probe
LOM  light optical microscopy
LSCM  laser scanning confocal microscopy
PWHT  post weld heat treatment
ROI  region of interest
SANS  small angle neutron scatter
SAXS  small angle X-ray scatter
SCHAZ  sub critical heat affected zone

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<table>
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<th>Abbreviation</th>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TOF</td>
<td>time of flight</td>
</tr>
<tr>
<td>TRXRD</td>
<td>time resolved x-ray diffraction</td>
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1.1 Multi-scale characterization

Understanding microstructure and phase transformation in HAZ is important for solving weldability problems related to HAZ. One or two characterization techniques will be not sufficient to understand HAZ microstructure. For example, electron microscopy is one the most popular technique for materials scientists. However, electron microscopy cannot provide 3D information of the material. Sometimes the result may be biased since electron microscopy image use 2D projection to represent 3D features. Atom probe tomography can be used to obtain steel 3D composition and help to understand electron microscopy result. In addition, most electron microscope characterizations are ex-situ. Phase transformation information can be only speculated from ex-situ results.

To gain comprehensive understanding of HAZ in steels, multi-scale characterization techniques with both in-situ and ex-situ capability need to be used. The focus of the current research is to develop a scientific basis for evaluating HAZ microstructures of martensitic steels using the following multi-scale characterization techniques.

Optical microscopy techniques: Optical microscopy has been widely used to analyze steel microstructure. It is a technique that is easy to learn and use. According to Rayleigh criterion the resolution limit of a light microscope using visible light is about 200 nm. As a result, optical microscopy can be used to
look at steel grains, microstructure, precipitate, inclusions and so on from mm to μm scale.

Electron Microscopy techniques: Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the most commonly used electron microscopy. Electron microscopy is often used to look at features from μm to nm scale.

Time resolve X-ray diffraction techniques (TRXRD): TRXRD can track phase transformation in HAZ in real time. In welding, the phase transformation occurs during fast heating and cooling. As a result, TRXRD is an ideal tool to study phase transformation in HAZ. With X-ray generated by synchrotron source and high speed pixel camera, small amount of phase change (less than 0.5%) can be captured with a time resolution of 0.01-0.1 second.

Atom probe tomography: Atom probe is use to study steel composition in nano-scale. It is a good technique for the study of nano-scale precipitate, segregation, interfaces and so on.

Spatial hardness mapping: Traditional hardness test is used to evaluate mechanical properties of specific region. However, if multiple locations need to be tested, it is time-consuming. Recently, automatic microhardness testing is developed and microhardness maps can be generated. Microhardness map can be used to determine HAZ width, segregation bands, comparing hardness in different regions and so on.
Two steels, blast-resistant naval steel and creep strength enhanced ferrite steel, will be studied using above characterization techniques. The observed microstructure and strengthening behavior will be rationalized using existing strengthening models.

1.2 Motivation

1.2.1 Blast-resistant naval steel

To meet the rigorous requirements for US Navy hull and deck application, a blast resistant steel, BlastAlloy 160 (BA-160), was developed by Northwestern University researchers [1,2]. This steels is based on a low carbon martensitic matrix that is strengthened by nanometer sized Cu-rich precipitates and M_{2}C precipitates (where M = Cr, Mo, and V). The yield strength of BA-160 is 1104 MPa (160 ksi). Overarching goal of this development activity is to replace the currently certified high strength low-alloy 100 (HSLA-100, yield strength 100 ksi) steels for better blast-resistance in surface ship structure. In order to meet this goal, the steel has to be weldable. Previous research found softening and abnormal hardening in heat-affected zone (HAZ) [3]. Current research pertains to the study of strength recovery of HAZ and kinetics of martensitic transformation. The activities include electron microscopy and atom probe characterization, time-resolved X-ray diffraction by synchrotron radiation, as well as, thermodynamic and kinetic modeling of the microstructure evolution in HAZ region. The above
data can be used to fine tune the base metal, as well as, design welding process parameters.

1.2.2 Creep strength enhanced ferritic steels

Global warming is caused by greenhouse gases. 72% of the totally emitted greenhouse gases are carbon dioxide (CO₂). Due to the heavy use of fossil fuels, fossil fired power plants are a major CO₂ producer. The worldwide annual emission of CO₂ from fossil fuel combustion is over 5.4 billion tons [4]. The reduction of CO₂ emission and improve efficiency can be achieved by increasing the steam parameters in the power plant. For example, the increase in steam parameter (steam temperature and steam pressure) from conventional 538 °C and 24.1 MPa to 650°C and 34.3 MPa can save the energy used by 6.5%, which results in a significant decrease in coal use, and hence the reduction of CO₂ emission [5].

The increase in steam parameters requires extensive research and development on the steels associated with the construction of reliable boilers and turbines. A large variety of steels were developed and used for different purposes in fossil fired power plant in the past several decades. Creep strength-enhanced ferritic (CSEF) steels (such as the ASTM A387 Grade 91) are widely used as tubing and piping in fossil fired power plants to increase efficiency.

The performance of CSEF steels, however, does not always meet expectations, and there have been reports of numerous failures in HAZ of CSEF steels after only a few years in service [6]. The optimum properties in CSEF steels are
achieved by producing a fully-tempered martensitic microstructure through a specific normalization and tempering sequence of heat treatment. However, traditional welding and subsequent post-weld heat treatment (PWHT) significantly alters this microstructure which results in welded joints with a variety of microstructures that includes weld metal with large compositional gradients, as well as both coarse and fine-grained heat-affected zones (HAZ). It is well-established that microstructures developed in the fine-grained HAZ regions can significantly reduce creep life up to 20% or less when stress is low [7, 8, 9, 10]. Also, the size and orientation of the fine-grained HAZ can lead to high triaxial stress states that may contribute to accelerated creep damage [11,12]. This combination results in so-called 'Type-IV' failures in CSEF steels and studies show that the creep strength reduction of such joints can be on the order of 50% compared to base metal. The implications of such failures include disruptions of electrical supply, increased cost of electricity, and the potential for failure endangering the safety of power plant personnel. There is an urgent need to improve the creep strength of the weldments. Current study is going to investigate the effect of pre-weld tempering temperature on weldments creep performance.
Chapter 2. Background

This chapter will provide background information of two steels in the current study: BA-160 and Grade 91 steel. HAZ issue of both steels will be discussed. In addition, literature review also is done on different characterization techniques.

2.1 BlastAlloy160 (BA-160) Steel

Since BA-160 steel is one of the steels in the current study, its design and development will be elaborated in this section. The strength and toughness of BA-160 is achieved by a combination of dispersed Ni-enriched austenite for transformation toughening and nano-size Cu and M$_2$C precipitate strengthening within martensitic matrix. Prototype evaluation tests were also performed to confirm the microstructure and mechanical properties.

2.1.1 Alloy design

The steels requirement for naval hull materials in the year 2020 are the achievement of high impact toughness (C$_V$>85 ft-lbs or 115J corresponding to fracture toughness, K$_{IC}$>200 ksi in$^{1/2}$ or 220 MPa m$^{1/2}$ and K$_{IC}$> 250 ksi in$^{1/2}$ or 275 MPa m$^{1/2}$) and high yield strength (150-180 ksi or 1030-1240 MPa). To achieve the requirement, proper materials design method should be applied. According to Olson [13], materials design can be achieved by breaking down the structure into
subsystems. Each of the subsystems has an interaction with the others. The flow block diagram can be used to present the interaction between subsystems. Systems design chart for BA-160 is shown in Figure 2.1. In steel-making, from Iron Ore to final steel, there are many processes involved, as shown in the left column of Figure 2.1. Each process will have one or more affects on the microstructure. On the other hand, microstructure will control mechanical properties and weldability of steels. The aim of the alloy design is to maximize toughness-strength combination without decreasing weldability. Since it is well known that all strengthening methods (except grain refinement) will reduce the toughness, it is a difficult job to design steel with both high strength and high toughness.

Figure 2.1 system chart for design of blast resistant naval hull steels [1]
According to Saha [1], BA-160 matrix is a mixture of secondary hardened bainite and martensite to get good toughness. However, our later analysis on BA-160 found it is 100% martensitic microstructure. In addition, Ni stabilized austenite
dispersion will be designed to provide transformation toughening. The strength of the steel will be achieved by designing a fine dispersion of precipitates, including M$_2$C carbides and Cu precipitates. The strength contribution from M$_2$C carbides and Cu precipitates were quantitatively determined. Since hardness has a monotonical relationship with yield strength, it is used to assess the yield strength of steel. Figure 2.2 plots the hardness vs. yield strength for low carbon steels with a best-fit power-law curve and linear curve. According to Figure 2.2, for the target yield strength of 160ksi, the design hardness of the steel should be 389 VHN. Graville diagram (Figure 2.3) shows the tendency of hydrogen induced cracking with respect to carbon content and carbon equivalent. To avoid hydrogen-induced cracking, carbon content is set to be 0.05 wt.% However, Figure 2.3 is only used for low alloy steel. Steel with high alloy content may not be relevant for the diagram. Since carbon equivalent of BA-160 is larger than 1.5, 0.05 wt.% carbon cannot guarantee avoiding hydrogen-induced cracking.

When the size of M$_2$C is larger than 3nm, the strengthening mechanism is Orowan bypass. Wise [14] developed strengthening model shows the relationship between hardness increment by M$_2$C and nominal carbon content (Figure 2.4). The model assumed full equilibrium carbide volume fraction at tempering temperature and carbides size is fixed. Based on Figure 2.4, for 0.05 wt.% carbon, the maximum hardness increment by M$_2$C could be 175 VHN. Saha also claimed that the hardness contribution from lath martensite matrix is 67 VHN according to Wise. The rest of the hardness contribution, which is 151 VHN, should be from BCC Cu precipitates. The strengthening mechanism of BCC Cu is explained in Chapter
2.1.2. Figure 2.5 shows the hardness increment due to BCC Cu strengthening vs. Cu content in Cu bearing steel. A best-fit one-half power curve is superimposed. Based on this model, if hardness contribution from BCC Cu is 151 VHN, the Cu content should be 3.25 at.%.

However, the hardness contribution from lath martensite is much higher than 67 VHN. Yu [3] shows in coarse-grained HAZ of BA-160, no precipitates are found in the matrix. The hardness is 340 VHN, which is purely from the contribution of martensite. As a result, martensite should be the major contributor for high strength of BA-160. Figure 2.4 and Figure 2.5 are either incorrect or does not apply to BA-160.

Good fracture toughness is another major priority for the design of blast-resistant steel. However, it is difficult and expensive to measure fracture toughness parameters (e.g. $K_{IC}$ and $K_{ID}$). Saha used Charpy V-notch impact energy ($C_v$), which is inexpensive, can be used to estimate fracture toughness parameters ($K_{IC}$ and $K_{ID}$). For $K_{IC}$ fracture toughness of 250 ksi in$^{1/2}$, the corresponding $C_v$ is 85 ft-lbs. However, this approximation may not be correct. Charpy impact has a high strain rate and CTOD which used to measure fracture toughness is a process with slow strain rate. These failure mechanisms are totally different [15].
Figure 2.4 Effect of $M_2C$ carbides (measured by alloy carbon content) on Vickers hardness

[1]

Figure 2.5 Effect of Cu precipitates (measured by alloy Cu content) on Vickers hardness [1]
2.1.2 Strengthening mechanism

Understanding strengthening mechanism is important for both steel design and weldability evaluation. Since there is a misunderstanding on strength contribution from Cu precipitates and martensite matrix, strengthening mechanism is discussed in this section.

For martensitic strengthening, the yield stress of the lath martensite is calculated by the summation of the hardening mechanisms [16]:

\[ \sigma_{ys} = \sigma_0 + \sigma_s + \sigma_\rho + \sigma_g + \sigma_p \]

(2.1)

where \( \sigma_0 \) is the friction stress to move dislocations for pure Fe, \( \sigma_s \) is the yield strength increment due to solid solution hardening, \( \sigma_\rho \) is the strengthening term as a function of dislocations density, \( \sigma_g \) is the grain boundary strengthening and \( \sigma_p \) is the precipitate strengthening.

2.1.2.1 Cu precipitation Strengthening

It is generally agreed that the maximum strengthening of Fe-Cu steels is achieved by BCC Cu precipitates that are coherent with the matrix. On the other hand, the strengthening induced by FCC Cu precipitates is limited. FCC Cu precipitates have a KS orientation relation with the BCC Fe matrix. Due to the presence of many common slip planes, dislocations are easy to glide [17] with negligible hardening effect. As a result, only precipitation strengthening from Cu rich BCC precipitates is discussed here. The mechanism of strengthening from fine precipitates can be explained by the interaction between precipitate and
dislocation. Two mechanisms exist: one is cutting through mechanism for weak precipitate and the other is the Orowan looping mechanism for strong precipitates. Since BCC Cu precipitate is recognized as week precipitate, the cutting through mechanism is applied. It is generally believed that there are four contributions for strengthening when a dislocation cuts through a precipitate [18].

**Misfit strengthening**

Misfit effect is also named coherency strain effect. Since BCC Cu has a different atomic volume with the Fe matrix, a strain field is produced around the precipitate and acts as an internal stress against the movement of dislocation [19]. For strengthening by precipitate which has an ordered structure, Brown and Ham [20] reported the increment of shear stress ($\Delta \tau_{mis}$) by coherency strain effect as following:

$$\Delta \tau_{mis} = 4.1G(\varepsilon_s)^{3/2}f^{1/2}(r/b)^{1/2}$$

where $G$ is the shear modulus of the matrix (Pa), $\varepsilon_s$ is the coherency strain or misfit parameter, $f$ is the volume fraction of the precipitates, $r$ is the precipitate radius (nm) and $b$ is magnitude of Burgers vector (nm). The misfit parameter $\varepsilon_s$ is expressed as:

$$\varepsilon_s = 2\Delta d/3d$$
$d$ is the lattice parameter of the matrix and $\Delta d$ is the lattice parameter difference between precipitate and matrix. The lattice parameter of BCC Fe ($d_{Fe}$) is 0.28665 nm at the room temperature. For precipitate with 60 at. % Cu and 40 at. % Fe, the lattice parameter is estimated to be 0.2891 nm, which gives $\Delta d_{Fe-Cu}/d_{Fe}=0.0085$. The volume fraction of BCC Cu precipitates at aged condition is found to be 0.03 [21]. Shear modulus for iron is considered to be 80 GPa and $r/b$ is taken to be 2.5. The calculated misfit strengthen $\Delta \tau_{mis}$ is found to be 38.7 MPa, which is small compared to the overall yield strength of BA-160 (1097 Mpa).

**Elastic modulus difference strengthening**

The energy in dislocation is a function of local modulus. As a result, precipitate with significant difference in modulus from matrix will either raise or lower the dislocation energy in the interaction of dislocation and precipitate. Strengthening of low carbon Fe-Cu steels is usually described by modulus strengthening based on the model developed by Russell and Brown [15]. This difference in the shear modulus of BCC Cu precipitates and BCC Fe (ferrite) matrix result in a large difference in dislocation energy between these phases. The difference impedes the dislocation movement. Fine [16] cited the wrong equation from Russell and Brown by considering a term in condition as a multiplier in strengthening equation. The conclusion is drawn that the modulus difference played an insignificant role in strengthening. The misuse of the modulus difference equation leads to the wrong conclusion. Since modulus difference strengthening model play an important role in strengthening, it should not be ignored. It is realized Russell and Brown model has some limitations in BCC Cu precipitate
strengthening, such as using FCC Cu bulk shear modulus to estimate BCC Cu precipitate shear modulus.

Spherical precipitates are assumed as secondary phase distributed in the martensite matrix. The shear modulus of precipitates is smaller than the matrix. If a stress is applied on the material, dislocations will move and cut through an array of precipitates. The yield stress induced by precipitates is a function of effective inter-precipitate distance and the critical angle:

\[
\tau = 0.8 \frac{Gb}{L} \cos \left( \frac{\Phi_c}{2} \right)^{1/2}, \Phi_c \leq 100^\circ \quad (2.4)
\]

\[
\tau = \frac{Gb}{L} \left[ \cos \left( \frac{\Phi_c}{2} \right) \right]^{3/4}, \Phi_c > 100^\circ
\]

where \( G \) is the shear modulus of the matrix, \( b \) is the burger vector, \( L \) is effective inter-precipitate distance and \( \Phi_c \) is the critical angle. The critical angle is defined as the cut through angle when dislocation is about to break though the precipitate, which is shown is Figure 2.7(b).
For the case that one dislocation is cutting through a precipitate, the equilibrium of the dislocation requires that

\[ E_M \sin \alpha_M = E_P \sin \alpha_P \quad (2.5) \]

where \( E_M \) and \( E_P \) are the dislocation energy in matrix and dislocation energy in precipitate. \( \alpha_M \) and \( \alpha_P \) are the angles shown in Figure 2.6 (a).

If the dislocation energy in precipitate is smaller than that in matrix, the cutting angle has a minimum value when the precipitate is about to cut through the precipitate, which is the critical angle shown in Figure 2.6 (b). The dislocation equilibrium and critical angle can be expressed as:

\[ E_M \sin(\phi_c/2) = E_P, \quad \phi_c/2 = \sin^{-1}(E_P/E_M) \quad (2.6) \]

Substituting the critical angle into equation 2.3, the yield stress as a function of dislocation energy in precipitate and in matrix can be given by:
According to Russell and Brown, for a spherical precipitate with a radius of \( r \), the ratio of dislocation energy in precipitate can be described as:

\[
\tau = 0.8 \frac{G_b}{L} \cos \left(1 - \left(\frac{E_P}{E_M}\right)^2\right)^{1/2} \sin^{-1}\left(\frac{E_P}{E_M}\right) \leq 50^\circ \tag{2.7}
\]

\[
\tau = \frac{G_b}{L} \cos \left(1 - \left(\frac{E_P}{E_M}\right)^{3/4}\right) \sin^{-1}\left(\frac{E_P}{E_M}\right) \leq 50^\circ \tag{2.8}
\]

According to Russell and Brown, for a spherical precipitate with a radius of \( r \), the ratio of dislocation energy in precipitate can be described as:

\[
\frac{E_P}{E_M} = \frac{E_P^0 \log \frac{r}{r_0}}{E_M^0 \log \frac{R}{r_0}} + \frac{\log \frac{R}{r}}{\log \frac{R}{r_0}} \tag{2.9}
\]

where \( E_P^0 \) is dislocation energy per unit length in precipitate, \( E_M^0 \) is dislocation energy per unit length in matrix, \( r \) is the average radius of precipitates. \( r_0 \) is inner cut-off radius, which is 1.2 nm and \( R \) is outer cut-off radius, which is 1000 \( r_0 \). It is assumed that bcc Cu has the same shear modulus as FCC Cu. Estimated dislocation energy ratio per unit length \( E_P^0/E_M^0 \) is around 0.6. Assume 3.5 vol.% Cu precipitates with a size of 3nm, \( \Delta \tau_{EMD} \) is 283Mpa.

**Chemical strengthening**

When a dislocation passes through a precipitate, some atoms in the precipitates will be dissolved in the matrix and form solid solution. The force required to cut through a precipitate is given [17]:

\[
F_{cs} = (\Delta U / b)(2r / b) \tag{2.10}
\]
$\Delta U$ is the change in energy per atom for on slip step, $r$ and $b$ is the same as described before. The shear stress increment is a function of the force required to shear a precipitate according to Friedel-Bronm-Ham equation:

$$\Delta \tau_{cs} = \frac{2}{bL(0.5Gb^2)^2} \left( \frac{F_{cs}}{2} \right)^{3/2}$$  \hspace{1cm} (2.11)

From calculation of Fine [17], $\Delta \tau_{cs}$ is less than 75 MPa. As a result, chemical strengthening should not be major contributor to the increase of yield stress.

Dislocation core-precipitate interaction strengthening

Recently, it is realized that the effect of dislocation core on BCC Cu structure also plays an important role in BCC Cu strengthening. Since the Cu precipitate discussed in the present study is about several nanometers, which is not much larger than the dislocation core radius (>1nm), the interaction between dislocation core and precipitate should not be ignored. The interaction energy of dislocation core and precipitate could be estimated by first principle [22,23] and molecular dynamic calculation [24]. The flow stress to move the dislocation through precipitate is a function of interaction energy. As a result, the strengthening due to dislocation core-precipitate interaction could be calculated. Fine estimated $\Delta \tau$ is about 170MPa. However, it is assumed that the dislocation moves through the precipitate as a straight line, which is not true. As a result, the estimated interaction energy is much higher. $\Delta \tau$ should be much less than 170MPa.

2.1.2.2 Maternsite Sub-structure Strengthening

In ferrous alloy, martensite can be divided into three groups based on morphologies: lath martensite, lenticular martensite and thin plate martensite [25].
Due to the superior industrial significance, lath martensite is widely studied [26, 27, 28, 29, 30]. The size of the martensite lath is about 300 nm in thickness, 2.8 μm in width and 100μm in length [31]. As a result, individual lath cannot be observed by optical microscope. However, when austenite is transformed to martensite, martensite laths tend to align themselves parallel one to another in a large area of the parent grain [29]. Therefore, lath martensite exhibits a characteristic microstructure at the optical microscopic scale. Figure 2.7 shows optical and TEM micrographs of lath martensite in Fe-0.2C steel.

![Optical and TEM micrographs of lath martensite in Fe-0.2C steel](image)

**Figure 2.7 Optical and TEM image showing lath martensite microstructure [29]**

The current theory of lath martensite states that martensite inside one prior austenite grain can be divided into packets (group of laths with the same habit
plane) with each packet being further subdivided into blocks (group of laths of the same orientation or same variant), as illustrated in Figure 2.9 [29]. Since packet and block size are considered as the effective grain sizes in lath martensite, packet and block size play an important role in the strengthening of martensite. As a result, characterizing lath martensite morphology and crystallography become a critical aspect to understand the strengthening of martensite. Recently, many studies have been conducted on the morphology and crystallography of lath martensite [24-29]. Basically, two orientation measurement techniques are used, either convergent-beam electron diffraction (CBED) from a local region using transmission electron microscopy (TEM) or electron backscatter diffraction (EBSD) in a scanning electron microscopy (SEM). Since orientation maps can be obtained by EBSD but not CBED, EBSD is used in current investigation to study martensite sub-structure.
Figure 2.9 shows schematic comparison of martensite sub-structure between low carbon and high carbon martensite. In low carbon martensitic steels, there are two variants in the same block. However, there is only one variant in the same block in high carbon steel. In addition, there is no specific pair of block variant is formed in a packet.
2.2 Weldability of BA-160

The BA-160 steel has been assumed to be weldable without susceptibility to hydrogen-induced cracking based on a low-carbon concentration (<0.05 wt.%). This assumption is based on the tendency for hydrogen embrittlement in the heat-affected-zone (HAZ), which requires a hard microstructure (such as martensite with a high carbon content), hydrogen concentration and a triaxial state of stress.

In addition to hydrogen-induced cracking, the weldability of steel must consider solidification cracking in the weld metal (WM) region, liquation cracking in the HAZ and WM region, ductility dip cracking, reheat cracking, along with the final mechanical properties of the various weld regions. Yu et al [3] studied hardness and microstructure of different HAZ regions. A plot of Vickers microhardness vs. peak temperature for the simulated HAZ samples is presented in Fig. 2.10. Also
shown is a dashed line indicating the base metal microhardness value of 402 HV. The microhardness profile exhibits a maximum value in the ICHAZ, with the lowest microhardness occurring in the CGHAZ sample. A slight decrease in microhardness was experienced for both the SCHAZ and FGHAZ samples.

Figure 2.10 Measured Vickers microhardness as a function of peak temperature for the simulated HAZ samples exhibits anomalous hardening in samples heated to 750°C.

EBSD maps for all simulated HAZ samples are displayed in Figure 2.11. The samples exhibit a typical lath martensitic microstructure for all heat treatments. Since no detectable phase transformation occurs for the SCHAZ sample, no significant martensite and prior austenite grain morphology change is observed.
compared to the reference base metal specimen. Fine martensite packets with
diameters of approximately 1 μm are found in the ICHAZ. The fine packet size
results from small austenite grains formed during heating which did not have
sufficient time to grow, due to the short time above the Ac1 temperature. Also
visible in the ICHAZ are some larger martensite packets (indicated by arrows in
Figure 2.11c) which suggests they did not transform to austenite. Fine and coarse
prior austenite grains are clearly revealed in Figure 2.11c and d. In the base metal
and simulated HAZ samples with a peak temperature larger than 900°C, the
martensite packet size is close to the prior austenite grain diameter, which implies
there is only one packet inside each prior austenite grain. There are several
packets, however, in one prior austenite grain in the CGHAZ: two packets,
designated P1 and P2, and two blocks, designated B1 and B2, are shown in Figure
2.11e.
Figure 2.11 Measured EBSD images from (a) base metal; (b) SCHAZ; (c) ICHAZ; (d) FGHAZ; and (e) CGHAZ show different martensite sub-structures
The evolution of Cu precipitates in the HAZ was characterized by Atom probe tomography. Cu atom maps for different simulated HAZ conditions are displayed in Figure 2.12a, c, e, and g. The regions of high Cu concentration are clearly discernible in Figure 2.12a and c. The presence of high Cu concentration regions in the SCHAZ and ICHAZ indicates that the Cu precipitates are not fully dissolved. In Fig. 5e and g, no Cu-enriched zones are observable as the Cu atoms are almost homogeneously distributed in the FGHAZ and CGHAZ samples. The absence of Cu precipitates implies their dissolution in the FGHAZ and CGHAZ.

To interpret the hardening and softening phenomena in Figure 2.10, Yu applied available models to evaluate the microstructural strengthening in the HAZ regions. Emphasis has been put on the effects of lath martensite morphology and the size of Cu precipitates on strengthening. The predicted strength difference change vs. hardness increment is plotted in Figure 2.13. A near linear relationship between the predicted strength and measured microhardness implies that the strengthening models can be used to evaluate the strengthening of the HAZ regions.
Figure 2.12 Three-dimensional LEAP reconstructions of simulated HAZ regions: Cu atom maps are shown in (a) SCHAZ; (c) ICHAZ; (e) FGHAZ; (g) CGHAZ. Corresponding reconstruction of copper atoms in precipitates, as detected by the envelope method, are shown in (b) SCHAZ; (d) ICHAZ; (f) FGHAZ; and (h) CGHAZ.
Figure 2.13 Predicted strength increment due to martensite sub-structure and Cu precipitate compared with experimentally measured hardness changes in the corresponding regions.

To validate the preceding thermal simulations, gas tungsten arc (GTA) spot welds were made on BA160 samples [71]. Vickers microhardness traverse...
across spot weld HAZs showed a similar phenomenon as that observed from Gleeble samples. Softening is shown close to the fusion line (i.e., CGHAZ) and hardening is observed in the ICHAZ. These results confirmed the presence of four distinct HAZ regions in the spot welds.

Figure 2.14 Vickers microhardness traverse across GTA spot weld [71]

It is conceivable that PWHT could reinstate strength in the HAZ. For example, autogenous spot welds in the BA160 sample were post weld heat treated at 823 K (550 °C) for 30 minutes or 723 K (450 °C) for 5 hours. [71] Strength recovery was
observed after PWHT in the fusion zone and HAZ (Figure 2.15). The observed strength increase was assumed to be the result of reprecipitation during the PWHT. The PWHT is not feasible for naval applications due to the size or complexity of the structures that are welded. Alternatively, strength recovery in the HAZ (or weld metal) could be achieved by designing an appropriate multi-pass welding procedure that leads to a similar extent of re-precipitation during PWHT. Most of the HSLA structural steel plates currently used in shipyards are in the range of 6 to 30 mm (0.25 to 1.25 in.) with yield strength from 448 to 689 MPa (65 to 100 ksi). The thickness of heavier gage plate could be as high as 83 mm (3.25 in.). Though the plate thickness of BA160 will be reduced due to the high yield strength, the envisioned thickness for naval applications (>6 mm) is still too high for single pass welding. As a result, multi-pass welding is required for most applications.
Figure 2.15 Hardness traverse across microstructural regions of BA-160 spot weld following each step of PWHT procedure [71]

Caron also performed hot-ductility tests on BA-160. The hot ductility test result is shown in Figure 2.16. Nil-Ductility Temperature (NDT) for BA-160 is 1419°C, Nil-Strength Temperature (NST) is 1451°C, and Ductility Recovery Temperature (DRT) is 1303°C. Liquation Cracking Temperature Range (LCTR) is 148°C, which implies HAZ liquation cracking susceptibility is not severe.
Simulated Reheat Cracking test result for BA-160 is shown in Figure 2.17. When temperature is in the range between 450°C and 700°C, BA-160 ductility values is above 50% reduction. The result indicates BA-160 is not susceptible to reheat cracking.
The weldability of BA-160 has been evaluated. Previous research showed softening in HAZ. As a result, there is a need to mitigate softening in HAZ based on the understanding of BA-160 microstructure. Hot ductility test showed slow ductility recovery of BA-160. However, the reason of this slow recovery is not fully understood. In addition, the tendency of hydrogen-induced cracking still needs to be evaluated.

### 2.3 Creep Strength Enhanced Ferritic (CSEF) Steels

The second steel studied is creep strength enhanced ferritic steel (CSEF). First, fundamentals of creep mechanism will be discussed. Then history of CSEF and Type IV failure will be reviewed.
2.3.1 Creep

Creep can be described as a slow and continuous deformation of a solid material when exposed to a constant load or stress [32], which is below the yield strength of the material. Creep deformation is a thermally activated process. For a certain material with a certain load, the creep rate is a function of time and temperature. A typical strain-time curve, which describes the creep behaviors, is shown in Figure 2.18 [4].

![Figure 2.18 A typical creep curve shows three distinct stages with different creep rates. [4]](image-url)
Figure 2.18 shows the creep behavior is temperature dependent. Creep rate is defined by:

\[ \dot{\varepsilon} = \frac{d\varepsilon}{dt} \]  \hspace{1cm} (2.12)

where \( \varepsilon \) is strain and \( t \) is time. At low temperature, the creep rate is usually small and the chance of failure due to creep is very small. Understanding the creep deformation at high temperature (\( T > 0.4T_M \)) is very important. The high temperature creep curve can be divided into three distinct stages: 1) after an initial rapid elongation, the creep rate decrease with time until reaching the steady-state. Primary creep provides decreasing creep rate. The decreasing creep rate is due to strain hardening or reduction of free or mobile dislocations. 2) Beyond primary stage, the creep rate become constant and creep deformation reaches a steady-state stage, which is called secondary creep. The steady-state creep is due to the balance between work hardening and recovery processes [4]. 3) After the steady-state stage, tertiary creep yields a rapid creep rate till failure.

The creep rate at steady-state stage is usually expressed by Norton’s law as [31]:

\[ \dot{\varepsilon}_s = A\sigma^n \]  \hspace{1cm} (2.13)
\[ A = A' \exp \left( -\frac{Q}{RT} \right) \]  \hspace{1cm} (2.14)

Where \( n \) is the stress exponent, \( Q \) the activation energy for creep, \( R \) the gas constant and \( T \) the absolute temperature. \( A' \) is a parameter which is related to microstructure. The relationship between \( \dot{\varepsilon}_s \) and time of rupture \( (t_r) \) is described by Monman-Grant equation:

\[ \dot{\varepsilon}_s = C/(t_r)^m \]  \hspace{1cm} (2.15)
Where $C$ is a constant depending on total elongation during creep and $m$ is a constant often nearly equal to 1.

Frost and Ashby developed the mechanisms for deformation [33]. For creep deformation, there are two major mechanisms, dislocation creep and diffusion creep. At low stress, the diffusion creep is controlled by volume diffusion or grain boundary diffusion. At high stress, dislocation creep is controlled by volume diffusion (high temperature power law creep) or pipe diffusion (low temperature power law creep) [8].

![Figure 2.19 Deformation mechanism map with respect to stress and temperature][32]
2.3.1.1 Dislocation creep

The movement of a dislocation can be impeded by obstacles, such as precipitates, grain boundaries or other dislocations. When a dislocation encounters the precipitates, their movement will not be continued until the dislocation passes through the precipitates. Atomic diffusion can assist dislocation bypass over the precipitates. Since diffusion creep is mostly the mechanism for the creep of CSEF steels (at ultra supercritical condition), mechanism of dislocation creep will not be discussed here.

2.3.1.2 Diffusion creep

When the stress level is low, the diffusion creep mechanism is dominant. Diffusion creep is a result of transporting atoms and condensation of vacancies by diffusion. Diffusion creep can be further divided into Nabarro-Herring creep and Coble creep.

Nabarro-Herring creep

Nabarro-Herring creep occurs when the stress is low ($\sigma/G<9\times10^{-4}$ in Figure 2.11) and temperature is high ($T/T_m>0.6$ in Figure 2.11). The creep is controlled by volume diffusion. The steady-state creep rate can be expressed:

$$\dot{\varepsilon} = \frac{B\sigma \Omega D_V}{d^2 kT}$$

(2.16)

where $\sigma$ is applied stress, $\Omega$ is atomic volume, $D_V$ is grain boundary diffusion coefficient, $d$ is grain size, $k$ is Boltzmann constant and $T$ is temperature. $B$ is a numerical constant, which takes the value of 10.

Coble creep
Coble creep occurs when stress is low ($\sigma/G<10^{-3}$ in Figure 2.11) and temperature is low ($T/T_m<0.4$ in Figure 2.11). The creep is control by grain boundary diffusion. The steady state creep rate can be expressed:

$$\dot{\varepsilon} = \frac{B'\sigma\Omega w_D gb}{d^3 kT}$$  \hspace{1cm} (2.17)

where $w$ is the width of grain boundary, $B'$ is a numerical constant, which take the value of 150/$\pi$.

### 2.3.1.3 Inhibition of diffusion creep by precipitates

Precipitates at grain boundaries can inhibit creep deformation. It is known that grain boundary can act as an efficient vacancy sink. During diffusion based creep deformation, grain boundaries perpendicular to loading direction will emit vacancies, whereas boundaries parallel to loading direction will absorb vacancies. As depicted in Figure 2.20 [34], as creep deformation continues, those boundaries parallel to loading direction will move toward to each other. Precipitates will hinder the movement of grain boundaries. As a result, grain boundaries have to drag precipitates on the boundaries for creep to continue. Consequently, grain boundaries parallel to loading direction collect precipitates. As the creep continues, vacancies will condense and gradually forms void at the boundaries parallel to tensile direction.

If there is no precipitate at the grain boundary which is parallel to tensile direction, vacancies tend to diffuse to grain boundary. As the creep continues, vacancies condense at grain boundaries and two grain boundaries separate. However, if precipitates exist on the grain boundaries, vacancy condensation is difficulty
occur at precipitate/matrix interface. As a result, grain boundaries cannot be further separated unless the matrix deform plastically around the precipitates. Harris [98] proposed that creep continues by “punching” of prismatic defect loops into the matrix, as shown in Figure 2.21. Due to the fact that defect loop will shrink by absorption of vacancies, the size of defect loops is decreasing with increase distance from grain boundaries.

Figure 2.20 Schematic showing distribution of precipitate before (a) and after creep (b). Diffusion direction of vacancies is indicated by arrows, small circles represent precipitates
Figure 2.21 Schematic showing condensations of vacancies cause grain boundary separation.

The stress at dislocation is released by forming interstitial loops.

In order to form the interstitial loop, the line energy the loops must be smaller than the energy gained on condensing a single layer of vacancies at the grain boundary, which can be expressed:

$$\frac{4\Delta F \pi \lambda^2}{a^2} > \frac{Gb^2r}{2} \ln \frac{r}{r_0}$$

(2.18)

where $\Delta F$ is average energy to induce a vacancy to condense at the grain boundary, $\lambda$ is the inter-precipitate spacing, $a$ is inter-atomic distance, $G$ is elastic shear modulus of the matrix, $b$ is Burgers vector, $r$ is the radius of the loop (which
is assumed to be the same as precipitate radius) and \( r_0 \) is the radius of dislocation core.

If tensile stress is \( \sigma \), average energy \( \Delta F = \sigma \Omega \). Assuming \( a \approx b \approx r_0 \approx \Omega^{1/3} \), the minimum stress \( \sigma_0 \) for plastic deformation to occur is:

\[
\sigma_0 = \frac{2G \sigma r}{\pi \lambda^2} \ln \left( \frac{r}{a} \right) \tag{2.19}
\]

Harris also calculated the number of precipitate intersected and collected parallel grain boundaries. He derived that inter-precipitate spacing can be expressed as:

\[
\lambda = (8 \pi r^3 / 3 f d) ^{1/2} \tag{2.20}
\]

where \( \varepsilon \) is macroscopic strain and \( d \) is grain size. As a result, \( \sigma_0 \) can be expressed as:

\[
\sigma_0 = \frac{3Gafed}{16\pi^2r^2} \ln \left( \frac{r}{a} \right) \tag{2.21}
\]

If \( \sigma_0 \) is considered, equation 2.6 can be modified as:

\[
\dot{\varepsilon} = \frac{B(\sigma-\sigma_0)\Omega wDg_b}{d^3 kT} \tag{2.22}
\]

Harris equation did not consider temperature effect on \( \sigma_0 \). On the other hand, Burton [35] proposed another mechanism for plastic deformation near the precipitates. Burton believed stress concentration near the precipitates should be relaxed by nucleation and growth of defect loops in the precipitate/matrix interface since interfacial defects has lower line energy than lattice defects. Burton assumed that at steady state condition, one defect loop must be nucleated on each precipitate in the time taken to condense one layer of vacancies on the adjacent precipitate free boundary. By using this assumption, he calculated:

\[
\sigma_0 = \left( \frac{2U}{r b} - \frac{55kT}{\pi l^2 b} \right) f, (r < 55kT/\pi U) \tag{2.23}
\]
where $U$ is line energy of defect loop. Burton’s calculation shows when precipitate size is smaller than $55kT/2\pi U$, $\sigma_0$ is zero, which indicates small precipitates cannot inhibit vacancy condensation. When precipitate size is larger than $55kT/2\pi U$ and smaller than $55kT/\pi U$, $\sigma_0$ is increasing as precipitate size increase. When precipitate size is larger than $55kT/\pi U$, $\sigma_0$ is independent of precipitate size and only a function of volume fraction. Both Burton and Harris predict $\sigma_0$ is a function of precipitate volume percentage $f$. The above mechanism will be discussed later with reference to Grade 91 steel.

2.3.2 History of high chromium ferritic steels and Grade 91

Due to the need for improving power plant efficiency and increasing the stream parameters, researchers have spent many decades on the development of creep-resistance steels. The development progress of power plant ferritic steels is summarized in Figure 2.22 [36]. The High Cr ferritic steels were first developed based on classical 2.25Cr-1Mo grades in the Center for Metallurgical Research of Liege in Belgium in the mid 1960s. In the 1970s, EM12, which is 9Cr-2Mo steel alloyed by V and Nb, was developed in France for power plant application. However, this steel exhibits poor impact toughness which is caused by the existence of delta-ferrite in the steel. Meanwhile, 12Cr-1Mo steel was developed in Germany, which was named as HT91. HT91 had been used in pipes and headers in many fossil fuel power plants mainly in Europe. However, HT91 is difficult to weld since the carbon content is high (0.2 wt.%). Improved 12Cr-1Mo steels, such as HCM12 and HCM12A, are further developed with low carbon content. In 1970s, a
modified 9Cr-1Mo steel was developed in the Oak Ridge National Laboratory (ORNL) in the US. In 1980s, this modified 9Cr-1Mo steel was standardized as ASTM SA-335 P91 for piping, ASTM SA-213 T91 for boiler, superheater and tubes, and ASTM SA-387 Grade 91 for pressure vessel plates.

Figure 2.22. Development of creep strength enhanced ferritic steels. Strength shown is rupture strength for $10^5$ hours at 600 °C [33]

Grade 91 is 9Cr-1Mo high temperature creep-resistant steel used primarily for welded boilers and pressure vessels. The microstructure of Grade 91 steel is tempered martensite with precipitates. A typical martensitic microstructure for 0.1C-0.36Si-0.41Mn-0.015P-0.003S-0.059N-0.022Al-8.43Cr-0.92Mo-0.04Cu-0.068Nb-0.11Ni-0.20V at normalized and tempered condition is shown in Figure 2.23. Prior austenite grain boundaries, martensite packet and block boundaries are high angle boundaries (15-180°). Low angle boundaries were observed in
martensite blocks (2-15°). The width of martensite block is in the order of microns. Generally, Grade 91 steels are strengthened by two kinds of precipitates: 1) $\text{M}_2\text{C}_6$ ($\text{M}=\text{Cr, Fe, Mo}$) precipitates located mostly at martensite lath boundaries and prior austenite grain boundaries (PAGB); 2) MX ($\text{M}=\text{V, Nb}$ and $\text{X}=\text{C, N}$) precipitates dispersed within laths.

![Figure 2.23](image)

**Figure 2.23.** a) Electron backscatter micrograph, b) inverse pole figure and c) EBSD boundaries of Grade 91 steel showing martensitic microstructure. EBSD images shows lath martensite blocks and packets sub-structure [36]

$\text{M}_2\text{C}_6$ is a face-centered cubic precipitate enriched with Cr. The precipitate may contain Fe and Mo, and sometimes W and V, depending on the alloy composition. $\text{M}_2\text{C}_6$ precipitate is usually the equilibrium phase in 9 wt.% Cr steels. However,
M₃C (M=Fe, Cr, Mo) or M₇C₃ (M=Fe, Cr, Mo) forms first during the initial stages of tempering. Subsequently, M₂₃C₆ precipitate forms by the dissolution of M₃C or M₇C₃. Finely dispersed M₂₃C₆ precipitates can pin the dislocations and grain boundaries during creep. As a result, M₂₃C₆ is one of the contributors to the high creep strength of CSEF.

MX is vanadium and niobium carbonnitride with face center cubic structure. Since MX is small (usually from 5 to 20 nm) [37] and very stable at high temperature, it can act as inhibitor for creep. It is favorable in CSEF steels.

Locations of those precipitates in 9Cr-steel are studied by Kaneko et al. using electron microscopy [38]. Figure 2.24 shows both M₂₃C₆ and MX appear on PAGB. The size of M₂₃C₆ is much larger than MX precipitates. One the other hand, M₂₃C₆ is also seen on martensite lath boundary (Figure 2.25). M₂₃C₆ precipitates on the lath boundary are much finer (~20 nm).

![Figure 2.24 a) Bright field TEM image showing M23C6 at PAGB and b) dark field TEM image showing MX precipitates on PAGB][37]
2.3.3 Welding process and related issues of CSEF

CSEF steels are supplied in a normalized and tempered condition. Preheat is recommended before welding to reduce hydrogen and avoid cold cracking. Preheat temperature is very important and usually ranges from 200 to 250°C. However, for root and hot-pass weld layers where Gas tungsten arc welding (GTAW) is used, the preheat temperature could be as low as 121°C. A typical maximum interpass temperature is 300 °C. To reproduce a tempered martensitic microstructure and to relieve some of the stresses induced by welding, PWHT is generally required after welding. A typical temperature cycle and heat control for a welded joint in P91 steel is presented in Figure 2.26 [39]. The steel is welded with the interpass temperature of 250 to 300°C, and then slowly cools to a temperature below 100°C to ensure the full formation martensite. Welding is
followed by PWHT at 750°C for 2-4 hours. After PWHT, the welded structure is air-cooled.

Figure 2.26. A typical temperature cycle and heat control for a welded joint in P91 steel [38]

In general, all arc welding processes can be applied to weld Grade 91 power plate steels, such as GTAW, manual metal arc welding (MMAW), flux cored arc welding (FCAW), and submerge arc welding (SAW). GTAW is often used to produce root pass. Complex joint is often welded by MMAW and deep welds require high productivity processes such as FCAW and SAW. Electron beam welding is also reported to have been used in the welding of CSEF steels [40].
Filler metals for CSEF steels are required to match the creep strength of the parent material in service. Ideally the impact toughness of base metal and filler metal should be matching also at ambient temperatures. However, since some welding process rely on fluxes and slag systems for alloying and/or shielding gases for protection of the molten weld pool (such as SAW, FCAW), many factors in the welding process may reduce the toughness of weld metal [41]. A typical reduction of toughness for different welding process is summarized in Table 2.1.

Table 2.1 Toughness reduction for different welding process

<table>
<thead>
<tr>
<th>Welding Process</th>
<th>Typical Toughness Reduction</th>
<th>Wetting Agents, Crack Inhibitors, Deoxidizers or Slag Formers</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTAW</td>
<td>None</td>
<td>Si, Mn, Ti</td>
</tr>
<tr>
<td>SAW</td>
<td>25-50%</td>
<td>SiO₂, MnO₃, etc.</td>
</tr>
<tr>
<td>SMAW</td>
<td>40-50%</td>
<td>CaCO₃, etc.</td>
</tr>
<tr>
<td>FCAW</td>
<td>50-70%</td>
<td>Varies</td>
</tr>
</tbody>
</table>

**2.3.4 Type IV failure**

In the welding of steels, there are four distinct HAZ regions (Figure 2.27): (1) In subcritical HAZ regions \( T_p < A_{c1} \), no detectable transformation of ferrite-to-austenite occurs; (2) In the inter-critical HAZ, partial transformation of ferrite-to-
austenite occurs because the peak temperature is in between \( A_{c1} \) and \( A_{c3} \); (3) In the fine-grained HAZ, the samples are heated to a temperature slightly above the \( A_{c3} \) temperature, after complete austenitization; and (4) In the coarse-grained HAZ, the sample in the austenite state is heated to a peak temperature significantly above the \( A_{c3} \).

---

Figure 2.27. Schematic shows classification of different regions in steel weldments [42]
The premature failures are commonly seen at the welded joint of CSEF, particularly in HAZs of the welds. The definitions of different failure types in the weldments are illustrated in Figure 2.28 [43]. The classification of failure type depends on location of failure. Type I mode occurs within the weld metal. If the failure starts at the fusion line, it is characterized as Type II mode. Type III occurs in the CGHAZ. Type IV is the form of failure which occurs in the FGHAZ or the ICHAZ.

Figure 2.28. Classification of failure locations in CSEF steel weldments
It is widely accepted that the microstructure gradient in the HAZ of welds leads mostly to Type IV failure in CSEF steels [44]. Even though PWHT is usually given after welding to allow precipitation in newly formed martensite formed adjacent to the weld, a microstructure gradient still exists. This results in the gradients in mechanical properties, such as creep strength of the overall weldments.

Since a creep test can take years to complete, researchers tried to explore the correlation between creep properties and hardness. Albert et al. [45] simulated HAZ regions of 12Cr steel by using a furnace and simulated HAZ samples were subjected to creep tests and hardness measurements. The results showed that sample with the peak temperature 30°C above $A_{c1}$ (simulated ICHAZ) has the lowest hardness. However, in the creep test, the lowest rupture time is observed in the sample with peak temperature 30°C above $A_{c3}$ (simulated FGHAZ). Though the rupture location changes with load, hardness could not be used to indicate creep strength/failure location in HAZ.

The mechanism of Type IV failure is still not clear. There are several mechanisms proposed from aspect of microstructure evolution. Hirata and Ogawa [46,47] studied simulated HAZ microstructure in 9Cr steels by using induction heating and laser scanning confocal microscopy. Three different HAZ regions were studied with peak temperature of 830°C, 1000°C and 1200°C. After the HAZ simulation, all the samples were subject to a post-weld heat treatment at 740°C for 0.5 hour. Creep tests showed HAZ with peak temperature of 1000°C (FGHAZ)
had the lowest creep strength. Microstructure evolution was investigated by using LSCM. It is discovered when the peak temperature is 1000°C, $M_{23}C_6$ is partially dissolved in the FGHAZ. Large MX enriched with Cr is found in the sample after post-weld heat treatment. Hirata and Ogawa concluded that $M_{23}C_6$ partially dissolve and accelerate coarsening of MX phase (Figure 2.29). In HAZ with peak temperature of 830 °C, since the peak temperature is low, both MX and $M_{23}C_6$ are undissolved during welding. During PWHT and creep test, those carbides may coarsen. The coarsening of MX is controlled by V diffusion. On the other hand, when peak temperature is 1000°C, $M_{23}C_6$ carbides were seen partially dissolved by laser scanning confocal microscope (LSCM). Cr-enriched regions were left around carbides [45]. During PWHT and initial stage of creep, new small $M_{23}C_6$ and MX carbides formed in those Cr-enriched regions. The growth and coarsening of MX were controlled by Cr diffusion. Due to the fact that Cr diffusivity in steel is higher than V (according to the parameters form [48], at 650°C, diffusivity is $1.62\times10^{-13}$ cm$^2$s$^{-1}$ for Cr and $4.72\times10^{-16}$ cm$^2$s$^{-1}$ for V), MX coarsened much faster in HAZ with 1000°C. Coarse MX in this region yield very poor creep strength. However, Hirata and Ogawa did not give any direct evidence of Cr-diffusion governed MX growth and coarsening. According to ThermoCalc, the solubility of Cr in austenite at 1000°C is about 13 wt.%, which indicates the maximum Cr content at the periphery of the carbides. 13 wt.% Cr may not be sufficient to accelerate coarsening of MX. Even though MX in this region is coarser, it may not significantly affect creep strength.
Figure 2.29. Schematic illustration of carbides evolution in HAZ [46]

Tsukamoto et. al. [49] studied Grade 92 steel and discussed type IV failure from a standpoint of carbides stability. Two conditions were studied, as-normalized and fully tempered. Two conditions were subjected to FGHAZ simulation and post-weld heat treatment. Surprisingly, as-normalized condition had a better creep strength than fully tempered condition. Tsukamoto et. al. proposed undissolved carbides at ghost austenite grain boundaries in fully tempered weldments is the reason for Type IV failure (Figure 2.30). Ghost austenite grain boundaries are defined as locations where prior austenite grain boundaries are in steel before welding. In base metal, most of M_{23}C_{6} carbides were on PAGs and martensite
block boundaries. Those carbides did not go into fully solution during welding when peak temperature is low (a little over $A_{c3}$). During post-weld heat treatment, since there were pre-existing carbides on ghost austenite boundaries, supersaturated carbon in solution will diffuse to pre-existing carbide instead of nucleating new carbides on newly formed austenite grain boundaries. Accordingly, lack of carbides on prior PAGs and martensite block boundaries cause low creep strength in FGHAZ. However, Tsukamoto et.al. ignored effect of coarse carbides in FGHAZ in the fully tempered condition. Possible ferrite formation in HAZ of fully tempered conditions was also not considered.

Figure 2.30. Schematic diagram of microstructure evolution in HAZ simulated Gr.92 at the peak temperature of just above $A_{c3}$
Besides metallurgical reasons, the mechanical aspect also plays a role in Type IV failure. There are many studies on the stress and stain state in FGHAZ during creep test using finite element analysis [50, 51, 52, 53]. Li [51, 52] shows that at the same tensile stress, the strain rate at the interface for the FGHAZ matrix is about six times higher than that for the CGHAZ, and 17 times higher than that for the 9Cr steel base metal. These results suggest a tendency towards the occurrence of creep voids in the FGHAZ. Another mechanism of Type IV failure is proposed by Kimmins et al. [54]. The creep mechanism is considered as grain boundary sliding accommodated by diffusional (Ashby–Verrall's model). They constructed a finite element model of weld and allow grain boundary sliding. The model contains the different HAZ regions with different mechanical properties. When the weld is under certain tensile stress, the microstructure gradients in the HAZ induce constraint in the HAZ. The constraint is further relaxed by grain sliding in FGHAZ due to the large amount of grain boundaries in that region.

2.4 Scope of current research

By reviewing the problems and existing literatures, it can be found that understanding HAZ microstructure is critical to solve weldability problems in HAZ.

Previous research has discovered abnormal hardness variation in HAZ of BA-160. Even though the variation was explained by strengthening model, the softening in HAZ still needs to be addressed. PWHT was one of the methods to solve the softening problem. However, PWHT is not feasible in the field condition.
Manipulating multi-pass welding parameter can also mitigate softening. As a result, multi-scale characterization is needed to study microstructure in multi-pass HAZ. EBSD will be used to study micro-scale martensite sub-structure. APT will be used to study nano-precipitates. Since martensite is the major strength contributor, understanding martensite transformation kinetics is also very important. TRXRD coupled with LSCM will be used to study martensitic transformation in BA-160 in real time.

On the other hand, to understand the mechanism of Type IV failure, it is also important to understand microstructure in HAZ of CSEF steels. Limited previous research has report comprehensive understanding of FGHAZ in CSEF. Therefore, multi-scale characterization can be used to get a comprehensive understanding of FGHAZ in CSEF steels. Microhardness mapping can be used to see hardness variation in the weldments. Due to the hardness difference amount weld metal, FGHAZ, CGHAZ and base metal, difference regions can be indentified and further characterized by other tools. Optical microscopy and SEM can be applied to look at large carbides, martensite sub-structure, creep voids. Carbon extraction replica technique can be use to extract carbides out of matrix and get them characterized in TEM. Carbide morphology, type and composition information can be obtained. In addition, phase transformation can be studied by TRXRD, dilatation measurement and LSCM in real time. Due to high flux of X-ray by synchrotron radiation, secondary phase with small fraction can be characterized by TRXRD. Martensite, austenite and carbide fraction can be acquired as a function of temperature. With LSCM, it is possible to observe martensitic
transformation by characterize surface deformation. Dilatation measurement can be used to study transformation start/finish temperature and transformation rate.

### 2.5 Characterization techniques

Characterization techniques at different scale levels used in current study will be discussed in the following sections.

#### 2.5.1 Optical microscopy

Light optical microscopy (LOM) is widely used for microstructure characterization for more than 200 years. LOM can be used to characterize opaque material’s surface (all metals, many ceramics and polymers) in a reflective mode. Due to the difference in reflectivity of different regions, contrast can be obtained in LOM images. Usually, LOM is used for etched or unetched samples to determine characteristics of grains and various phases or microstructures. These parameters can be also further quantified by image analysis techniques. Different regions in the weldments can be also indentified by LOM. An example is given in Figure 2.31 [55], showing optical images of T-joint on alloyed steels welded by laser welding process. The two work pieces have the same composition but different initial microstructure.
Figure 2.31 Detailed optical images of a high alloyed steel weld, (A) annealed base metal showing ferrite and carbides (B) and (D) HAZ showing martensite (C) weld metal showing martensite (E) over tempered regions in base metal [55]
Figure 2.3 clearly shows at least five distinctive regions in the weld. Region A is in unaffected based metal. The microstructure is equiaxed ferrite and fine carbides. Region B and D are in the HAZ, which have untempered martensite. In addition, regions C in the weld metal also shows martensitic microstructure. Region E is in the base metal but it is darker than other regions in base metal in the macrograph. Since the steel is fully tempered before welding, the difference may due to the over-tempering during welding.

Even though LOM has many advantages (i.e. easy to use and simple sample preparation), there are also some limitations. A major drawback of LOM is that images obtained are 2 dimensional (2D). The real 3 dimensional (3D) microstructure can only be “guessed” from LOM images. David [56] obtained 3D solidification microstructure of 308 stainless steel weld by using 3D edge detection techniques (Figure 2.32). By using this technique, comprehensive understanding of material microstructure can be achieved. Figure 2.32C shows there is a difference in morphology between top-view image and left-view image. Figure 2.32D also shows the similar phenomenon. In addition, Figure 2.32A and B also shows different ferrite number for the same solidification morphology. As a result, if only one LOM is obtained, the result will be biased.

Recently, there are many reports on getting 3D microstructure data by serial sectioning and optical microscopy [57, 58, 59]. In order to get one set of 3D data, it usually requires tens or hundreds times of sectioning, polishing, etching and picture taking. It is time-consuming. To solve this problem, UES, Inc developed a
fully automated serial sectioning system, Robo-Met 3D®, for 3D microstructural investigations [60].

Figure 2.3 2D solidification morphologies in 308 stainless steel welds [56]
Another drawback of traditional LOM is that it is an ex-situ characterization technique. Phase transformation in the weldments can only be interpreted by analyzing images of final microstructure. Recently, thanks to the development of high speed camera, the characteristics of weld pool, arc, and solid/liquid interface can be observed by optical microscopy. However, high speed camera cannot reveal material microstructure in micro-scale.

On the other hand, laser scanning confocal microscopy (LSCM) can track in-situ phase transformation during welding in micro-scale. LSCM is a high resolution optical imaging technique with depth sensitivity. LSCM is widely used for characterization in cell biology and materials science. For welding applications, usually the LSCM system is composed of three parts (Figure 2.33): an infrared furnace with computer control and laser scanning confocal microscope [61].
Using LSCM, the surface of the samples can be imaged continuously while subjected a pre-programmed thermal cycle [62, 63, 64]. LSCM system has been used to study the transformation kinetics of allotriomorphic ferrite [65], observe the solidification and ferrite to austenite transformation of high strength steel [66], transformation kinetics from ferrite to austenite [62] and investigate ferrite nucleation sites in weldments [67].
2.5.2 Hardness mapping

Mechanical testing is also an important aspect of understanding material microstructure and behaviors’. In the weldments, due to its microstructure and mechanical property gradient, measuring and interpreting mechanical test results is complex [55]. Hardness testing, which is a traditional tool to evaluate hardness of the materials, now is widely used to assess the strength of the materials. With the help of automatic hardness testing system, spatial microhardness mapping can be obtained easily. Microhardness testing is a useful technique for weldments characterization. The weldments are comprised of weld metal, HAZ and base metal. In different regions, microstructure gradient or heterogeneity may also exist. Hence, microhardness map can be used to observe hardness variation due to microstructure gradient.

Figure 2.34 shows an example of X100 steel weld microhardness map [55]. The weld metal has a hardness varied from 280 to 320 VHN. Base metal hardness is about 250. A softening in HAZ is observed, with hardness of 200 to 220. The width HAZ indentified based on hardness variation in the hardness maps may be different from the width determined by microstructure [55].
Figure 2.34 Macrograph and corresponding microhardness map of X100 steel weld [55]
2.5.3 Electron microscopy

Conventional scanning and transmission electron microscopy techniques are widely used for materials characterization. Morphology, composition and structure can be determined by electron microscopy techniques. For microstructure in ferritic weld characterization, the use of electron microscopy includes, but not limit to:

1. Electron backscattering diffraction (EBSD) techniques in SEM can be applied to determine prior austenite grain size, martensite sub-structure size. In addition, orientation relationship between bainite/martensite and prior austenite can be determined.

When martensite is formed from austenite during quenching, the crystal orientation relationship between martensite and the parent austenite is fixed. To minimize the strain energy the martensite forms on specific crystallographic plane of austenite phase, which is defined as habit plane [68]. The approximate habit plane for low alloy low carbon steel is \{111\}_\gamma. The near close-packed plane in the ferrite is parallel to the close-packed planes in austenite. Three approximate relationships describe the orientation relationship of martensite and austenite [36]:

\[
\begin{align*}
\{111\}_\gamma & \parallel \{011\}_\alpha' \\
<10-1>_\gamma & \parallel <11-1>_\alpha' & \text{Kurdjumov-Sachs (KS)} \\
\{111\}_\gamma & \parallel \{011\}_\alpha' \\
<10-1>_\gamma & \text{about 5.3° from } <11-1>_\alpha' \text{ towards } <-11-1>_\alpha' & \text{Nishiyama-Wasserman} \\
\{111\}_\gamma & \text{about 0.2° from } \{011\}_\alpha' \\
<10-1>_\gamma & \text{about 2.7° from } <11-1>_\alpha' \text{ towards } <-11-1>_\alpha' & \text{Greninger-Troiano}
\end{align*}
\]
It is generally believed that for low carbon steels, the orientation relationship between martensite lath and austenite follows near KS relationship. There are 24 variants in KS relationship. Since four crystallographical plane parallel relations exist, four different packets can appear in a given austenite grain. In a packet there are six variants with different orientation parallel aligned to each other. Typical Orientation maps obtained by EBSD are shown in Figure 2.35. Three kinds of blocks (B1, B2, and B3) and six kinds of variants (V1 to V6) are recognized. Different color in the maps indicates different orientation. Inside each block, slightly color difference could be seen. The slight difference in color indicates two variants co-exist in one block with small misorientation (V1-V4, V2-V5, and V3-V6). The corresponding orientation is presented in pole figure in Figure 2.35 (c) and (d). The misorientation between sub-blocks inside a single block is around 7°.
2. Crystal structure of an unknown phase can be determined by TEM.

One example on characterizing Cu precipitate crystal structure is shown here. During aging of Fe-Cu or Fe-Cu-Ni alloy, the transformation sequence for Cu precipitates is bcc→9R→3R→fcc with increasing aging time. 9R is twinned structure with (009) close packed plane. 3R is a more stable distorted fcc structure with (003) close packed plane. At the early stage of aging of Cu bearing steels, bcc Cu nucleate from the ferritic or martensitic matrix. As the bcc Cu clusters grow to a critical size (5–12 nm), which is depended on the aging temperature,
bcc Cu will transform martensitically into a twinned 9R structure [69]. The 9R Cu precipitate is roughly spherical and is recognized by a characteristic herring-bone pattern in high resolution transmission electron microscopy (HRTEM), as shown in Figure 2.36 [70].

![Figure 2.36 9R Cu precipitate with herring-bone pattern shown in HRTEM image](image)

3. TEM can be used to determine characteristics of precipitates in steels. One example on the study of carbides in power plant steel is shown here. Thomson [70] investigated carbide distribution and composition in 2.25Cr-1Mo steels tempered at different temperature and time. At one condition, the sample was tempered for 178 hours at 565°C. Carbides were extracted using carbon extraction replica
technique. Figure 2.37 (a) and (b) shows the carbides morphology at low and high magnification. Acicular shape carbides in Figure 2.37b are $M_2C$ carbides, which were confirmed by diffraction. In addition, large carbide indicated by arrow in Figure 2.37b was cementite according to selected area diffraction.

Figure 2.37 (a) low magnification and (b) high magnification TEM images of 2.25Cr-1Mo steel tempered at 565°C for 178h (c) selected area diffraction from a cementite
It is realized that there are many other capabilities of electron microscopy, such as backscatter imaging to show a contrast in atomic number, determination of chemical composition using electron energy loss spectrometry and Z contrast imaging to show alloy elements in HRTEM. Since discussion of characterization techniques in details is out of the scope of current study, only some techniques used were discussed. A comprehensive review on characterization of ferritic weld by electron microscopy can be found in [71].

2.5.4 Atom probe tomography

Field ion microscope was invented by Prof. Erwin W. Müller by utilizing phenomena of field-ionization. The needle shape prepared sample was placed in front of phosphor screen in an ultra-high vacuum system (10^{-10} Torr). When a high DC voltage is applied on the needle, high electric field is produced on the tip. If the imaging gas, typically He or Ne, is admitted in the chamber, gas atoms will be ionized by an electron tunneling process. As a result, the gas ions are positively charged and projected away from specimen. This will generate an image with high magnification on a screen. The tip, with a radius of about 50 nm is cryogenically cooled to low temperatures (20-80 K) to minimize the vibration of atoms at the sample tip.
Atom probe microscopy is based the concept of field evaporation. When an electric pulse with a high static voltage is applied to the sharp specimen, the electric field generated at the apex of the specimen is large enough to ionize surface atoms. This process is called field evaporation. Once the atoms are ionized, the positively charged ions are projected away from the specimen, just as gas ions are projected away from the specimen in the field ion microscope mode. Time-of-flight mass spectrometry is used to identify the ion, and the position of impact gives the original position on the specimen surface. The frequency of
electric pulses is from 1 to 200 kHz and the steady-state DC voltage $V_{dc}$ is up to 20 Kv.

For conventional 3DAP microscopy, the analysis area is limited to about 15 x 15 nm$^2$. The local-electrode atom-probe or LEAP$^\text{®}$ microscope is developed, as shown in Figure 2.38 [72] to have the capability of large volume analysis, typically 100 x 100 nm$^3$. In addition, the collection rate of LEAP is at least 600 times faster than conventional 3DAP microscopes. Recently, instead of voltage pulse, laser pulse is used in LEAP to assist the field evaporation on the specimen tip (Figure 2.38). Laser pulsing atom probe has the advantage of high mass resolution without the need for energy-compensating devices [73].

APT is a very good technique to characterize microstructures in nano-scale. As a result, it is ideal to analyze Cu precipitates and carbide in BA-160. Size and distribution of precipitates, which are important to understand strength contribution from precipitates, can be obtained by APT. In addition, composition in the both precipitates and matrix can be analyzed. APT can also be used to study carbides and matrix composition in CSEF steels.

2.5.5 Time-resolved X-ray diffraction

In HAZ of steels, the microstructure is a function of thermal cycle, composition and sometimes strain. In order to understand and control the microstructure, it is very important to study the phase transformation (ferrite-austenite-ferrite) in steels. Most of ex-situ characterization tools, e.g. SEM and TEM, can only study the phase transformation by characterizing the final product microstructure. In-
situ phase transformation information is also very important. In addition, since ex-situ experiments are time-consuming and expensive, there is a need to develop comprehensive computational phase transformation model for HAZ in steels. As a result, in-situ characterization is necessary to measure the kinetics of microstructure evolution (fraction transformed and morphology) during continuous cooling conditions typical to that of welding. Although, the dilatation measurements during Gleeble® thermal simulation can be considered as an indirect in-situ measurement, the transients in morphological changes and crystallographic information are not accessible by this technique.
One of the in-situ approaches to investigate phase transformation in steels is LSCM, which has been discussed in section 2.5.1. Though LSCM has the
capacity of tracking real time morphology, the crystal structure information cannot be obtained. On the other hand, time resolved X-ray diffraction (TRXRD) technique is capable of characterizing lattice parameter and volume fraction of phases (fcc and bcc) as a function of imposed thermal cycles. In the past decade, Synchrotron based in-situ TRXRD systems have been used extensively to investigate phase transformations in steels [74, 75, 76, 77, 78, 79].

Considering the advantages of the LSCM and synchrotron TRXRD techniques, Komizo and Terasaki [80] developed a hybrid in-situ system that combines both the methods (Figure 2.39). Current research uses this hybrid in-situ system to characterize martensitic transformation in BA-160 and Grade 91 steels subjected to HAZ thermal cycles.

Phase transformation study by high-speed X-ray diffraction technique using synchrotron radiation allows one to obtain the crystal structure information, such as lattice parameter, of all the phases presented in the sample, as well as, their phase fractions (~ 0.01) under in-situ conditions. Moreover, changes in chemical composition of phases could be estimated from lattice parameter data. For example, Babu et al [15] derived carbon concentration in both austenite and ferrite during bainitic transformation in steel. However, analyzed volume by X-ray diffraction is indeed small and located on the top surface of the sample. Even though synchrotron radiation X-ray has a high penetration in to materials, the volume analyzed is estimated to be in the order of 0.01 mm$^3$. The results will be biased if the sample contains large grain size due to free surface effects. The phase transformation can also be studied by measuring relative length or radius
change of the sample using dilatometer. This is relevant to decomposition of austenite (FCC) to ferrite or martensite (BCC or BCT) due to large differences in coefficient of thermal expansion (typically in 18–20×10⁻⁶/K for austenite and 7–15×10⁻⁶/K for ferrite). The volume analyzed in dilatometer could be as large as several mm³. Since the dilatation is measured throughout the sample length or diameter, the results correspond to the average transformation behavior. Although, the carbon concentration of austenite can be calculated from dilatometry data, however the methodology requires the following assumptions [81]: (a) negligible change in coefficient of thermal expansion with temperature and (b) equilibrium carbon concentration in ferrite.

The transformation kinetics derived from synchrotron TRXRD are compared with dilatation study, as well as, predictions from a martensite kinetics model. In this research, specific focus is given to the correlation between austenite grain size and martensite start temperature (Ms).
Chapter 3. Objectives

Since weldability of steel is very important aspect of steel design, the objective of current study is to develop a methodology for studying HAZ microstructure evolution in steels. Multi-scale characterization techniques towards comprehensive understanding of HAZ in steels will be used. Two challenging problems will be studied using this multi-scale characterization technique in BA-160 and Grade 91 steels.

The goal of HAZ characterization of BA-160 includes:

1. Previous research discovered HAZ softening in BA-160. Current study will study mitigating the softening problem by manipulating multi-pass welding parameters. Simulation of two-pass weld HAZ will be performed. The aim of second pass is to re-precipitate Cu and carbide in the HAZ. Precipitates will be characterized by atom probe tomography and martensite sub-structure will be investigated by EBSD. Contribution of strengthening will be studied

2. Since martensite sub-structure is very important to the strengthening of steels, a hybrid system combined TRXRD and LSCM will be used to study martensitic transformation in HAZ.

The task of HAZ characterization of Grade 91 steel includes:
1. To understand microstructure in HAZ of ASTM Grade 91 steel pre-weld tempered at different temperature, using various characterization techniques:
   
i) Determine carbides type in FGHAZ of Grade 91 steels.

ii) Characterize martensite sub-structure using both optical microscopy and electron backscatter diffraction technique. Study the prior austenite grain size, martensite block size and packet size.

2. Study martensite to austenite to martensite transformation kinetics and carbide evolution using in-situ synchrotron X-ray diffraction and LSCM.

3. Apply existing creep strengthening model to explain the variation in strength (by following mechanism) along different region in the HAZ at different pre-weld tempering temperature
Chapter 4. Experimental procedure

4.1 Materials

4.1.1 BA-160 steel

The BA-160 experimental material was provided by QuesTek Innovations LLC, Evanston, IL in the form of 1.375-inch diameter bar stock. The measured chemical composition of the BA-160 experimental material is provided in Table 4.1. The details of the heat treatment procedure for BA-160 are outlined in Table 4.2. Test samples were machined using the wire Electro Discharge Machining (EDM) process. The hardness following the heat treatment procedure was verified to be in accordance with the expected 41HRC in the fully hardened condition. The microstructure of heat treated steel is a mixed bainitic/martensitic matrix microstructure with optimized nano-scale Cu precipitates and M2C carbides.
Table 4.1 Chemical composition of the BA-160 experimental material

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>0.059</td>
<td>0.015</td>
<td>0.001</td>
<td>3.39</td>
<td>6.8</td>
<td>1.9</td>
<td>0.61</td>
<td>0.016</td>
<td>Balance</td>
</tr>
<tr>
<td>At.%</td>
<td>0.277</td>
<td>0.03</td>
<td>0.001</td>
<td>3.005</td>
<td>6.527</td>
<td>2.058</td>
<td>0.358</td>
<td>0.019</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 4.2 The heat treatment procedure for BA-160 steel

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature, °C</th>
<th>Duration</th>
<th>Post-Step Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Austenitization</td>
<td>900</td>
<td>1 hr</td>
<td>water quench</td>
</tr>
<tr>
<td>2. Liquid nitrogen hold</td>
<td>-196</td>
<td>30 min</td>
<td>Air warm to room temp</td>
</tr>
<tr>
<td>3. Tempering</td>
<td>550</td>
<td>30 min</td>
<td>water quench</td>
</tr>
<tr>
<td>4. Tempering</td>
<td>450</td>
<td>5 hr</td>
<td>air cool to room temp</td>
</tr>
</tbody>
</table>

4.1.2 Grade 91 steel

The chemical composition and fabrication conditions of ASTM Grade 91 (heat number 30176) are shown in Table 4.3 and Table 4.4. After fabrication, the steels are normalized at a temperature of 1080°C for 2.5 hours. Two tempering temperatures are investigated in the current study: 650°C and 760°C. The samples were tempered in the furnace for 1.5 hours. GTAW is used to join the plates,
followed by PWHT at 760°C for 4 hours. The information of welding process can be found in chapter 4.2.1

<table>
<thead>
<tr>
<th></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></td>
<td>0.081</td>
<td>0.37</td>
<td>0.01</td>
<td>0.003</td>
<td>0.11</td>
<td>8.61</td>
<td>0.89</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.09</td>
<td>0.2</td>
<td>0.072</td>
<td>0.055</td>
<td>0.007</td>
<td>0.002</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 4.3. Chemical composition (wt.%) of heat 30176 Grade 91 steel [43]

<table>
<thead>
<tr>
<th></th>
<th>Melter</th>
<th>Melting Practice</th>
<th>Product</th>
<th>Thickness</th>
<th>Fabrication method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cartech</td>
<td>AOD-ESR</td>
<td>Plate</td>
<td>25 mm</td>
<td>Hot forged, hot rolled</td>
</tr>
</tbody>
</table>

Table 4.4. Summary of information on fabrication of heat 30176 Grade 91 steel [43]

4.2 Experimental Procedures

4.2.1 Welding Experiments

Two 1 inch plates, which were tempered at two different temperatures (650°C and 760°C), were later machined with V grooves. The plates are pre-heated at 121°C before welding. Welding was performed on the plates with one root pass and two
fill passes. Welding current, voltage and speed are 260A, 8V and 2.5mm/s respectively. Filler wire is 1.6mm in diameter and its composition is listed in Table 4.5. The welded plates were post-weld heat treated in the furnace at 760°C for 4 hours. Then the plates were sectioned and machined for creep tests.

<table>
<thead>
<tr>
<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>0.08</td>
<td>0.41</td>
<td>0.01</td>
<td>0.005</td>
<td>0.31</td>
<td>8.62</td>
<td>0.92</td>
</tr>
<tr>
<td>Ni</td>
<td>V</td>
<td>Nb</td>
<td>N</td>
<td>Al</td>
<td>Cu</td>
<td>O</td>
</tr>
<tr>
<td>0.15</td>
<td>0.24</td>
<td>0.08</td>
<td>0.04</td>
<td>0.002</td>
<td>0.005</td>
<td>0.008</td>
</tr>
</tbody>
</table>

**Table 4.5 Chemical composition (wt.%) of 9Cr-1Mo filler wire**

### 4.2.2 Heat-Affected Zone simulation by Gleeble

To investigate the multi-pass HAZ microstructural evolution of BA-160, thermal-cycle simulations representative of the various HAZ regions were performed. For actual welding conditions, the thermal history is complicated. The thermal profile for a specific location may contain several thermal cycles, depending on the number of passes. Current research pertains to only re-precipitation in double thermal cycle HAZ. Peak temperature of the second thermal cycle is lower than Ac1. As a result, four single-pass and simplified multi-pass HAZ regions are selected (Figure 5.1): (1) CGHAZ with high heat input, (2) CGHAZ+650 °C
reheat with high heat input, (3) CGHAZ with low heat input, and (4) CGHAZ+650 °C) reheat with low heat input. The Δt_{8/5} (time to cool from 800 °C to 500 °C) was approximately 45 seconds for high heat input and 15 seconds for low heat input. The thermal cycle simulations were performed with a GLEEBLE 3800 thermomechanical simulator using solid cylindrical samples of 5 mm in diameter and 101.6 mm in length. The sample temperature was controlled with a type- thermocouple wire percussion welded at the midsection. The samples were heated to the peak temperature at a linear rate of 100°C/s. The simulations were conducted with the test chamber in a high vacuum state of 10^{-6} torr to limit surface oxidation and thermocouple detachment. Phase transformation temperatures for the HAZ simulations were determined using a dilatometer, which provides an accurate determination of the change in specimen diameter during the thermal cycle. This data provided an estimate of the Ac$_1$ and Ac$_3$ temperatures, the on-cooling phase transformation temperatures and the fraction of austenite transformed as a function of temperature. The selection of the peak temperatures for the HAZ simulations was made in reference to the dilatometry data.

The same approach is used to study HAZ phase transformation and microstructure of Grade 91 steels. Since type IV failure occurs at FGHAZ in CSEF steels, current study only focused on FGHAZ simulation. Three peak temperatures were selected: 950°C, 1000°C and 1050°C. Constant heating rate (20°C/s) and cooling rate (10°C/s) were used.
4.2.4 Creep tests

The creep tests of those welded plates were done at Oak Ridge National Laboratory. Sample dimension is shown in Figure 4.1. The tests were performed according to ASTM E139-06. Lever-arm creep machines were calibrated to a load accuracy of ±0.5%. The temperature was measured by three Chromel vs. Alumel thermocouples (±0.4% accuracy) wired to the gage section. The temperature variation among these was less than +1.0 °C, and the highest temperature was taken as the nominal test temperature. Creep test were done at 650°C with a load of 10ksi (70MPa). Proportioning temperature controller was used to obtain control to ±1.0 °C with the highest temperature being the nominal test temperature.

Length change was measured by an averaging extensometer attached by set screws to a small groove in the specimen shoulder. The tension reading was converted to strains by dividing by the reduced section length. The dial gage used in measuring the extension had a resolution of 2.5 μm. The strain was recorded every 36 seconds in the first 37 minutes. Then it was recorded every 360 seconds.
4.3 Microstructure Characterization

4.3.1 Metallographic Preparation

Samples for metallographic analysis were sectioned with a LECO® VC-50 Precision Diamond Saw and mounted in Konductomet conductive mounting powder. Mounted samples are grinded with metallurgical sand paper with grit steps of 180, 320, 600, and 800. Then samples were polished by 9μm, 3μm, and 1μm diamond in suspension. Final polish was done on a Buehler Vibromet II with 0.05 μm colloidal silica. For light optical and SEM viewing, samples were etched with Fry’s reagent. Olympus GX-51 scope was used to look at steel microstructure at magnification up to 1000x.
4.3.2 Microhardness testing

The microhardness Grade 91 steels was measured with a LECO LM100AT micro-hardness tester using a 300g load with a dwell time of 10 seconds, in accordance with ASTM Designation E-384-08. For each hardness map, there are 2500 to 3000 indents with a spacing of 150μm. After the indents were made, micro-hardness tester measure each indents automatically. Those hardness data were interpolated and were plotted as color maps with the assist of IgorPro software.

4.3.3 Scanning Electron Microscopy and Electron Backscatter Diffraction

In order to characterize the original microstructure of the steel and the microstructure evolution in the HAZ, a Philips ESEM FEG-30 scanning electron microscope (SEM) equipped with an EDAX® TSL EBSD detector was used. SEM images were taken at accelerating voltage of 20kV and spot size of 5nm. The working distance is set to be 10mm. For EBSD, prior to scanning, the sample was tilted to 70° in accordance with standard EBSD procedures. Pattern acquisition and indexing was performed using TSL OIM Data Collection 5 with ferrite phase. The accelerating voltage was 20kV and spot size was 5nm. The scanning step size was 0.1 micron. For subsequent analysis, TSL OIM Data Analysis 5 was utilized for the production of inverse pole figures, pole figures, grain size distributions, and grain boundary misorientation distributions. During the processing of EBSD data, the data point with confidence index (CI) smaller
than 0.2 were cleaned up using the functions of grain dilation provided in TSL software.

4.3.4 Extraction Replica and Transmission Electron Microscopy

In order to quantify carbides, extraction carbon replica sample preparation technique was applied. A well-polished sample was prepared and then etched by Fry’s reagent. As a result, carbides are revealed on the sample’s surface. Then a thin layer of carbon film was deposited on the etched sample surface. 2-3 mm squares were cut from the carbon film with razor blades. The sample was then soaked in 50% HCl for to remove the carbon replica from the sample. After one hour soaking in HCl, the sample was put in to water and replicas would float on the water surface. 3mm Cu grid is use to hold carbon replicas for later TEM examination.

A Philips CM-200 TEM operated at 200 kV accelerating voltage was used to study carbides. The composition analysis is achieved by the EDAX X-Ray Energy Dispersive Spectrometer CM-200. A spot size of 9 was used since this spot utilizes a lower amount of beam current, and thus lowers the X-Ray dosage the detector receives. This ultimately leads to more accurate results. Diffraction patterns that were collected with the TEM were indexed and subsequently compared to simulated patterns generated with SingleCrystal.

4.3.5 Carbides quantification in Cr-Mo steels

Carbides were extracted by carbon replica technique and examined by TEM as
discussed in the previous section. All the carbides were identified by EDS. Electron diffraction and X-ray diffraction has confirmed that $M_{23}C_6$ and MX are the only two kind carbides in all condition. As a result, EDS only is sufficient to determine carbide type. If the carbide was enriched with Fe and Cr, the carbide was identified as $M_{23}C_6$. On the other hand, if V and Nb were major component in the carbide, it was identified as MX. The diameter of each indentified carbide was measured by mean intercept method. For carbon extraction replica technique, replicas only extracted precipitates on the sample surface. Accordingly, the thickness of analyzed volume should be close to the diameter of the largest precipitates. In current investigation, analyzed volume were estimated by the area of TEM image times the diameter of largest precipitates. As the volume was obtained, number density and volume fraction can be calculated.

4.3.6 Atom Probe Tomography

Coupons (0.3×6×6 mm$^3$) were cut utilizing a LECO® VC-50 Precision Diamond Saw. Atom probe tomography (APT) tip blanks, 0.3×0.3×6 mm3, were cut from the coupons and a standard two-stage electropolishing method was applied. Initial polishing was performed with a solution of 10 vol. % perchloric acid in acetic acid at 10 – 25 Vdc at room temperature. This was followed by a manually controlled pulsed final-polishing step using a solution of 2 vol. % perchloric acid in butoxyethanol at 10 – 25 Vdc at room temperature, producing a tip with a radius <50 nm. The APT data was collected utilizing the LEAP tomography at the Northwestern University Center for Atom-Probe Tomography (NUCAPT),
Evanston, IL. The data was acquired at a specimen temperature at 25K under ultra-high vacuum (UVHN) conditions of ca. $1.0 \times 10^{-8}$ Pa ($7.5 \times 10^{-11}$ torr). Voltage mode is used to get a more accurate composition. The voltage applied to the specimens is up to 8kv.

Data collected by LEAP is stored in file with the extension of RHIT. The RHIT file contains all the parameters and conditions during data collection, such as flight path, temperature, pressure, target pulse frequency, laser frequency. In addition, information about ions on the sample tip is included in RHIT file, including time of flight (TOF), position on the detecting screen, and ion type (single, multiple or partial). Calibration was carried out to get position information of ions from information stored in RHIT file. Reconstruction was made to visualize 3 dimensional distributions of ions. The acquired atomic position data are calibrated and reconstructed by using the Imago Visualization and Analysis (IVAS®) program (Imago Scientific Instruments). The data flow of LEAP system is shown in Figure 4.2.
Before calibration, the voltage range and region of interest (ROI) on the detector was selected to reconstruct ions in specific region. Since the sample was prepared by electropolishing with a Cu based holder, Cu, water, or some other elements from the electropolishing solution may contaminate the tip of sample. As a result, the first $10^5$ to $10^6$ ions will be eliminated during voltage range selection. TOF correction will be carried out after voltage range and ROI selection. TOF correction consists of a series of iterations and each iteration is comprised of a
voltage and flight path correction. The resolution should continue to improve with each iteration until convergence. TOF correction can be calculated by IVAS automatically. After TOF correction, mass to charge ratio was calibrated. With calibrated mass and TOF, reconstruction was made. In general, the following equation is used in IVAS to determine the initial radius from the initial voltage, which is determined in the voltage selection.

\[ r = \frac{v}{kF} \]  

(4.1)

where \( V \) is initial voltage (V), \( r \) is tip radius (nm) and \( F \) is evaporation field (V/nm). According to Miller [43], the evaporation field for Fe is 27 V/nm. However, the evaporation of Cu precipitate is preferred in steel compared with evaporation of Fe matrix. If 27 V/nm is used for reconstruction, the morphology and composition of Cu precipitate will be skewed from reality. Since information regarding the Cu precipitate is critical in the current study, a higher evaporation field, 30 V/nm is used to get close to real Cu morphology and composition. Reconstruction done by IVAS could generate a POS file, which contains atomic position \((x, y, z)\) and mass to charge values \((m/a)\). With atom position and mass information, all kinds of analysis could be done to evaluate nanostructure of sample.

The number density \((N_v)\), average radius \(<R>\) and composition of the Cu precipitates were determined by the envelope method [43]. The following parameters were used: a maximum Cu-atom separation = 0.6 nm, minimum
number of Cu atoms in a cluster = 30, and grid resolution = 0.12 nm. Precipitate characteristics including radius of gyration, Guinier radius, center-of-mass of the precipitates, and number of atoms in the precipitates were determined for the Cu precipitates. The $N_v$ is calculated using equation (1) [43]:

$$N_v = \frac{N_p \varsigma}{n\Omega},$$

where $N_p$ and $n$ are the number of particles and total number of atoms detected in the volume, respectively, $\Omega$ is the average atomic volume, $1.2 \times 10^{-29} \text{ m}^3$ for bcc Cu, and $\varsigma$ is the detection efficiency of the multichannel plate (MCP), which is taken to be 0.5.

In order to study the precipitate in Grade 91 steels, 4 at.% isoconcentration interface is generated by IVAS. Composition profiles were obtained by generating a proxigram across 4% V isoconcentration interface with a selected bin size of 0.2 nm [82].

4.3.7 Hybrid in-situ characterization

A hybrid in-situ characterization system, which has been described in section 2.5.5, was used. Cylindrical samples were prepared with the dimension of 5mm in diameter and 2mm in height. The surfaces of the samples were final polished (0.02µm colloidal silica) to be suitable for LSCM observation. Figure 2.39 shows the experimental set-up of the hybrid in-situ observation system situated within a 46XU beamline at Spring-8 in Hyogo, Japan. The infrared furnace was set on the
theta-axis of the goniometer. The LSCM system containing a laser head and the furnace was attached to the theta-axis.

Samples were placed inside a boron nitride (BN) crucible, which was held by a platinum holder. A thermocouple was attached to the platinum holder to measure the temperature. The measured temperature was used to control the heat flux generated by the halogen lamps. The sample was placed at the focal point of the halogen lamp and mirror systems. During the experiments, the furnace was filled with pure argon (99.99996%) after evacuation to prevent oxidation. The LSCM recorded the images at a rate of 30 frames per second (time resolution = 0.03s). The current work has shown a small temperature gradient from the top to bottom of the sample, under rapid heating/cooling conditions. A correction factor has been used to account for these gradients. The methodology for correcting the same and impact of temperature gradients on accuracy of measurements will be discussed later.

A large-area pixel detector, Pilatus 2M [83] was placed on the 2-theta axis (Figure 2.39b). The incident beam (30keV) shines on the sample surface placed in the furnace and the resulting diffraction rings were recorded by the pixel detector. The time resolution (TRXRD) dictated by the detector hardware is 0.3s. The X-ray with a wavelength was set at 0.413269Å. The glancing angle of the beam on the sample surface was chosen to be 5° and this leads to a total irradiated area on the sample surface to be 2.07 mm². The depth of X-ray interaction in the sample is estimated to be around ~16 µm [18].
For each thermal cycle, 1000 diffraction images were collected from pixel detector with a time resolution of 0.3s. The diffraction rings on each image were integrated to give one-dimensional scans of intensity versus interplanar spacing [84, 85]. In order to take care of possible changes in the incoming X-ray intensity, the diffraction intensity at each time interval was normalized with reference to the highest peak intensity. The diffraction data are then synchronized with measured thermal cycles. In the next step, the scans were analyzed by using automatic peak fitting algorithms. The methodologies for these are described in published literature [75, 77].
Chapter 5 Strength Recovery of BlastAlloy-160

Weldability testing techniques, such as Heat-Affected Zone (HAZ) simulations, hot ductility testing and reheat cracking testing, have been employed to evaluate the weldability of BA-160 [86]. Prior research on four HAZ regions of BA-160 steels, using a Gleeble3800 thermomechanical simulator, showed no strength change in the SCHAZ, some hardening in the ICHAZ, and softening in both the FGHAZ and CGHAZ. Atom probe tomography (APT) characterization and strengthening analyses correlated the softening to the dissolution of Cu precipitates and carbides. To validate the preceding thermal simulations, gas tungsten arc (GTA) spot welds were made on BA-160 samples. Vickers microhardness traverse across spot weld HAZs showed a similar phenomenon as that observed from GLEEble samples. Softening is shown close to the fusion line (i.e., CGHAZ) and hardening is observed in the ICHAZ. These results confirmed the presence of four distinct HAZ regions in the spot welds.

Based on the preceding results, thermal simulations were considered to be an effective tool to evaluate the HAZ regions of BA-160. The fusion zone of GTA spot welds contained cellular/dendrite solidification substructure with an average hardness of 364VHN. Since both microstructure and hardness are not favorable in
The fusion zone, consumables for BA-160 have to be designed in the future. The focus of the current research is to develop methods to mitigate the softening in the HAZ region.

It is conceivable that post weld heat treatment (PWHT) could reinstate strength in the HAZ. For example, autogenous spot welds in the BA-160 sample were post weld heat treated at 550 °C for 30 minutes or 450 °C for 5 hours. Strength recovery was observed in the fusion zone and HAZ. The observed strength increase was assumed to be the result of reprecipitation during the PWHT. The PWHT is not feasible for naval applications due to the size or complexity of the structures that are welded. Alternatively, strength recovery in the HAZ (or weld metal) could be achieved by designing an appropriate multi-pass welding procedure that leads to a similar extent of re-precipitation during PWHT. Most of the HSLA structural steel plates currently used in shipyards are in the range of 6 to 30 mm with yield strength from 448 to 689 MPa. The thickness of heavier gage plate could be as high as 83 mm. Though the plate thickness of BA-160 will be reduced due to the high yield strength, the envisioned thickness for naval applications (>6 mm) is still too high for single pass welding. As a result, multi-pass welding is required for most applications. For some HAZ regions (CGHAZ and FGHAZ), the first thermal cycle with high peak temperature (>Ac3) causes the dissolution of precipitates. Subsequent thermal cycles with low peak temperatures (500 °C to 650 °C)) may trigger re-precipitation. It is realized that the thermal history of multi-pass HAZ is complex and depends on many variables, such as plate thickness, welding procedure, and field condition. The current
chapter only focuses on validation of the hypothesis of re-precipitation and strength recovery during the second thermal cycle in multi-pass welding. Thermal simulations and microstructural characterizations are used to prove the hypothesis. In addition, an appropriate strengthening model is used to rationalize the results.

5.1 Gleeble simulation and hardness measurement

The experimental measured thermal profile is plotted in Figure 5.1. The dilatation curves are presented in Figure 5.2. The on-cooling dilatation curve for both CGHAZ+650 HHI and LHI shows martensite transformation starts approximately at 356 °C. No phase transformation was observed during the thermal cycle with peak temperature of 650°C based on the dilatation curve.

![Figure 5.1 experimental measured thermal profile for double thermal cycle HAZ simulation](image)

Figure 5.1 experimental measured thermal profile for double thermal cycle HAZ simulation
Figure 5.2 Relative sample radius change and temperature trace during (a) coarse-grained HAZ+650 with high heat-input and (b) coarse-grained HAZ+650 with low heat-input thermal cycles from dilatometry experiment.
A plot of Vicker microhardness for different samples was provided in Table 5.1. For single pass HAZ simulation samples (CGHAZ with HHI and CGHAZ with LHI), Vicker hardness is about 340VHN, which is much lower than that of as-received materials (402VHN). For double-pass HAZ samples, the Vicker microhardness is approximately 405VHN. The hardness of the double-pass samples was regained to that of the base metal. The hardness recovery is believed to be caused by re-precipitation during the heat treatment of second thermal cycle.

Table 5.1 Microhardness of As-Received Materials and Different HAZ Regions (Average Hardness of 10 Measurements)

<table>
<thead>
<tr>
<th>Material</th>
<th>VHN</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>402</td>
</tr>
<tr>
<td>Coarse Grained HAZ (High Heat-Input)</td>
<td>340</td>
</tr>
<tr>
<td>Coarse Grained HAZ+ 650 (High Heat-Input)</td>
<td>405</td>
</tr>
<tr>
<td>Coarse Grained HAZ (Low Heat-Input)</td>
<td>351</td>
</tr>
<tr>
<td>Coarse Grained HAZ + 650 (Low Heat-Input)</td>
<td>404</td>
</tr>
</tbody>
</table>

5.2 Precipitate characterization

Cu atom maps for all samples are summarized in Figure 5.3. In Figure 5.3a and c, no Cu-enriched regions are observable or as the Cu atoms are almost homogenously distributed in CGHAZ for both HHI and LHI condition. The
presence of Cu rich precipitates can be clearly seen in Figure 5.3b and d. In order to get quantitative information of Cu-rich precipitates, a cluster searching algorithm called envelope method was applied [7]. The following parameters were used: maximum Cu atom separation = 0.6 nm; minimum number of Cu atoms in a cluster = 30; grid resolution = 0.12 nm. Cu precipitates found by the program are shown in Figure 5.4. Precipitate characteristics including radius of gyration, Guinier radius, center-of-mass of the precipitates and number of atoms in the precipitates were determined for the Cu precipitates. The number density \( N_v \) is calculated using equation:

\[
N_v = \frac{N_p \varsigma}{n \Omega}
\]

(5.1)

where \( N_p \) and \( n \) are the number of particles and total number of atoms detected in the volume, respectively, \( \Omega \) is the average atomic volume, 1.2 × 10^{-29} m^3 for BCC Cu, and \( \varsigma \) is the detection efficiency of the multichannel plate (MCP), which is taken to be 0.5. The summary of the results for the Cu precipitates is given in Table 5.2. The concentration of Cu precipitates matrix, as determined by the precipitate searching algorithm, is also provided in Table 5.3.
Figure 5.3 3-D LEAP tomographic reconstruction displaying Cu atoms for (a) coarse-grained HAZ with high heat input, (b) coarse-grained HAZ+650 with high heat input, (c) coarse-grained HAZ with low heat input (d) coarse-grained HAZ+650 with low heat input.

Even though Cu-enriched regions cannot be seen in CGHAZ for HHI and LHI, Cu precipitates with small radius are still detected by the precipitates searching algorithm (Figure 5.5). It is noted that the size and distribution of Cu precipitates is strongly related to the parameters chosen during precipitate searching. The small precipitates in CGHAZ could represent artifacts produced in the current
analysis. However, the emphasis of this study is to compare the Cu precipitates characteristics between single thermal cycle HAZ and double thermal cycle HAZ.

The absolute properties of Cu precipitates are of secondary importance.

<table>
<thead>
<tr>
<th></th>
<th>Radius (nm)</th>
<th>Number density ($10^{23} \text{ m}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>2.4±1.2</td>
<td>4.2±2.2</td>
</tr>
<tr>
<td>Coarse Grained HAZ (High Heat-Input)</td>
<td>1.7±0.5</td>
<td>2.0±1.1</td>
</tr>
<tr>
<td>Coarse Grained HAZ+ 650 (High Heat-Input)</td>
<td>2.4±1.5</td>
<td>9.4±3.1</td>
</tr>
<tr>
<td>Coarse Grained HAZ (Low Heat-Input)</td>
<td>1.9±1.4</td>
<td>2.0±1.40</td>
</tr>
</tbody>
</table>

Figure 5.4 Major alloy element composition profile across the copper precipitates boundary in (a) coarse-grained HAZ+650 with high heat input and (b) coarse-grained HAZ+650 with low heat input.
Table 5.3 Composition of Martensite Matrix (Atomic Percent) Measured by Atom Probe

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse Grained HAZ (High Heat-Input)</td>
<td>0.11</td>
<td>1.94</td>
<td>87.84</td>
<td>6.73</td>
<td>0.36</td>
<td>2.86</td>
</tr>
<tr>
<td></td>
<td>± 0.001</td>
<td>± 0.003</td>
<td>± 0.007</td>
<td>± 0.006</td>
<td>± 0.001</td>
<td>± 0.004</td>
</tr>
<tr>
<td>Coarse Grained HAZ + 650 (High Heat-Input)</td>
<td>0.05</td>
<td>1.98</td>
<td>90.28</td>
<td>6.43</td>
<td>0.38</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>± 0.001</td>
<td>± 0.007</td>
<td>± 0.015</td>
<td>± 0.012</td>
<td>± 0.003</td>
<td>± 0.004</td>
</tr>
<tr>
<td>Coarse Grained HAZ (Low Heat-Input)</td>
<td>0.37</td>
<td>1.95</td>
<td>86.33</td>
<td>7.82</td>
<td>0.48</td>
<td>2.95</td>
</tr>
<tr>
<td></td>
<td>± 0.003</td>
<td>± 0.006</td>
<td>± 0.016</td>
<td>± 0.012</td>
<td>± 0.003</td>
<td>± 0.008</td>
</tr>
<tr>
<td>Coarse Grained HAZ + 650 (Low Heat-Input)</td>
<td>0.16</td>
<td>2.15</td>
<td>89.45</td>
<td>6.73</td>
<td>0.37</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>± 0.002</td>
<td>± 0.008</td>
<td>± 0.017</td>
<td>± 0.014</td>
<td>± 0.003</td>
<td>± 0.005</td>
</tr>
</tbody>
</table>

Table 5.2 shows for single pass CGHAZ, both radius and number density of Cu precipitates is low. The data indicates nearly full dissolution of Cu precipitates.
Compared with single pass CGHAZ, double pass HAZ samples have larger Cu radius and number density. The Cu precipitates should be formed during the second thermal cycle of double pass HAZ simulation. Besides, after the second thermal cycles in double pass HAZ, Cu concentration in matrix decrease from approximately 2.85 at.% to 0.9 at.% . About 2 at.% Cu re-precipitate from the matrix during the heat treatment of second thermal cycles.

Major component concentration profile across one representative Cu precipitate interface in CGHAZ+650 with HHI and LHI samples is plotted in Figure 5.4. Cu concentration in precipitate core is about 66 at.%, which is lower than Cu concentration in Cu precipitate at aged condition (above 90 at.%) [87].
Figure 5.5 1 pct carbon (plum) and 8 pct copper (golden) isoconcentration surface from (a) coarse-grained HAZ with high heat-input sample and (b) coarse-grained HAZ+650 with high heat-input sample. (c) Composition profile across the metal carbide boundary shown by the arrow in (a).
1 at.% C and 8 at.% Cu iso-concentration surface in CGHAZ and CGHAZ+650 with HHI is shown in Figure 5.6. Few precipitate-like C and Cu iso-concentration surface could be generated by analyzing the data from CGHAZ-HHI. In CGHAZ+650-HHI sample, many Cu precipitates and carbides, which are represented by C and Cu iso-concentration interface, could be observed. One precipitate is selected by the bold arrow shown in Figure 5.6b. Major component concentration profile across the carbide interface is plotted in Figure 5.6c. The carbide is enriched with Cr and Mo. Since the C concentration in the core of carbide is approximately 30 at.%, this carbide is most likely to be M$_2$C (where M=Fe, Cr, Mo). Cu is depleted in carbide and enriched near carbide boundary.
This observation supports the report of co-locate of Cu precipitates and Mo/Cr-enriched carbide [9].

### 5.3 Martensite sub-structure

Current investigation employs EBSD technique to study the morphology and crystallography of martensitic matrix. Martensite sub-structure of single pass BA-160 HAZ has been studied extensively [5]. Two EBSD maps of CGHAZ with HHI and LHI are shown in Figure 5.7. Since dilatation data has already indicates no matrix transformation during the second thermal cycle of double pass HAZ, martensite morphology should be the same for single pass and double pass. As a result, properties of martensite sub-structure in double pass HAZ were not measured and assume to be the same as single pass HAZ. The characteristics of martensite sub-structure are summarized in Table 5.4.

<table>
<thead>
<tr>
<th></th>
<th>Packet Size (μm)</th>
<th>Block width (μm)</th>
<th>Slip plane length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG HAZ (HHI)</td>
<td>56.0±7.5</td>
<td>12.4±3.5</td>
<td>25.3±5.0</td>
</tr>
<tr>
<td>CGHAZ+650 (HHI)</td>
<td>56.0±7.5</td>
<td>12.4±3.5</td>
<td>25.3±5.0</td>
</tr>
<tr>
<td>CGHAZ (LHI)</td>
<td>52.3±7.2</td>
<td>11.9±3.4</td>
<td>24.0±4.9</td>
</tr>
<tr>
<td>CG HAZ +650 (LHI)</td>
<td>52.3±7.2</td>
<td>11.9±3.4</td>
<td>24.0±4.9</td>
</tr>
</tbody>
</table>
Figure 5.6 Measured EBSD images from (a) coarse-grained HAZ with high heat input and (b) coarse-grained HAZ with low heat input.
5.4 Precipitate evolution in HAZ

APT results show re-precipitation of Cu precipitates and carbides during the second heat treatment of double pass HAZ. In the HAZ of BA-160, the solid state transformations involved are complex due to on-heating transformation of martensite to austenite; precipitate growth and coarsening; precipitate dissolution; reformation of precipitates during cooling; and on-cooling transformation of austenite to martensite. Figure 5.8 [5] is a schematic of the thermal history of the CGHAZ divided into five stages.

Figure 5.7 (a) Predicted solubility of Cu in austenite and ferrite is displayed as a function of temperature. (b) Schematic illustration of different stages in microstructure evolution in coarse-grained HAZ region.
The Cu solid solubility in austenite and ferrite is also plotted as a function of temperature, evaluated with ThermoCalc® software using the TCFE5 thermodynamic database [88]. For double pass HAZ in current analysis, during the first CGHAZ thermal cycle, when the material is heat from P1 to P4, martensite transformed to austenite and all precipitates go into solution. On-cooling, from P4 to P5, due to high solubility of Cu and C in austenite and short period of time, re-precipitation is limited. At the temperature below Ms, precipitation is not expected since the diffusivity of Cu and C is very low. During the second thermal cycle, the material is heated to a temperature below Ac1, the nucleation and growth of Cu precipitates and carbide is expected. Figure 8a shows the solubility of Cu in ferrite at 650 °C is about 0.7 at.%. Since the Cu concentration in the material is 3.3 at.%, Cu is still supersaturated at this temperature. High Cu diffusivity and supersaturation of Cu promote Cu precipitates nucleation and growth.

5.5 Modeling of strengthening mechanism

Previous study [5] proposed a strengthening model by considering Cu precipitation and martensite sub-structure strengthening to interpret the hardening and softening phenomena in simulated HAZ of BA-160. However, due to dissolution of carbide, strengthening model for single pass HAZ did not consider carbide contribution. Since carbide re-precipitates during the second thermal cycle of double pass HAZ, strengthening contribution from carbide should be considered. Orowan harden mechanism is used here to model the strength
contribution by carbide. The Orowan-Ashby [89] equation for looping of precipitate is expressed by:

\[
\tau_c = \frac{0.81Gb}{2\pi(1-\nu^2)D} \ln\left(\frac{2r_0}{b}\right) \quad (5.2)
\]

Where \( \tau_c \) is the resolved shear strength increase due to carbide, \( G \) is the shear modulus (77 GPa), \( \nu \) is Poisson’s ratio (0.3), \( D \) is the effective inter-precipitate spacing, \( r_0 \) is the mean precipitate radius, and \( b \) is the Burger vector (0.25nm). The properties of carbides can be estimated from the ATP analysis. Results are listed in Table 5.5.

By plugging all martensite, Cu precipitates and carbides properties into the current strengthening model, strengthening contribution could be calculated (Table 5.6). Data from [5] is concluded here to have a comprehensive understanding of current strengthening model. Figure 5.9 shows the predicted strength difference change vs. hardness difference change for all HAZ regions. The base metal hardness is used as a reference. A near linear relationship between predicted strength difference and hardness difference indicates the validation of current strength model.
Table 5.5 Strengthening Contributions in Different HAZ Samples ($\sigma_p$—Strengthening by Cu Precipitates, $\sigma_g$—Strengthening by Martensite Lath Boundaries, $\sigma_c$—Strengthening by Metal Carbides, and $\Delta\sigma$—Overall Strengthening)

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\sigma_p$ (Mpa)</th>
<th>$\sigma_g$ (Mpa)</th>
<th>$\sigma_c$ (Mpa)</th>
<th>$\Delta\sigma$ (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sub-critical HAZ (HHI)</td>
<td>282.5</td>
<td>127.0</td>
<td>0.0</td>
<td>409.5</td>
</tr>
<tr>
<td>Inter-critical HAZ (HHI)</td>
<td>190.0</td>
<td>290.0</td>
<td>0.0</td>
<td>480.0</td>
</tr>
<tr>
<td>Fine Grained HAZ (HHI)</td>
<td>4.8</td>
<td>213.0</td>
<td>0.0</td>
<td>217.8</td>
</tr>
<tr>
<td>Coarse Grained HAZ (HHI)</td>
<td>15.8</td>
<td>72.3</td>
<td>0.0</td>
<td>88.1</td>
</tr>
<tr>
<td>Coarse Grained HAZ (LHI)</td>
<td>57.3</td>
<td>74.1</td>
<td>0.0</td>
<td>131.4</td>
</tr>
<tr>
<td>Coarse Grained HAZ + 650 (HHI)</td>
<td>182.5</td>
<td>72.3</td>
<td>110.9</td>
<td>365.7</td>
</tr>
<tr>
<td>Coarse Grained HAZ + 650 (LHI)</td>
<td>176.0</td>
<td>74.1</td>
<td>105.3</td>
<td>355.4</td>
</tr>
</tbody>
</table>

Table 5.6 Radius and Number Density of M2C Precipitates for As-Received Material and Different HAZ Regions

<table>
<thead>
<tr>
<th></th>
<th>Radius (nm)</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse Grained HAZ (HHI)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Coarse Grained HAZ+ 650 (HHI)</td>
<td>1.23±1.1</td>
<td>0.00023</td>
</tr>
<tr>
<td>Coarse Grained HAZ (Low Heat-Input)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Coarse Grained HAZ + 650 (Low Heat-Input)</td>
<td>1.19±0.7</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Most of the research on Cu strengthened steel is focused on isothermal aging [90, 91, 92]. The aging time is usually between 0.5 to 320 hours. Heat treatment by isothermal aging is time and energy consuming. Current study shows Cu precipitation can occur during rapid heating and cooling. It is suggested quick heat treatment to 650 °C followed by air-cooling is sufficient for Cu precipitation.
Future investigation of non-isothermal heat treatment of Cu precipitate strengthened is recommended for steel making.

Figure 5.8 Predicted strength increase due to martensite substructure and copper precipitates compared with experimentally measured microhardness changes in the HAZ regions.
5.6 Summary

The softening in the CGHAZ region of BA 160 is partly attributed to the dissolution of Cu and metal carbide precipitates. Recovery of strength during multipass welding was demonstrated through two-cycle thermal simulations.

During the first cycle, on heating the steel above $A_{c3}$, softening was observed due to precipitate dissolution. During the second thermal cycle, on heating the steel below $A_{c1}$, re-precipitation of copper precipitates and carbides was promoted. This leads to an increase in hardness from 340 to 405 HV.

A strength model, including precipitation and martensite substructure strengthening, describes the observed softening and hardening in the HAZ simulated samples.

The current study also suggests a rapid nonisothermal aging treatment (heating rate = 100 °C/s and peak temperature = 923 K (650 °C)) for strengthening of the original BA160 steel, instead of long isothermal aging treatments.
Chapter 6. In-situ phase transformation study of BlastAlloy-160

Previous studies also demonstrated that martensite substructure plays an important role in strengthening of BA-160 [3]. For example, fine martensite substructure contributed to the hardening in the samples subjected to the intercritical HAZ thermal cycle. This was attributed to the reduced martensite plate/lath/packet size, which in turn is related to small austenite grain diameter. This observation is in agreement with the research of Morito et al.[15] The preceding microstructure evolutions were rationalized with ex-situ characterization tools including optical microscopy and electron backscattered diffraction imaging. However, to develop a comprehensive computational model for HAZ, there is a need to measure the kinetics of microstructural evolution (fraction transformed and morphology) during continuous cooling conditions typical of that of welding. Although the dilatation measurements during GLEEBLE thermal simulation can be considered as an indirect in-situ measurement, the transients in morphological changes and crystallographic information are not accessible by this technique. Hybrid in-situ characterization system, discussed in section 4.3.7 is applied to study phase transformation in BA-160.
6.1 Analysis of transformation kinetics by TRXRD

Thermal cycles used to simulate different HAZ regions are plotted in Figure 6.1. Figure 6.2 shows two snapshots of X-ray diffraction rings recorded by the pixel detector. The images (CGHAZ sample) show the diffraction characteristics during heating at 880°C and 1243°C. In both the cases, the austenite is the only phase that is present in the sample. The data obtained at 880°C, show continuous diffraction rings from \{111\}_FCC and \{200\}_FCC lattice planes (see Figure 6.2a). In contrast, the data obtained from 1243°C show spotty diffraction images from the same and other lattice planes. Diffraction rings from BN crucible are also clearly visible under this condition. An ultra-bright diffraction spot (shown by the arrow in Figure 6.2b) is from \{111\}_FCC planes and this spot overlaps with diffraction ring from BN. This is indeed expected since there are many small austenite grains (at 880°C) with random orientation on heating just above the Ac₃ temperature. This diffraction conditions are similar to that of powder diffraction and we observe continuous rings. If we assume that the average austenite grain size of 10 μm at this temperature, using the estimated irradiated surface area (2.07 mm²) and penetration depth (16 μm), the estimated number of austenite grains that may be in diffraction condition may be greater than 30,000. However, continued heating above 880°C to 1243°C will lead rapid austenite grain growth and the average grain size may increase above 130 μm. Under these conditions, only few (< 10) austenite grains are estimated in the ideal diffraction condition within the irradiated volume. Continued growth of austenite grain size will
eventually lead to a transition from powder diffraction to single crystal diffraction conditions. Moreover, our experimental setup does not allow for recording of diffraction from all solid angles (Debye - Scherer cones) that satisfies Bragg’s law. As a result, the integrated intensity of austenite at these temperatures will be close to the background levels [see Fig. 6.3]. This is expected to produce low signal to noise ratio (SNR) while analyzing the data from austenite. A rapid change in austenite grain growth (~ 130 µm) is also supported by the LSCM images to be discussed later.

Figure 6.1 Thermal cycles applied to simulate regions (ICHAZ, FGHAZ, and CGHAZ) of the HAZ with different peak temperatures are shown
Figure 6.2 Snapshots of images, showing diffraction rings, on heating the sample to different peak temperatures are shown. The dark bands are the region with no data due to the presence of masks. (a) On heating to 1153 K (880 °C), continuous rings are observed, indicating many small austenite grains that interact with the beam. (b) On heating to 1516 K (1243 °C), spotty features are observed due to the small number of large austenite grains that interact with the beam. These conditions lead to low SNR.

Phase transformations from austenite to martensite were analyzed using TRXRD data. The crystal structure of martensite is body centered tetragonal (bct) and the tetragonal distortion (c/a ratio) is related to the carbon concentration. Since the carbon content in BA-160 is low (0.06 wt.%), current experiments cannot
distinguish the peak splitting in martensite. Therefore, in current study martensite data is represented as body centered cubic (BCC) structure in all the results. Furthermore, diffraction data from \{111\}_{\text{FCC}} and \{011\}_{\text{BCC}} plates are selected for further analysis. The normalized intensities of \{111\}_{\text{FCC}} and \{011\}_{\text{BCC}} diffraction data in an image format, for all the HAZ samples with corresponding thermal cycles, are shown in Figures 6.3. In CGHAZ sample (see Figure 6.3a), immediately after the completion of martensite to austenite transformation, the data from \{111\}_{\text{FCC}} show good SNR. As expected from our previous discussions, the SNR reduce significantly (< 0.3) when the sample temperature reaches the peak temperature of 1243°C. Interestingly, as soon as the austenite decomposition starts, SNR of \{111\}_{\text{FCC}} increase to 5.6. This is consistent with the data from Terasaki and Komizo [93]. The above increase in SNR is rationalized by the geometrical considerations. On reaching the martensitic start temperature, the first martensitic plate will subdivide the large austenite grain into two major compartments. This will also result in small surface reliefs in the sample. This phenomenon is supported by the LSCM images (see Figure 6.4). As a result, the austenite grains in diffraction condition increases. With continued cooling, the next set of martensite plates forms and sub-divides the austenite grains furthermore. The above phenomena will be repeated with continued cooling and the number of austenite compartments will increase in geometric progression. This leads to a transition of diffraction condition form single crystal to powder diffraction conditions and thereby increasing the SNR. The above discussions are consistent with the data obtained from FGHAZ (see Fig. 4b and 4c) and ICHAZ.
samples. In both the cases, the austenite grain size remains lower than 10 µm. As a result, the SNR of austenite diffraction peaks remains at or about 50. It is noteworthy that in case of ICHAZ samples, the transformation to austenite is not complete [see Fig. 4c]. On reaching the peak temperature, approximately 25% of original martensite structure is calculated to be present still. Therefore, the austenite grain size is expected to be much smaller than 10 µm.
Figure 6.3 Overview of the TRXRD data in the image format and associated time and temperature variations are presented here. (a) Data from CGHAZ sample: Low SNR (<0.3) is observed for austenite diffraction peaks during cooling. SNR is improved after the start of martensite transformation. (b) Data from FGHAZ sample: High SNR (51.2) is observed in the austenite region throughout the thermal cycle. (c) Data from ICHAZ sample: The presence of bcc/bct peaks all the time indicates incomplete martensite to austenite transformation (75 pct).
Figure 6.4 LSCM images obtained at some typical temperatures during the onset and completion of the austenite-to-martensite transformation are presented. CGHAZ: Images from CGHAZ samples show (a) large austenite grain size and (b) large martensite packets. FGHAZ: Images from the FGHAZ show (c) fine austenite grains (mottled pattern) and the onset of the first martensite packets (black regions). (d) After the completion of transformation, the refinement of the martensite packet size is clear compared to CGHAZ samples. ICHAZ: Images from the intercritical HAZ samples showing (e) featureless polished surfaces due to lack of clear austenite/austenite boundaries due to incomplete transformation and the onset of the first martensite plate (dark region). (f) After completion of transformation, similar to FGHAZ, refined martensite packet size is observed. Note the temperature correction of 57 deg was made for the above data.
Careful analyses of the data shown in Fig. 6.3c also showed puzzling behavior with reference to continued increase in volume fraction of austenite during early stages of cooling cycle. This behavior has been rationalized by recent measurements of top and bottom surface, which showed a phase lag in temperature between these locations [94]. Nevertheless, these recent measurements have also confirmed that the measured peak temperatures are indeed same and allowed us to compare the results from different HAZ samples. Since our focus is martensitic transformation characteristics, a temperature correction has to be made to analyze these TRXRD and LSCM data. Martensite start temperature derived from dilatation analysis for CGHAZ sample was found to be 347°C, which is 57°C higher than observed in the current hybrid technique. Previous research has shown that M_s measurements are accurate with dilatation technique [3]. Therefore, current investigation assumed a constant temperature gradient of 57°C from sample surface to bottom for subsequent analyses and
results. The above corrections are made for interpretation of all TRXRD and LSCM data and are specifically called out in all the figures.

6.2 LSCM observations

Figure 6.4 shows snapshots of LSCM images before and during austenite to martensite transformation during cooling for all HAZ samples. It is noteworthy that the images in LSCM are attained by a change in surface topology. The austenite (γ-γ) grain boundaries are imaged due to the surface grooving. In CGHAZ sample (see Fig. 5a), large austenite grains (~ 130 µm) can be seen at the onset of martensite transformation at 346°C. In this image, fresh martensite packets can be seen adjacent to γ-γ grain boundaries (left side of the image). The martensite packets are imaged in LSCM technique due to the surface relief that occurs during displacive transformation of austenite to martensite [95]. In this work, we cannot delineate individual martensite plate growth, because they form in less than 10⁻⁷ s [95], which smaller than LSCM time resolution of 0.03 s. LSCM image obtained at 146°C shows more or less completion of austenite to martensite transformation. Many variants of martensite plates can also be seen. In addition, one can conclude that the martensite packets and blocks (see Figure 6.4b) are larger in comparison to the data from other samples to be presented below.

In FGHAZ sample, austenite grains (see Figure 6.4c) with an average grain size of 10 µm are observed at 314°C. Interestingly, no martensite transformation can be discerned from the images at this temperature. In contrast, the LSCM images
from CGHAZ samples showed the onset of martensitic transformation at 346 °C. Sequential analyses of LSCM images from these samples showed dramatic reduction in martensite packet sizes. Fine martensite packets and blocks are also evident from the LSCM image at 91°C, when the transformation is nearly complete (see Figure 6.4d).

In ICHAZ sample, the LSCM did not show clear $\gamma$-$\gamma$ grain boundaries (see Figure 6.4e). This is indeed expected, because the austenite to martensite transformation is not complete on reaching the peak temperature. TRXRD data showed that, on heating to peak temperature, newly formed austenite and untransformed martensite must coexist. Since the surface of these samples is in the polished condition, the original martensite boundaries ($\alpha/\alpha$) cannot be visualized. The newly formed austenite may lead to the formation of $\alpha$-$\gamma$ interphase boundaries, as well as, $\gamma$-$\gamma$ grain boundaries. On cooling to 296°C, the first martensite packet formation was imaged at a temperature of 296°C. After cooling below 93°C, LSCM images show completion of martensite transformation (see Figure 6.4f). These images show fine martensite packet, as well as, the original featureless white regions (marked by arrows in Figure 6.4f). These regions are interpreted as the original martensite regions that have not been transformed on heating.

### 6.3 Dilatometry Measurements

Phase transformation strains were also measured using a dilatometer while subjected to different HAZ thermal simulations. A typical dilatation curve for
FGHAZ sample is shown in Figure 6.5. As the specimen is heated (at 20°C·s⁻¹) from room temperature, the relative radius change increases with a nearly constant positive slope dictated by coefficient of thermal expansion of ferrite. On reaching the Ac₁ (660°C) temperature martensite transforms to austenite, which is associated with a contraction. The dilatation curve becomes linear at Ac₃ (740°C), due to the completion of transformation to austenite. The thermal expansion coefficient for martensite (1.088±0.001×10⁻⁵) and austenite (2.375±0.001×10⁻⁵) can be calculated from these curves. Next, the volume fraction of austenite and martensite can be calculated by geometric methods developed by Eldis [96] and Babu [97]. The same approach is used in martensite fraction calculation during cooling in Figure 6.6b.

Figure 6.5 Relative radius change vs. temperature obtained from FGHAZ samples showing on-heating (martensite to austenite) and on-cooling (austenite to martensite) transformations.
6.4 Discussion on $M_s$ and Martensite Transformation Rates

The data shown in Figure 6.6 was analyzed further by fitting a Gaussian peak to \{111\}_\text{FCC} and \{011\}_\text{BCC} diffraction peaks of the form [98]:

$$I = I_0 \exp\left(\frac{d-d_0}{w}\right)^2$$

(6.1)

where $I$ is the observed intensity as a function of interplanar spacing, $I_0$ is the intensity for a given mean interplanar spacing $d_0$ and $w$ is given by the Gaussian peak width. After peak fitting, the areas under \{111\}_\text{FCC} and \{011\}_\text{BCC} peaks are integrated. Phase volume fraction was derived by using direct comparison method considering structure factor, multiplicity factor, Lorentz polarization, and temperature factor [99]. Martensite fraction ($f_m$) as a function of temperature is plotted in Figure 6.6a. The $M_s$ for CGHAZ, FGHAZ and ICHAZ are 349°C, 311°C, and 293°C, respectively. This reveals a reduction of $M_s$ temperature with a reduction in austenite grain size. This result is in agreement with the measured $M_s$ by Yang and Bhadeshia using dilatometric technique [100]. From Figure 6.6a, it can be seen that the martensite fraction has a nearly linear relationship with temperature when $0.1<f_m<0.5$. By fitting a linear curve through martensite fraction [$0.1<f_m<0.5$] as a function of temperature, the transformation rate $df_m/dT$ was calculated for all the data shown in Fig. 7a. The magnitudes of $df_m/dT$ are found to be 0.033/°C, 0.018/°C and 0.012/°C for CGHAZ, FGHAZ and ICHAZ, respectively. The above calculations also suggest that an increase in austenite grain size also promotes the transformation rate. It is realized that in our data
analyses only one pair of diffraction peaks \( \{111\}_{\text{FCC}} \) and \( \{011\}_{\text{BCC}} \) is considered to derive the martensite volume fraction. For FGHAZ and ICHAZ, the result is accurate since the prior austenite grain size is small (<10µm). However, for CGHAZ, since the prior austenite grain is large (>130µm), the analyzed volume has less than 10 austenite grains. This small number may give a less accurate result on martensite volume fraction. We believe that transmission type 3D X-ray diffraction methodology with large beam size may indeed improve these results and is indeed focus of the future work [101].
Figure 6.6 Measured fraction of martensite as a function of temperature on cooling from different techniques. (a) TRXRD data: This is determined by the direct comparison method using \{011\}-bcc and \{111\}-fcc peaks. Note the temperature correction of 57 deg was made for the TRXRD data. (b) Gleeble dilatation measurement: This is determined by the geometric method, which assumes linear dilatation in the pure martensite and austenite phase fields.
To reconfirm the above result, the dilatometry data is also analyzed (see Fig. 6.6b) further. Due to the uncertainty of the exact temperature in the TRXRD data, these comparisons are made in terms of trends only. First, the dilatation data from CGHAZ and FGHAZ regions are discussed. CGHAZ sample shows the highest $M_s$ ($348^\circ$C) compared to that of FGHAZ ($331^\circ$C). Thus, the data reconfirms the trend of decreasing $M_s$ with a decrease in austenite grain size, in both techniques. However, it is clear that there is a discrepancy in measurements with respect to ICHAZ ($M_s = 331^\circ$C) from TRXRD and dilatometric data. The following paragraph attempts to explain this discrepancy based on the inability to control the peak temperature with reference to $A_{c1}$ and $A_{c3}$ transformation temperatures during TRXRD measurements and resulting difference in extent of transformation to austenite. During dilatometry experiments, the ICHAZ sample shows nearly complete (99%) transformation of martensite to austenite on reaching the peak temperature of $738^\circ$C. However, in TRXRD data, the transformation to austenite is only 75% complete (see Figure 6.6a). Therefore, on reaching the peak temperature, the austenite is expected to have higher carbon concentration. According to thermodynamic calculation using Thermocalc® (with TCFE5 database) [56], the carbon concentration of ferrite (or original martensite) in equilibrium with austenite at $660^\circ$C will be 0.0007 wt.%. Taking 25% as untransformed martensite region, the carbon concentration in remaining (75%) austenite will be 0.08 wt.%. This is indeed higher than nominal carbon concentration (0.06%) of the steel. Therefore, the $M_s$ temperature will reduce
further due to a reduction in driving force for austenite to martensite on cooling to low temperature. According to Beres’s empirical formula [102], an increase in carbon concentration by 0.02% will reduce $M_s$ by 13.3°C.

In the next set of comparison, the calculated transformation rates ($df_m/dT$) from dilatation data are compared. The absolute value of $df_m/dT$ at $0.1 < f_m < 0.5$ are 0.032/°C and 0.055/°C for CGHAZ and FGHAZ, respectively. This trend is indeed inconsistent between the two techniques. Currently, we cannot rationalize these inconsistencies. Three possible hypotheses are put forward below. (i) The inconsistencies can be due to stochastic variations of prior austenite grain in different samples due to small variations in peak temperature. When the peak temperature is high, the austenite grain size is not sensitive to small variation in peak temperature. However, if the peak temperature is little above $A_{c1}$, a small change in peak temperature will result in large difference in austenite grain size. (ii) These inconsistencies also can be due to differences the sampled volume in TRXRD and dilatation techniques. TRXRD characterize the martensite transformation in a localized surface area of the sample. Sectioning effect and free surface may cause the transformation kinetics to be largely different. Dilatation, on the other hand, is a volumetric measurement and averages many grains. Martensite transformation kinetics derived from dilation shows the average of the sample. (iii) As discussed earlier, the extent of martensite to austenite transformation on heating may dictate the carbon concentration of freshly formed austenite. A change in austenite carbon concentration will also change the $\gamma \rightarrow \alpha'$ transformation rates.
Since the data from CGHAZ samples were consistent in both measurement techniques, this data was compared with published martensite kinetics model. Yang and Bhadeshia [100] derived the equation to describe martensite transformation kinetics in steels:

\[ f_m = 1 - \exp\left\{ m \ln\left\{ 1 + a V_\gamma \exp\left\{ b \left( M_s^0 - T \right) \right\} \right\} \right\} \]  \hspace{1cm} (6.2)

In the above equation, \( m \) is martensite block aspect ratio (0.05), \( a \) (1 mm\(^3\)) and \( b \) (0.2689) are empirically fitted parameters. The \( V_\gamma \) is the average volume of austenite grain before the onset of martensite transformation. The \( M_s^0 \) is the highest temperature at which martensite can form and can be calculated by considering thermodynamics and stored energy of martensite (~ 700 J/mol). Thermodynamic [TCFE5 database in Thermocalc®] models were used to calculate the \( M_s^0 \) of BA-160 steel to be 396°C. The predicted martensite fraction for CGHAZ condition by equation (2) was compared with experimental measurements (see Fig. 6.7) from TRXRD and dilatometry. It is interesting that the rate of martensite fraction is almost identical for both TRXRD and dilatometry when the extent of transformation is less than 0.6. However, the predicted martensite fraction by the equation (6.2) shows sluggish transformation rate. It is quite possible to modify the empirical parameters (a, b) to fit the data. However, we believe these parameters need to be derived by leveraging the spatial morphology of martensite packets that are derived from LSCM images. Specific focus needs to be given to extend the equation (2), which relies on geometric progression to consider the stabilization of austenite [103] at a given subdivision.
Some of the emerging research in analyzing the microstructure evolution in steels through fractal theories can be leveraged for the same [104].

Figure 6.7 Martensite fraction vs temperature values on cooling for samples with 130-lm prior austenite grain size derived from prediction (equation 6.2) and experimental (TRXRD and dilatometry) measurements are compared. Note the temperature correction of 57 deg was made for the TRXRD data.
6.5 Challenges in Hybrid Technique

The main challenge is related to the uncertainty in temperature measurements in the hybrid system. Such effects were not observed in earlier work due to relatively slow heating rates [78]. Recently, Sharma et al have developed a furnace for synchrotron based in-situ measurements [105]. In this work, authors have discussed the methodologies to control temperature in detail. However, their system does not rely on any optical microstructure analyses similar to the current hybrid system. Our ongoing research is focusing on re-designing sample holder to allow for comprehensive measurements of temperature on the surface without interfering with the diffraction geometry. In addition, in-situ measurements of inclusion locations on the surface of the sample can be leveraged through image analyses. These positional measurements can be used to calculate thermal expansion coefficients of the sample in the pure phase region (austenite or ferrite), through which the actual temperature of the surface could be corrected.

6.6 Conclusions

A hybrid in-situ technique, which combines a TRXRD method using synchrotron and a laser scanning confocal microscope, was used to track microstructure evolution in the HAZ of BA-160 steels. The kinetics of phase transformations during thermal cycling with different peak temperatures was tracked at a 0.3-second time resolution. The data were compared with dilatometric measurements. The measurements from hybrid TRXRD and LSCM showed the following.
1. SNR of austenite diffraction peaks increased with a decrease in austenite grain size.

2. Reduction in martensite start temperature was observed with small austenite grain sizes.

3. Significant changes in transformation rates were also observed with different austenite grain sizes.

4. LSCM analyses showed refinement of martensite structure with a reduction in austenite grain size.

5. Predicted martensite fraction vs temperatures show similar trends as that of a published theoretical model; however, the magnitude of predicted rates is lower than that of experimental measurements.

Comparison of the preceding measurements with dilatometric measurements revealed some difficulties. The volumetric (dilatometer) and surface (synchrotron and LSCM) measurements show inconsistent quantitative values in tracking kinetics of martensite transformation (dfm/dT). The highest martensite transformation rate is observed with austenite grain sizes of 130 μm in synchrotron X-ray diffraction. However, dilation analyses show the fastest transformation in the sample with austenite grain size below 10 μm.
Chapter 7. Microstructure in HAZ of Welded 9 Cr Steel Plates

Multi-scale characterization techniques are used to study HAZ in 9Cr creep strength enhanced ferritic steels. The focus of this chapter is to answer the following questions:

1. How pre-welding temperatures affect cross-weld creep properties?

2. How the microstructure evolves in the HAZ during welding and PWHT?

3. What is relationship between HAZ microstructure and creep properties?

First, welded steel plates with different pre-welding temper temperature were post-weld heat treated and then tested in the stress rupture testing frame, as discussed in Chapter 4. The creep test results (strains vs. time) are shown in Figure 7.1. The creep test results are further analyzed and summarized in Table 7.1. Table 7.1 shows that the sample with pre-welding temper temperature of 650°C has the lowest steady state creep rate and the longest creep life. Creep life of 650°C tempering is almost 5 times that of 760°C tempering and 8 times that of 700 or 800°C tempering. According to ASTM 387 specification, the temperature range for tempering is 730-790°C. As a result, 760°C tempering in current experiments represents the conditions of industry practice. Following study will
be focused on following samples: pre-welding tempered at 650°C (denoted as low tempering temperature, LTT) and pre-welding tempered at 760°C (denoted as high tempering temperature, HTT). In order to understand the creep data, there is a need to know the failure location and how microstructure evolves during welding at this specific location.

![Creep curves for welded samples with different pre-weld tempering temperature](image)

**Figure 7.1. Creep curves for welded samples with different pre-weld tempering temperature**

<table>
<thead>
<tr>
<th>Tempering temperature (°C)</th>
<th>650</th>
<th>700</th>
<th>760</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary creep strain (%)</td>
<td>0.21</td>
<td>0.17</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>Steady state creep rate ($10^{-4}$%/h)</td>
<td>4.1</td>
<td>36</td>
<td>16</td>
<td>60</td>
</tr>
<tr>
<td>Total strain (%)</td>
<td>3.24</td>
<td>4.3</td>
<td>2.14</td>
<td>6.6</td>
</tr>
<tr>
<td>Test time (h)</td>
<td>2414</td>
<td>333</td>
<td>518</td>
<td>358</td>
</tr>
</tbody>
</table>

**Table 7.1 Summary of Creep test results**
Fractured samples were later sectioned, polished and etched to reveal the failure location. Optical images were taken to see the weldments after creep (Figure 7.2). The samples after creep tests showed failure location is about 3.04 and 2.96 mm away from the fusion line for LTT and HTT respectively. Since the total sample gage length is 80 mm, the elongation calculated LTT and HTT is 2.59 and 1.71 mm. If it is assumed 80% of the deformation occurred in the HAZ and 50% of the same deformation occurred on each side, the failure location should be 2.00 mm from fusion line for LTT and 2.28 mm for HTT in the weldments. These regions are in the FGHAZ, as confirmed in section 7.4. Regions in marked by white circle in Figure 7.2 were characterized by EBSD (Figure 7.3). Due to recrystallization and recovery during creep test, lath martensite sub-structure cannot be seen. Microstructure near failure location is elongated ferrite. The average grain size of ferrite is less than 5 μm. In addition, fine elongated ferrite grains also confirm steel failed at FGHAZ for both condition. Larger grain size of LTT may be due to longer duration time during creep test.

Figure 7.2 also shows there is a big difference in reduction of area (RA) between two samples. RA is 31% and 82% for LTT and HTT respectively. The result of RA indicates high ductility and low resistance to creep of HTT.
Figure 7.2 LTT (a) and HTT (b) after creep test macro graph.

Figure 7.3 Orientation maps near the failure location of (a)LTT (b) HTT
Figure 7.3 shows regions near creep rupture has ferrite grain size less than 5μm. In addition, fracture location calculation shows sample failed at location in HAZ which is 2-2.2 mm from fusion line. Analysis on post-weld heat treated samples later also shows fine grain feature of this region. As a result, in both condition, creep failure is in FGHAZ. Since the creep failure is in FGHAZ and failure mode is Type IV for both conditions, current study will be concentrated on microstructure in FGHAZ. The schematic thermal profile of FGHAZ is shown in Figure 7.4. The thermal profile can be divided into five stages: normalizing, tempering, welding, post-weld heat treatment, creep. In order to understand effect of pre-weld tempering on the creep properties, there is a need to characterize the microstructure of each stage.

![Schematic of temperature-time profile of FGHAZ in Grade 91 steel](image)

**Figure 7.4. Schematic of temperature-time profile of FGHAZ in Grade 91 steel**
7.1 As-normalized condition (stage I)

The optical micrograph of as-normalized sample (Figure 7.5) shows a martensitic microstructure. The average Vickers hardness for as-normalized sample is 429, which also implies untempered martensite in as-normalized condition [106].

Carbides in as-normalized condition are hardly seen from optical image. As a result, TEM is used to exam carbides in this stage. Figure 7.6a shows five carbides are still present in the sample. Electron diffraction and EDS confirms the carbides are MX type. The normalizing temperature is 1080°C. According to ThermoCalc calculation equilibrium MX volume fraction at this temperature is $3.6 \times 10^{-4}$. MX is fully dissolved in austenite at 1128 °C. Both experimental and modeling data suggest MX exist in austenite as-normalized condition.

![Figure 7.5 Optical image of as-normalized condition showing small carbides.](image)
Figure 7.6 (a) TEM image on carbon replica showing presence of MX (b) SAD of carbide circled in 7.6a showing MX diffraction with zone axis (001), camera length is 360mm (c) EDS spectrum showing carbide is enriched with Nb and V. Cu peak is from the Cu grid holder.

7.2 As-tempered condition (Stage II)

Optical micrographs of LTT and HTT pre-weld tempering condition also show martensitic microstructure (Figure 7.7). The average Vickers hardness is 349 for
HTT and 230 for LTT. The existence of more untempered martensite in LTT may contribute to the higher hardness, which needs to be proved by later characterization. LTT shows a mixture of darkly etched and light etched regions present in LTT in Figure 7.7. Darkly etched region may contain high density of dislocations, which can be confirmed by microhardness or nanohardness measurement. On the other hand, HTT did not show darkly etched regions. Carbides nicely decorate PAGs and martensite block boundaries.

![Figure 7.7 Optical image of (a)LTT and (b) HTT, one of the prior austenite grain boundaries is indicted by arrows](image)

Obviously, resolution of light optical microscopy is not sufficient to observe and quantify carbides. As a result, SEM images are taken on etched samples. The images were reverted to show carbides in black (Figure 7.8). Some small carbides
are shown at PAGBs in LTT (indicated by arrows). The size of the carbides is smaller than 1 μm. On the other hand, carbides in HTT are much larger and mostly seen at PAGBs and martensite block boundaries. Though SEM image can show the difference in carbide size, it is hard to quantify the carbides. The SEM images can be converted to black/white images by thresholding. Then carbides can be extracted and studied. However, during image processing, some of the boundaries and martensite lath, which are also considered as carbides and affect the quantification result. To get a better quantification result and finer resolution, extraction replica is later prepared and examined by TEM (Figure 7.9). Carbides were measured using mean intercept method. In LTT, there are two types of carbide: large dark carbides on martensite lath boundaries and grey carbides inside martensite lath. The dark carbide on the boundaries indicated by the dark arrow is confirmed as M_{23}C_6 by EDS and electron diffraction. Figure 7.10a shows select area diffraction of M_{23}C_6. M_{23}C_6 is FCC crystal structure (space group: Fm3m). The lattice parameter varies from 1.057 to 1.068nm [107]. Since two beam conditions are difficult to obtain with carbon replica sample, a random zone axis is selected. The diffraction pattern is indexed with the assistance of Single Crystal software. Figure 7.10a is close to the diffraction pattern of M_{23}C_6 at zone (145). Lattice parameter calculated from the indexed pattern is close to 1.06nm. EDS spectrum is shown in Figure 7.10b. Further analysis found M_{23}C_6 has a composition of 39.8Fe-54.1Cr-6.1Mo (wt.%, Cu peaks are from the Cu grid holder). The carbides indicated by the white arrow are confirmed as MX using the same approach (Figure 7.11). MX has a FCC crystal structure with lattice
parameter varying from 0.435 to 0.441 nm [108]. Select area diffraction of MX is shown in Figure 7.10a. Zone axis indexed is (114). EDS result shows MX is enriched with Nb and V. Composition of MX is 71.2Nb-38.8V (wt.%). The existence of $M_23C_6$ and MX are also found in HTT, which are annotated in Figure 7.9b. In the rest of this article, $M_23C_6$ or MX, which is annotated, is confirmed by EDS.

Figure 7.8 SEM images of LTT (a) and HTT (b) as tempered condition
Figure 7.9 TEM images of LTT (a) and HTT (b) as tempered condition, potential martensite block boundaries is marked
Figure 7.10 (a) SAD of zone (145) and (b) EDS spectrum of $M_23C_6$ carbide
Characteristics of carbides are summarized in Table 7.2. Volume percentage of M_{23}C_6 in HTT is 1.8, which is very close to Thermocalc prediction of 1.59 wt%. The data indicates M_{23}C_6 is almost in equilibrium condition after tempering at
760°C for 1.5 hours. On the other hand, M₂₃C₆ volume percentage in LTT is only 0.5, which is much lower than ThermoCalc prediction (1.59). This result suggest that martensite in LTT is still supersaturated with carbon but hardness is lower than as-normalized condition. Average diameter of M₂₃C₆ in HTT is twice of that in LTT condition. In addition, characteristics of MX in both conditions are similar.

Table 7.2 Average diameter, number density and volume percentage of carbides in HTT/LTT conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>HTT</th>
<th>LTT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbide type</td>
<td>M₂₃C₆</td>
<td>MX</td>
</tr>
<tr>
<td>Diameter (nm)</td>
<td>164</td>
<td>25.1</td>
</tr>
<tr>
<td>Number Density ($10^{18}$ m⁻³)</td>
<td>4</td>
<td>7.6</td>
</tr>
<tr>
<td>Volume Percentage (%)</td>
<td>1.8</td>
<td>0.03</td>
</tr>
</tbody>
</table>

EBSD are used to characterize martensite sub-structure. Orientation maps of LTT and HTT and corresponding texture plot are shown in Figure 7.12 and Figure 7.13. Based on the appearance of two orientation maps, one may conclude LTT has a larger martensite blocks. However, further analysis shows average block width for LTT and HTT are 3.84 and 3.57 microns respectively. No obvious difference in martensite block size is observed.
The composition of the matrix is analyzed by atom probe tomography. Only one sample is analyzed for each condition. C, Cr, Mo, and V atom maps are shown in Figure 7.13. No alloy enriched region is observed in HTT and several V enriched regions are observed in LTT condition. In order to study the V enriched region, 4% V isoconcentration interface is plotted in Figure 7.14a. Concentration profile across one on the interface is plotted in Figure 7.14b. Both Cr and C are also enriched in this region. The maximum V and Cr concentration in the region is about 10 and 30 at.% respectively. These regions may be Cr and V enriched carbides. Since this V enrich region is very small, a significant amount of carbon are not detected by atom probe experiment. The detected carbon content is lower than that in actual sample. Table 7.3 presents the composition comparison. Since HTT has more carbide, low carbon and Cr content is expected. Since analyzed volume is in nm$^3$, the data listed in Table 7.3 can only represent composition in a
local region. Since one small region cannot represent the whole matrix, to get a more accurate matrix composition, more atom probe experiments are needed to get better statistics.

Figure 7.13 (a) Atom maps for C, Cr, Mo and V in LTT and HTT, the box size is 20×20×30 nm (b) the box size is 35×35×75 nm (showing 100% of detected C, 10% of detected Cr, 100% of detected Mo, 100% of detected V)
Figure 7.14 (a) 4% V isoconcentration surface, the box size is 20×20×30 nm and (b) composition profile across the highlighted interface
Table 7.3 Composition comparison of martensite matrix between atom probe results
nominal (only one atom probe sample is analyzed for each condition)(wt.%) 

<table>
<thead>
<tr>
<th>Component</th>
<th>LTT</th>
<th>HTT</th>
<th>Nominal</th>
</tr>
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<tr>
<td>C</td>
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<td>0.010</td>
<td>0.08</td>
</tr>
<tr>
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<td>8.39</td>
<td>8.61</td>
</tr>
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<td>0.37</td>
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<td>0.37</td>
</tr>
<tr>
<td>Ni</td>
<td>0.61</td>
<td>0.52</td>
<td>0.09</td>
</tr>
<tr>
<td>Mo</td>
<td>0.96</td>
<td>0.91</td>
<td>0.89</td>
</tr>
<tr>
<td>V</td>
<td>0.17</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>Si</td>
<td>0.18</td>
<td>0.16</td>
<td>0.11</td>
</tr>
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</table>

7.3 As-welded condition (stage III)

Two plates (LTT and HTT) were welded by GTAW. The welding process is
detailed in Chapter 4.2.1. Microhardness maps of as welded condition are shown
in Figure 7.15. Comparing the hardness of HTT base metal (230VHN), the
hardness of LTT base metal is higher (330VHN). The result shows similar trends
with as-tempered hardness in previous section. In Figure 7.15a, CGHAZ has the
highest hardness of 420 VHN. High hardness is due to dissolution of carbides
during heating and formation of untempered martensite during cooling. The weld
metal has a hardness range from 380 to 400 VHN. The hardness is a little lower
than CGHAZ. The microstructure of weld metal is martensite within large prior austenite grain size. Larger austenite grains yield large martensite sub-structure, which may cause hardness of weld metal slightly lower than CGHAZ. In FGHAZ, as the peak temperature reduces, the hardness gradually decreases may be caused by dissolution of carbides. The more carbide is dissolved, the more carbon in the untempered martensite, the higher the hardness. FGHAZ regions are annotated on the microhardness maps. The regions in hardness map marked by star were examined by SEM and images were shown in Figure 7.16. Fine martensite substructure and some undissolved carbides are seen. Clearly, size of carbides in HTT is much larger than that of LTT.

![Microhardness map with annotations](image)

**Figure 7.15** As-weld condition hardness distributions for LTT(a) and HTT (b)
In HAZ of as-weld specimens, it is hard to make a TEM sample out of FGHAZ. In addition, even if SEM and TEM image can be obtained from FGHAZ, the thermal profile of analyzed region is unknown due to severe thermal gradient. As a result, current study focuses on characterization of the samples of HAZ simulations, which is discussed in Chapter 8.
Figure 7.16 As-weld FGHAZ microstructure in LTT (a) and HTT (b), undissolved carbides are indicated by arrows.
7.4 Post-weld heat treatment condition (stage IV)

PWHT of current study was performed in conventional furnace at 760°C for 4 hours. After PWHT, the samples were air cooled. Microhardness was measured on the sample and the result is shown in Figure 7.17. The weld metal in these three welds has the highest hardness, which is about 220 VHN. For LTT condition, one soft region close to the fusion boundary is observed, with the hardness about 200 VHN. This over tempered base metal has the lowest hardness, about 190 VHN. On the other hand, HTT shows a different hardness distribution. From the fusion line to the base metal, the hardness gradually decreases to 170 VHN and then goes up to the hardness of base metal, 190 VHN. The soft region is close to the base metal in HAZ. The traverse hardness plot in HAZ for LTT and HTT is shown in Figure 7.18. Both samples show a soft region which is about 2.1 mm from the fusion line. However, LTT shows a hard region with a distance of 0.8 to 1.6mm from the fusion line. The lowest hardness in LTT sample is 15 VHN higher than that in 760°C tempered sample. Both HTT and LTT have the lowest hardness in FGHAZ. The low hardness in HTT may be caused by coarse carbides which were not dissolved during welding. Carbides in FGHAZ of HTT are coarser, which gives a lower hardness compared with that of LTT. This hypothesis needs to be proved by microstructure characterization.
SEM is used to examine the microstructure in those regions for both LTT and HTT weldments after PWHT condition (Fig. 7.17) both image shows equiaxed
ferrite grains with an average diameter of 2-3 μm. Martensite microstructure cannot be seen in SEM image. These ferrite microstructures are the result of recovery and recrystallization during post-weld heat treatment. However, existence of martensite structure still needs to be further confirmed by EBSD. In addition, white spot shown in the images are Cr enriched carbide (according to EDS analysis). Those carbides are most likely M$_{23}$C$_6$, which need to be further proved by diffraction. M$_{23}$C$_6$ is reported usually formed at prior austenite grain boundaries (PAGBs) and martensite lath boundaries [109,110,111,112]. However, some of M$_{23}$C$_6$ carbides present in a line through ferrite grains in both image in Fig. 7.19, as indicted by arrows. If M$_{23}$C$_6$ carbides were formed during PWHT, most of them will be located on boundaries instead of in ferrite grains. In addition, even M$_{23}$C$_6$ carbides formed in martensite, they will be randomly distributed. As a result, those carbides should not be newly formed carbides when plates are post-weld heat treated. They are identified as undissolved carbides in FGHAZ after welding. When the steels are tempered (for both LTT and HTT), M$_{23}$C$_6$ carbides formed at PAGBs. Then the steel plates are subjected to welding process. In some of regions in FGHAZ, M$_{23}$C$_6$ carbides at PAGBs are partially dissolved as well as new small austenite grains formed. During later PWHT, martensite became equiaxed ferrite while undissolved M$_{23}$C$_6$ grew and coarsened to what are shown in Fig. 7.19. Fig. 7.19 also clearly shows M$_{23}$C$_6$ in LTT is much smaller than that on HTT, which indicates FGHAZ of LTT should have less coarse M$_{23}$C$_6$ than that of HTT. Since failure occurs near this location (Figure 7.2), these undissolved carbides in HTT be responsible for the pre-mature failure in Grade 91 steels.
Figure 7.19 SEM image of FGHAZ after post-weld heat treatment in LTT (a) and HTT (b), some ghost austenite grain boundaries are indicated by dash line
7.5 After creep condition (stage V)

Microhardness of the samples after creep failure is shown in Figure 7.20. For both condition, weld metal has the highest hardness. However, HTT weld metal hardness is about 30 VHN higher LTT weld metal. Compared with hardness before creep test, HTT weld metal hardness is 10 VHN higher. The reason this hardening is unknown. Since study of weld metal is out of the scope of current investigation, no further discussion will be made on this matter. As discussed previously, both condition failed at FGHAZ. Hardness maps also show FGHAZ has the lowest hardness (160 VHN). Microstructure of location A and location B are shown in Figure 7.21 and 7.22 respectively. SEM images indicate martensite microstructure was completely gone after creep test. Equiaxed ferrite grains and carbides are dominant microstructure. In FGHAZ of LTT, creep voids are observed at grain boundaries without carbides. On the other hand, two kinds of voids can be seen in FGHAZ of HTT. First kind is the same as LTT (Figure 7.21). Secondly, creep void are also observed inside ferrite grain at the periphery of coarse carbides. The mechanism of void formation will be discussed in section 8.5 and 8.6.
Figure 7.20 Microhardness maps of welds after creep test for LTT (a) and HTT (b)

Figure 7.21 Microstructure of location A in LTT indicated in Figure 10 showing a void at grain boundaries.
Figure 7.22 Microstructure of location B in HTT indicated in Figure 10 showing creep voids (indicated by arrows) at grain boundaries (a) and near coarse carbide (b)
7.6 Summary

1. Low temperature pre-welding tempering significantly improved creep strength of the weldments. Creep life of LTT welded plate is 5 times higher than that of HTT welded plate.

2. In the tempered condition, HTT has about 1.8 vol\% $M_{23}C_6$ based on extraction replica image analysis. The measured fraction of $M_{23}C_6$ is close to ThermoCalc prediction, which indicates HTT is near equilibrium condition. On the other hand, LTT only has 0.5 vol \% $M_{23}C_6$. Size of $M_{23}C_6$ in HTT is much larger than that in LTT. The hardness of HTT is much lower than that of LTT due to higher amount of tempered martensite.

3. Hardness map of post weld heat treated condition shows LTT has less softening in the HAZ than HTT. The softest region of LTT HAZ is 20HV higher than that of HTT HAZ. The softening may be related to undissolved carbides in FGHAZ.

4. Disappear of martensite sub-structure is observed after creep. Two type of creep void is observed in HTT after creep samples. Some creep voids grain boundaries and some creep voids are observed near coarse carbide. Creep voids in LTT are only observed at grain boundaries.
Chapter 8 Heat Affected Zone Simulation

Previous chapter has revealed that creep failure occurs in FGHAZ. As a result, understanding FGHAZ microstructure evolution is very important. SEM images of as-welded FHGAZ show undissolved carbides. Those undissolved carbides may coarsen during post-weld heat treatment and reduce steel creep resistance. Even though some information is obtained in chapter 7, there are still a lot of questions need to be answered, such as “How much carbide is dissolved?”, “what is the relationship between initial microstructure and heat affected zone thermal cycle?”, “how the microstructure evolve during post-weld heat treatment?”. As described in the previous chapter, there are some difficulties to characterize the heat affected zone in real weld. This chapter will focus on study FGHAZ of Grade 91 steels by controlled HAZ thermal simulation. Two techniques were used to simulate HAZ thermal cycles: Infrared furnace and Gleeble thermal mechanical simulator. Phase transformation in furnace samples will be studied by TRXRD employing synchrotron radiation. On the other hand, phase transformation in Gleeble samples will be studied by dilatometry.

8.1.1 Time resolved X-ray diffraction

Six experiments were done to simulate FGHAZ with different peak temperatures. Due to technical problems, some experiments did not yield good data. Therefore,
only four experiments data are shown and analyzed in this chapter. These experiments are summarized in Table 8.1. The first two experiments, HTT-Tp1050 and LTT-Tp1050 was performed at heating rate of 20°C/s and time resolution (time interval between two diffraction spectra) of 0.2 second. Preliminary analysis shows carbides peaks are weak since only a small amount of carbides present in the sample, especially for LTT. Increasing exposure time can increase the intensity of diffraction peaks. Later experiments adopted higher time resolution to 0.5 second for HTT-Tp950 and 1 second for LTT-Tp1050. In order to get better temperature resolution, heating rate is reduced to 10°C/s.

<table>
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<th>ID</th>
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<tr>
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<tr>
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<td>1</td>
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</table>

Figure 8.1 presents the comparison of carbide evolution for HTT and LTT for thermal cycle of simulated FGHAZ, whose peak temperature is 1050°C. Current study focuses on $M_{23}C_6$ (420), $M_{23}C_6$ (422), MX (111) and MX (200) peaks since
they have relatively high signal to noise ratio and are not affected by martensite or austenite peaks. In HTT sample, the intensities at $M_{23}C_6$ peaks do not change until temperature reaches about 900°C, at which the dissolution $M_{23}C_6$ starts. Intensities of $M_{23}C_6$ peaks become very weak and near the background level at the peak temperature, 1050°C. MX peaks are weak and remain unchanged during the heat treatment (Figure 8.1a). The increase in d-spacing during heating is due to thermal expansion. Since the intensities at MX peaks are just a little is barely above the background, it is impossible to fit MX peaks. MX in current study is not quantified. On the other hand, peak intensity $M_{23}C_6$ in LTT sample is very weak and close to the background before HAZ heat treatment, which implies only small amount of $M_{23}C_6$ exist in as tempered condition. When the temperature reaches 1050°C, $M_{23}C_6$ peaks cannot be seen any more. The intensities at MX peaks are the same as HTT and remains unchanged (Figure 8.1b). The data shown in Figure 8.1a and 8.1b were analyzed further by fitting a Gaussian peak to austenite (111), ferrite (011) and $M_{23}C_6$ (420) diffraction peaks [16]. After peak fitting, the area under each peak is integrated. The phase volume fraction was derived by using the direct comparison method considering structure factor, multiplicity factor, Lorentz polarization, and temperature factor [113]. The details of data analysis can be found in [64].

Figure 8.1c shows $M_{23}C_6$ fraction in HTT and austenite fractions as a function of temperature. There is $1.53 \pm 0.22$ vol.% $M_{23}C_6$ in HTT before thermal cycling. This value is very close to the equilibrium volume fraction of $M_{23}C_6$ (1.59 vol.%) at 760°C predicted by ThermoCalc using TCFE5 database. During heating,
fraction of $M_{23}C_6$ is slightly decreased on heating of 400°C. When the sample is heated to $A_{c1}$ (998°C), martensite transforms to austenite. Due to high C solubility in austenite, $M_{23}C_6$ begin to dissolve. Volume fraction of $M_{23}C_6$ gradually decreases to 0.2 vol.%. When $M_{23}C_6$ is below 0.2 vol.%, $M_{23}C_6$ (420) and (422) diffraction intensities are close to the background and volume fraction cannot be obtained.

Benetoeau et al [114] shows $M_{23}C_6$ start to dissolve between 700 and 750°C before austenite formation in high nitrogen martensitic stainless steel. However, similar dissolution of $M_{23}C_6$ is not observed in the current study. The discrepancy maybe caused by difference heating rate used in the experiments. Benereaua use very slow heating rate of 0.194°C/s. On the other hand, current investigation used heating rate of 20°C/s, which do not give sufficient time for $M_{23}C_6$ to dissolve in martensite/ferrite matrix. In addition, composition difference between the two steels may also contribute the discrepancy.
Figure 8.1. Carbide intensity (shown in grey scale with arbitrary value) as a function of time and temperature in HAZ (Tp=1050°C) for (a) HTT and (b) LTT; (c) $M_{23}C_6$ and austenite fraction as a function of time and temperature, collected data between 2.25 and 2.30 in (b) is very noisy and has been removed
Carbides in the simulated HAZ samples are extracted by carbon replica and further analyzed using TEM (Figure 8.2). Even though TRXRD showed there is no carbide after thermal cycling, carbides still can be seen by SEM. In LTT, only MX is present indicating that all the $M_{23}C_6$ carbides have dissolved during thermal cycling. Both $M_{23}C_6$ and MX exist in HTT. However, the size of $M_{23}C_6$ is much smaller than pre-welding temper condition. Size, number density and volume fraction of the carbides are summarized in Table 8.2. Comparing Table 7.2 with Table 8.2, it can be concluded that about 90% $M_{23}C_6$ dissolved in HAZ with a peak temperature of 1050°C in HTT and 100% of $M_{23}C_6$ dissolved in LTT.
MX dissolution is also observed in HTT and LTT conditions. However, amount of MX dissolved during thermal cycling is very small and can be neglected.

Table 8.2 Average diameter, number density and volume percentage of carbides in simulated HAZ (Tp=1050°C)

<table>
<thead>
<tr>
<th></th>
<th>Diameter (nm)</th>
<th>Number Density ($10^{18}$ m$^{-3}$)</th>
<th>Volume Percentage</th>
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</thead>
<tbody>
<tr>
<td>HT</td>
<td>M$_{23}$C</td>
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</tr>
<tr>
<td></td>
<td>MX</td>
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<td>1.1</td>
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<td>LTT</td>
<td>M$_{23}$C</td>
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<td>0</td>
</tr>
<tr>
<td></td>
<td>MX</td>
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<td>1</td>
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</table>
Figure 8.2 TEM images of extraction replica of (a) LTT-Tp1050 and (b) HTT-Tp1050, carbides indicated were confirmed by diffraction and EDS analysis
Similar results for peak temperature 950°C is shown in Figure 8.3. Quantitative analysis shows about 1.8 vol.% M$_{23}$C$_6$ in HTT before thermal cycling, which shows agreement with quantitative analysis in Table 7.2. M$_{23}$C$_6$ decreased to about 0.8 vol.% after heat treatment. Austenite transformation kinetics for two conditions is different. Figure 8.3c shows $A_c1$ of HTT is a little lower than that of LTT. The difference in austenite transformation temperature is not seen in Figure 8.1. Contradictory may be due to high carbide fraction in HTT. When carbides dissolve, carbon enriched ferrite near carbides will form austenite prior to massive transformation occurs. Phase transformation will be discussed in details in the following section.

![Figure 8.3. Carbide peaks intensity as a function of time and temperature in HAZ (Tp=950°C) for (a) HTT and (b) LTT; (c) M23C6 and austenite fraction as a function of time and temperature](image)

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Figure 8.3 continued
In order to see if microstructure of HAZ simulated samples is similar to the microstructure in the real weld, SEM images on HTT-Tp950 and LTT-Tp950 were taken (Figure 8.4) and compared with Figure 7.16. LTT-Tp950 microstructure is very similar to the FGHAZ in the weld. However, HTT-Tp950 has more undissolved carbides than the FGHAZ in the weld. As a result, peak temperature of region in Figure 7.16b should be higher than 950°C.

Figure 8.4 SEM images (a)LTT-Tp950 and (b)HTT-Tp950
Besides SEM, carbides were studied by TEM (Figure 8.5) and the results were summarized in Table 8.3. Comparing with pre-welding temper condition (Table 7.2), $M_23C_6$ size and volume percentage of HTT were slightly reduced after thermal cycling. No significant change was observed with respect to MX.
Table 8.3 Average diameter, number density and volume percentage of carbides in simulated HAZ (Tp=950°C)

<table>
<thead>
<tr>
<th></th>
<th>Diameter (nm)</th>
<th>Number Density (10^{18} m^{-3})</th>
<th>Volume Percentage (%)</th>
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</thead>
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<tr>
<td>HTT M_{23}C_{6}</td>
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<td>1.2</td>
</tr>
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<td>MX</td>
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<td>LTT M_{23}C_{6}</td>
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</tr>
<tr>
<td>MX</td>
<td>23.3</td>
<td>5.6</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Figure 8.5 TEM images on extraction replica of (a)LTT-Tp950 and (b)HTT-Tp950
8.2 LSCM observation

Figure 8.6 shows snapshots of LSCM images during austenite to martensite transformation during cooling in HTT-Tp950. The austenite grain boundaries are imaged due to the surface grooving (Figure 8.6a). At 370°C, onset of martensite transformation is seen near austenite/austenite grain boundaries. Initially, the transformation occurs very fast. From 370°C to 362 °C (about 0.8 second), almost more than 50% austenite transforms to martensite (Figure 8.6c)

Figure 8.6 LSCM images obtained during HTT-Tp950 experiment during cooling at (a) 563°C (b) 370°C (c) 362 °C (d) 161°C
Figure 8.7 shows snapshots of LSCM images during austenite to martensite transformation during cooling in LTT-Tp950. Observed Ms for this condition is about 350°C (Figure 8.7b), which is much lower than LTT. From 350°C to 339°C, only about 20% transformation occurs (Figure 8.7c). Initial transformation rate of HTT is also lower than HTT.

Figure 8.7 LSCM images obtained during LTT-Tp950 experiment during cooling at (a) 448°C (b) 350°C (c) 339°C (d) 229°C

Figure 8.8 shows snapshots of LSCM images during austenite to martensite transformation during cooling in HTT-Tp1050. At 412°C, martensite is seen to form underneath the surface. When martensite forms underneath the surface, there
is only slightly contrast change in the picture. The change is difficult to see in the pictures, but it is obvious in the video.

Figure 8.8 LSCM images obtained during HTT-Tp1050 experiment during cooling at (a) 419°C (b) 412°C (c) 344°C (d) 214°C

Figure 8.9 shows snapshots of LSCM images during austenite to martensite transformation during cooling in LTT-Tp1050. Martensite on set formation underneath the surface is also observed at 404°C.
LSCM experiments shows sample with peak temperature of 950°C yield a lower Ms. The lower may be due to smaller austenite grain size in Tp950. Yang and Bhadeshia studied the relationship between PAGs with Ms [84]. The result is shown in Figure 8.10. As the PAGs increase, Ms increase. At small PAG size range, small PAG size increase give large Ms increase. Since PAGs of Tp1050 condition is larger than that of Tp950 condition, Tp1050 condition is expected to have higher Ms.
For 1050°C peak temperature, martensite transformation underneath the surface can be seen before surface transformation, which is not seen in Tp950 condition. This may be caused by larger martensite sub-structure formation. Since Tp1050 has a larger PAGs, it also forms large sub-structure during transformation. Larger sub-structure underneath the surface is more observable.

![Graph showing the relationship between grain size and martensite start temperature (Ms)].(84)

Figure 8.10 Relationship between prior austenite grain size and martensite start temperature (Ms) [84]

### 8.3 Gleeble simulation

Gleeble thermal-mechanical simulator was also used for HAZ simulation. Phase transformation kinetics was measured with dilatometry. Four peak temperatures was selected ranged from 900 to 1050 °C. Experiments are summarized in Table
8.4. Martensite transformation kinetics between TRXRD and dilatation measurement is compared in the following section.

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</tbody>
</table>
Accurate determination of the $A_1$ temperature in CSEF steels is crucial for the development of proper tempering temperature. Current research also studied $A_1/A_c1$ and $A_3/A_c3$ of two tempering conditions (LTT and HTT). Critical temperatures have been determined by ASTM 1033-4 procedure using dilatometry in Glleeble [115]. The result is shown in Table 8.5. The result shows $A_1$ difference between two conditions is very small. However, $A_3$ of HTT is 25°C lower. Martensite fraction as a function of temperature during heating is plotted in Figure 8.11. Both HTT and LTT show two stages in austenite transformation: first stage with a high transformation rate and second stage with a low transformation rate. A linear fitting has been performed for both stages to determine the transformation rate. This observation shows agreement with Yu et al. [116,117]. Yu proposed that the
two stages transformation is related to the dissolution of cementite in the steel. Similar phenomenon is observed in Grade 91 steel. Instead of cementite dissolution, $M_{23}C_6$ dissolution is the reason for two-stage transformation. Since HTT has more $M_{23}C_6$ carbide, more carbon-enriched regions are expected during dissolution of carbides. For this reason, austenite should have a higher transformation rate in HTT in the initial stage. The experiment result (Figure 8.11) does show a higher rate for HTT. For the first stage, transformation rate of HTT ($0.032/°C$) is much higher than that of LTT ($0.024/°C$). For the second stage, since carbon in untransformed marteniste is homogenized, transformation rate for HTT ($0.004/°C$) and for LTT ($0.006/°C$) are similar.

Measured $A_1$ and $A_3$ were also compared with ThermoCalc prediction and $A_{c1}$ and $A_{c3}$ at different heating rate (Table 8.5). ThermoCalc calculation shows a higher $A_1$. Since ThermoCalc assumes a homogenized carbon distribution in martensite, it is reasonable to predict a higher $A_1$. $A_3$ predicted by ThermalCalc is close to HTT condition. For $A_{c1}$ and $A_{c3}$, all experiments show HTT has a lower transformation temperature. During heating, carbide dissolves before austenite transformation, which was confirmed by TRXRD. As the carbide dissolves, carbon will be enriched in martensite/ferrite in the vicinity of dissolving carbides. This ferrite with high carbon will transform at lower temperature compared to the other regions with low carbon. Since HTT has more carbide, carbide dissolution start temperature and $A_{c1}$ is expected to be lower.
Table 8.5 Comparison of critical temperatures between software prediction and experimental measurement

<table>
<thead>
<tr>
<th>Conditions</th>
<th>heating rate</th>
<th>$A_1/A_{c1}$ ($^\circ$C)</th>
<th>$A_3/A_{c3}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTT-ASTM</td>
<td>28°C/h</td>
<td>793</td>
<td>912</td>
</tr>
<tr>
<td>HTT-ASTM</td>
<td>28°C/h</td>
<td>792</td>
<td>887</td>
</tr>
<tr>
<td>ThermoCalc</td>
<td>N/A</td>
<td>820</td>
<td>873</td>
</tr>
<tr>
<td>LTT- Tp1050-100</td>
<td>100°C/s</td>
<td>882</td>
<td>945</td>
</tr>
<tr>
<td>LTT- Tp1050-20</td>
<td>20°C/s</td>
<td>857</td>
<td>945</td>
</tr>
<tr>
<td>HTT- Tp1050-100</td>
<td>100°C/s</td>
<td>871</td>
<td>920</td>
</tr>
<tr>
<td>HTT- Tp1050-20</td>
<td>20°C/s</td>
<td>847</td>
<td>910</td>
</tr>
</tbody>
</table>

8.4 Phase transformation measured by TRXRD

Martensite transformation kinetics measured by TRXRD and dilatometry are compared in Figure 8.12. As discussed in chapter 6, 50$^\circ$C was added on TRXRD temperature for temperature correction. When peak temperature is 1050$^\circ$C, difference is martensite transformation kinetics between HTT and LTT is minimal. For dilatometry measurement, small amount of ferrite is observed in HTT before martensite formation. The ferrite formed in HTT condition may due enrichment of Cr at carbide interface, which will be discussed in section 9.2. In TRXRD measurement, martensite show very high transformation rate in HTT at initial stage. This may also be due to ferrite formation. Since ferrite and martensite has similar crystal structure (BCC and BCT), ferrite intend to grow on pre-existing
martensite instead of nucleate from austenite during cooling. If ferrite formed in 
HTT before Ms, martensite may nucleate and grow on pre-existing ferrite, which 
give a very high transformation rate. When peak temperature is 950ºC, TRXRD 
and dilatometry do not show good agreement. However, both measurement show 
HTT has a higher Ms. According to previous analysis, there are still about 0.9 vol.% 
M$_{23}$C$_6$ in HTT condition while M$_{23}$C$_6$ in LTT is less than 0.2 vol.% As a result, 
HTT has less carbon than LTT in austenite matrix. Since carbon is austenite 
stabilizer, HTT is expected to have a higher Ms. Moreover, TRXRD shows two 
stages transformation phenomenon. Two stages feature may be due to 
inhomogeneous distribution of carbon. Since there are still some undissolved 
carbides at peak temperature, carbon concentration at regions adjacent to carbides 
is very high. On the other hand, due to the dissolution of carbides, there are two 
regions with different carbon concentration in austenite. Austenite near dissolving 
carbides has high carbon concentration. Austenite away from undissolved 
carbides has low carbon. As a result, martensite transformation starts at low 
carbon region and later at high carbon region. Carbon content affect 
transformation rate, which yield two stages transformation phenomenon.
Figure 8.12 Martensitic transformation kinetics measured by dilatometry and TRXRD (a)
for simulated HAZ with peak temperature of 1050°C (b) for simulated HAZ with peak
temperature of 950°C
To further understand the transformation, d-spacing as a function of temperature is studied. In addition, carbon content in ferrite and austenite is estimated based on d-spacing data. Ferrite (011) d-spacing as a function of temperature during heating is plotted in Figure 8.13. When temperature is below 200 °C, the data is reasonable. HTT has a higher due to its lower carbon content in the matrix. However, when the temperature is above 200 °C, d-spacing change cannot be explained by thermal expansion only. In HTT-Tp1050 experiment, increase of noise level is observed when temperature is above 200 °C, which causes the inaccurate d-spacing measurement. Carbon content in martensite matrix is estimated based on d-spacing at room temperature before heating. The equation used is [64]:

$$d_{001}^{bcc} = \frac{a_{bcc}}{\sqrt{2}}$$

$$a_{bcc} = 2.8664 + \frac{(a_{Fe} - 0.279M_{C})^2(a_{Fe} + 2.496M_{C}) - a_{Fe}^3}{3a_{Fe}} - 0.03M_{Si} + 0.06M_{Mn} + 0.07M_{Ni} + 0.31M_{Mo} + 0.05M_{Cr} + 0.096M_{V}$$  \hspace{1cm} (8.1)

where $M_i$ is the mole fraction of elements “$i$” in the ferrite.

Calculation shows carbon in HTT matrix is 0.003 wt.% and in LTT matrix is 0.04%. As mentioned earlier, the nominal composition for carbon is 0.081 wt.%.

As a result, HTT is almost in equilibrium condition, which shows agreement with previous analysis.
Austenite (111) d-spacing a function of temperature during cooling is plotted in Figure 8.14. In heating of HTT-Tp1050 condition, austenite (111) d-spacing decreases first before it increases (as indicated by the arrow). It implies austenite initially forms at the regions that have the highest carbon content (carbides or adjacent to carbide). As austenite transformation continue, average carbon concentration in austenite decrease. There is a competition between d-spacing decrease by average carbon concentration decrease and d-spacing increase by thermal expansion. During cooling, austenite d-spacing for each condition is very similar. There are two dash lines in Figure 8.14. The upper dash line shows d-spacing calculated based on nominal composition of the steel. The lower dash line shows d-spacing calculated based on 0.025 wt.% carbon (everything else is the
same as nominal). Low dash line overlaps the cooling curve very well. It indicated after thermal cycling, the carbon content in the steel is low.

![Figure 8.14 Austenite (111) d-spacing as a function of temperature](image)

8.5 Simulated post-weld heat treatment

HAZ furnace simulation samples were later post-weld heat treated at 760 °C for 4 hours. Post mortem TEM investigations were performed on carbon extraction replica to analyze properties of carbides. Martensite substructure was studied by
EBSD. Carbides after post-weld heat treatment of HTT-Tp1050 and LTT-Tp1050 are shown in Figure 8.15 and Figure 8.16. By comparing LTT and HTT, one cannot easily tell the difference in carbide. Moreover, SEM images show equiaxed ferrite grains instead of martensite blocks feature. It implies martensite recovery and recrystallization may occur during post-weld heat treatment. Quantification result of carbides in Figure 8.16 is shown in Table 8.6. Size of M$_{23}$C$_6$ in HTT is slight larger these in LTT, which may be due to coarsening of undissolved carbides seen in Figure 8.4. For both condition, volume percentage of M$_{23}$C$_6$ is close to equilibrium condition. Compared with HAZ simulated condition (Table 8.3), MX volume percentage after post-weld heat treatment increased increase from 0.03 to 0.04. Orientation maps are shown in Figure 8.17. Even martensite sub-structures cannot be seen in SEM, they still exist according to EBSD result (Figure 8.17). Parallel martensite blocks still present after post-weld heat treatment. Martensite sub-structure size is summarized in Table 8.8. As discussed in section 8.1, HTT has a lower A$_{c3}$, it stays at austenite region for longer time than LTT. Consequently, HTT has a larger PAGs and martensite blocks.
Table 8.6 Average diameter, number density and volume percentage of carbides in simulated HAZ after post-weld heat treatment (Tp=1050°C)

<table>
<thead>
<tr>
<th></th>
<th>Diameter (nm)</th>
<th>Number Density ($10^{18} \text{m}^{-3}$)</th>
<th>Volume Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTT</td>
<td>M$_2$C$_6$</td>
<td>134</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>30.4</td>
<td>5.6</td>
</tr>
<tr>
<td>LTT</td>
<td>M$_2$C$_6$</td>
<td>122</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>27.8</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Figure 8.15 SEM images of (a)LTT-Tp1050 after PWHT (b)HTT-Tp1050 after PWHT
Figure 8.16 TEM images on extraction replicas of (a)LTT-Tp1050 after PWHT (b)HTT-Tp1050 after PWHT
LTT-Tp950 after post-weld heat treatment shows fine distribution of carbides mostly on prior austenite grain boundaries. Some carbide is also seen on martensite block boundaries. On the other hand, much coarser carbides at ghost austenite grain boundaries are seen (Figure 8.18). Ghost austenite grain boundaries are steel’s PAGBs before welding. After welding in FGHAZ, carbides on PAGs are not dissolved and remained in the boundaries. Those carbides grow and coarsen to a very large size. In addition, newly formed PAGs are free of carbides, as indicated by arrows in Figure 8.18b. TEM image on extraction replica shows a higher magnification of carbide (Figure 8.19). Properties of carbides are summarized in Table 8.7. As we expected, M$_{23}$C$_6$ carbide in HTT has a larger size and lower number density due to coarsening of undissolved carbides. Size of LTT is small and close to simulated HAZ with peak temperature of 1050°C. PAG size and martensite block size is also listed in Table 8.8. Similar phenomenon is observed that HTT has a slightly larger PAGs and martensite blocks due to its lower $A_{c3}$.

Figure 8.17 shows martensite substructure (blocks and packets) still exist after post-weld heat treatment. However, some areas with high angle boundaries are observed. Similar phenomenon is also observed when peak temperature is 950°C. Image quality maps (Figure 8.17b and 8.17d) show high image qualities in those area. As a result, those high angle boundaries are not artifact. Orientation map at high magnification (Figure 8.17e) shows small ferrite grain in those blocks. Those ferrite grains may form during post-weld heat treatment due to recrystallization. Further analysis on recrystallization need to be performed.
Figure 8.17 LTT-Tp1050 after PWHT Orientation maps (a) and image quality map (b);
HTT-Tp1050 after PWHT Orientation maps, lower magnification (c) higher magnification (e) and image quality map (d); solid line represent boundaries with misorientation from 15 to 180° (the same for the rest EBSD images)
Table 8.7 Average diameter, number density and volume percentage of carbides in simulated HAZ after post-weld heat treatment (Tp=950°C)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Diameter (nm)</th>
<th>Number Density ($10^{18}$ m$^{-3}$)</th>
<th>Volume Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTT M$_{23}$C$_6$</td>
<td>172</td>
<td>2.8</td>
<td>1.8</td>
</tr>
<tr>
<td>HTT MX</td>
<td>27.7</td>
<td>6.7</td>
<td>0.04</td>
</tr>
<tr>
<td>LTT M$_{23}$C$_6$</td>
<td>114</td>
<td>6.0</td>
<td>1.6</td>
</tr>
<tr>
<td>LTT MX</td>
<td>26.9</td>
<td>5.9</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 8.8 Prior austenite grain size and block width of after post-weld heat treatment condition

<table>
<thead>
<tr>
<th>Conditions</th>
<th>PAGS (μm)</th>
<th>Block width(μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTT Tp950+PWHT</td>
<td>5.7</td>
<td>2.4</td>
</tr>
<tr>
<td>HTT Tp950+PWHT</td>
<td>7.9</td>
<td>2.7</td>
</tr>
<tr>
<td>LTT Tp1050+PWHT</td>
<td>9.28</td>
<td>2.94</td>
</tr>
<tr>
<td>HTT Tp1050+PWHT</td>
<td>11.1</td>
<td>3.62</td>
</tr>
</tbody>
</table>
Figure 8.18 SEM images of (a) LTT-Tp950 after PWHT (b) HTT-Tp950 after PWHT
Figure 8.19 TEM images on extraction replicas of (a)LTT-Tp950 after PWHT (b)HTT-Tp950 after PWHT
Figure 8.20 Orientation maps of LTT-Tp950 after PWHT (a) HTT-Tp950 after PWHT (b)
8.5 Summaries

1. TRXRD experiments shows almost full dissolution of $\text{M}_2\text{C}_6$ when peak temperature in HAZ is 1050°C for HTT. When peak temperature is 950°C, about 1% dissolution of $\text{M}_2\text{C}_6$ is observed. Due to weak peaks, $\text{M}_2\text{C}_6$ in LTT and MX in both conditions cannot be quantified.

2. In both Gleeble and synchrotron experiments, two stages martensite to austenite transformation phenomenon is observed during heating. Carbide dissolution in the austenite may be responsible to two-stage transformation, which need to be confirmed in the future.

3. TRXRD samples were later post weld heat treated. Undissolved carbides are mostly seen in HTT-Tp950 condition. HTT and LTT HAZ with the same peak temperature have similar prior austenite grain size and martensite sub-structure size.
Chapter 9 Creep resistance mechanism

9.1 Hypothesis of carbides evolution

Figure 9.1 provides the schematics of carbide evolution based on data from chapter 8.

Preweld-temper: When the steel is tempered at HTT condition, $M_{23}C_6$ is in near equilibrium condition. $M_{23}C_6$ are located on PAGBs, martensite block and packet boundaries. MX is also present at martensite block boundaries and inside martensite blocks. HTT also has $M_{23}C_6$ and MX but $M_{23}C_6$ is much smaller.

Welding: During welding in the FGHAZ, new small austenite grains are formed. Small $M_{23}C_6$ are dissolved and large $M_{23}C_6$ are partially dissolved, but MX remains the same. Undissolved $M_{23}C_6$ carbides are present in martensite matrix after welding. Since solubility of carbon in ferrite is very low, martensite matrix is expected to be still supersaturated with carbon. On the other hand in LTT, $M_{23}C_6$ are all dissolved in FGHAZ.

Post-weld heat treatment: When the steel is subject to PWHT, supersaturated carbon in HTT will come out of martensite matrix and supports the growth of undissolved $M_{23}C_6$ instead of forming new $M_{23}C_6$. As a result, number of newly formed and MX will be limited. However in LTT, since there is no pre-existing $M_{23}C_6$, there will competition between $M_{23}C_6$ nucleation and MX
growth/nucleation. MX is larger and $M_{23}C_6$ is smaller compared with HTT. In addition, carbon content of HTT in martensite matrix is lower than that of LTT. $M_{23}C_6$ carbides in HTT condition will reach coarsening stage sooner than that in LTT condition. Coarser $M_{23}C_6$ and less number of MX give poor creep strength of HTT.

![Figure 9.1 Schematic showing microstructure evolutions during welding and PWH for LTT and HTT conditions (courtesy of Dr. Yamamoto)](image)

### 9.2 Strengthening mechanism

Chapter 7 and chapter 8 shows how microstructure in Grade 91 steels evolve during welding. Microstructure in FGHAZ of HTT and LTT post weld heat
treated condition shows different carbide distribution. How the microstructure affect the final creep properties need to be understood by creep strengthening model.

Figure 9.2 shows stress vs. minimum creep result for commercial Grade 91 steels at normalized and tempered condition. Test temperature is 650°C. The results of HTT and LTT are also plotted in the diagram. By fitting the data, calculated $n$ value in Norton’s law (equation 2.13) is 2.73. As a result, the creep mechanism is dislocation creep. In addition, Figure 9.2 clearly reveals the behavior of LTT weldments is close to normalized and tempered condition (base metal). However, minimum creep rate of HTT is much higher than base metal.

![Figure 9.2 Stress vs. minimum creep rate for Grade 91 steels](image)

*Figure 9.2 Stress vs. minimum creep rate for Grade 91 steels*
Grade 91 steel is mainly strengthened by $\text{M}_2\text{C}_6$ and MX. There are two precipitate strengthening mechanisms. One is that $\text{M}_2\text{C}_6$ and MX act as obstacles to dislocation motion. During creep, dislocations have to bypass those carbides to continue. Orowan strengthening mechanism can be used to evaluate the phenomenon. The other is that they slow down recovery of the dislocation substructure.

Orowan stress in high Cr steels can be expressed as [118]:

$$\sigma = 0.8MGb/\lambda$$  \hspace{1cm} (9.1)

where $M$ is the Taylor factor (=3), $G$ is shear modulus (=65Gpa at 650ºC), $b$ is the value of Burger vector (=0.25nm) and $\lambda$ is inter-particle spacing. The relationship between $\lambda$ and number density $N$ can be described as:

$$\lambda = N^{-1/3}$$  \hspace{1cm} (9.2)

As a result, using the data in Table 8.7, the orowon stress for $\text{M}_2\text{C}_6$ of HTT and LTT calculated are 51 and 71 Mpa respectively.

### 9.3 Ferrite formation at the periphery of undissolved carbide

The other mechanism for significant lose of creep strength in FGHAZ of HTT is formation of ferrite near undissolved $\text{M}_2\text{C}_6$ carbides. In TRXRD experiment of HTT-Tp950, the evidence of ferrite formation was observed. Figure 9.4 shows ferrite (011), $\text{M}_2\text{C}_6$ (511) and austenite (111) peak intensity as a function of time and temperature in HTT-Tp950 experiment. It can be seen that the intensity of ferrite (011) is increasing during cooling before onset of martensitic transformation. Similar ferrite formation phenomenon is also observed in other
HTT experiments. Furthermore, post mortem EBSD investigation was performed and the result is shown in Figure 9.4. Image quality maps show some regions with very high image quality (indicated by the circles). High image quality regions are potentially ferrite. Moreover, those high image quality regions look like near ghost austenite grain boundaries. It is very possible that ferrite were formed at ghost austenite grain boundaries during cooling.

![Diagram showing X-ray diffraction results](image)

**Figure 9.3 Time-resolved X-ray diffraction result showing forming of ferrite before onset of martensitic transformation**
During welding, $M_23C_6$ carbides at PAGs are partially dissolved in FGHAZ. When $M_23C_6$ is dissolving, both Cr and C diffuse into austenite. The diffusivity of C is very fast but diffusivity of Cr is slow. In addition, solubility of Cr in austenite is very low (less than 13%). As a result, Cr will be accumulated at carbide
austenite interface. Austenite with high Cr concentration tend to transform to ferrite during cooling before Ms. Since austenite to ferrite transformation is reconstructive, there is no carbon supersaturation in ferrite. Consequently, ferrite will be carbides free after post-weld heat treatment. Ferrite will be very vulnerable during creep.
Chapter 10. Conclusion and Future work

10.1 Conclusion

1. The softening in the CGHAZ region of BA-160 is partly attributed to dissolution of Cu precipitates and carbides. A recovery of strength during multi-pass welding was shown through double-pass thermal cycle simulations. Both Cu precipitates and carbides were shown to re-precipitate during the second thermal cycle. The re-precipitation recovers the strength loss found in the CGHAZ region. A strengthening model, with consideration of precipitation strengthening and martensite sub-structure strengthening, gives good prediction of strength increment. An innovative approach to heat treat Cu bearing steel is proposed that that a quick heat treatment is sufficient for Cu precipitation.

2. A hybrid in-situ technique, that combines a time-resolved X-ray diffraction method using synchrotron and a laser scanning confocal microscope, was used to track microstructure evolution in HAZ of BA-160 steels. The kinetics of phase transformations during thermal cycling with different peak temperatures was tracked at 0.3-second time resolution. The data was compared with dilatometric measurements. The measurements from hybrid TRXRD and LSCM showed the following:
I. Signal to noise ratio of austenite diffraction peaks increased with a decrease in austenite grain size; A reduction in Martensite start temperature was observed with small austenite grain sizes; II. Significant changes in transformation rates were also observed with different austenite grain sizes. III. The LSCM analyses showed refinement of martensite structure with a reduction in austenite grain size. The predicted martensite fraction versus temperatures shows similar trends as that of a published theoretical model, however, the magnitude of predicted rates are lower than that of experimental measurements. IV. Comparison of the above measurements with dilatometric measurements revealed some difficulties. The Volumetric (dilatometer) and surface (synchrotron and LSCM) measurements show inconsistency quantitative values in tracking kinetics of martensite transformation. Highest martensite transformation rate is observed with austenite grains size of 130 μm in synchrotron X-ray diffraction. However, dilation analyses show fastest transformation in the sample with austenite grain size below 10 μm.

3. For Grade 91 steels, low temperature pre-welding tempering significantly improved creep strength of the weldments. Creep life of LTT welded plates is 5 times higher than that of HTT welded plate, Hardness map of post weld heat treated condition shows LTT has less softening in the HAZ than HTT. The softest region of LTT HAZ is 20VHN higher than that of HTT HAZ. The softening is related to larger carbides in FGHAZ. Current hypothesis suggest different carbides size and distribution in FGHAZ contribute to difference in creep properties. In FGHAZ of HTT condition, undissolved M_{23}C_{6} will remain on the
ghost austenite grain boundaries and coarsen faster and suppress the formation of M_{23}C_6 formation on PAGs and martensite block boundaries during PWHT, which give low creep strength in this region compared with LTT condition.

4. Creep strength difference is also studied by Burton’s models, which predict minimum strain rate based on fraction of precipitate on grain boundaries. When defect line energy for steel is 48 pN, the predicted steady state creep rate ratio shows agreement with experiment data. In addition, ferrite formation during cooling near carbide interface in HTT condition is also a factor for low creep strength.

10.2 Future work

Initial evaluation of BA-160 HAZ microstructure and mechanical properties was performed. Caron also performed many weldability tests on BA-160, such as hot ductility test and reheat cracking tests. Overall, BA-160 has a relatively good weldability compared with other naval steels. However, there is no matching filler metal for BA-160. Cu-bearing steel is one of the candidates. Recently, Wang [119] showed with 2.5 wt.% in the filler wire, 350 VHN hardness can be achieved in the weld. Two bead welds were performed. Since the first bead was tempered by the second bead, the first bead shows higher hardness (Figure 9.1). Atom probe confirm precipitation of Cu in the first bead (Figure 9.2). Cu-bearing filler wire with careful design temper bead technique can be used for filler wire design. Cautions need to be taken on solidification cracking since Cu has a low melting
point and notorious for wetting austenite grain boundaries. Varestraint testing and Cast-Pin Tear Test can be used to evaluate tendency for solidification cracking.

![Microhardness map of Cu-bearing filler metal weldments](image1.png)

**Figure 10.1** Microhardness map of Cu-bearing filler metal weldments

![Cu atom map from Cu-bearing filler wire](image2.png)

**Figure 10.2** Cu atom map from Cu-bearing filler wire shows Cu precipitation in the first bead due to the tempering from second bead
Experiments and analysis has showed pre-welding temper at lower temperature (650°C) will give welded structure a better creep strength. However, other factors will also need to be taken into consideration. High hardness (350VHN) of 650 °C tempering indicates low toughness and high susceptibility of hydrogen induced cracking. Usually, P91 pipes are tempered in the shop and then brought to power plant. Pipes with low toughness may not survive the vibration and impact during transportation. There is no evidence of hydrogen induced cracking in our plate butt joint experiments. However, field condition is so different from the lab condition. In addition, welding of pipes will induce much more restraint on the weld, which may lead to hydrogen induced cracking. Tendency of HIC, especially for field condition, need to be evaluated.

Current study emphasized on HAZ simulation. Microstructure evolution during welding, post-weld heat treatment, and creep test was studied. In-situ phase transformation on HAZ simulation in has been characterized. Microstructure evolution during post-weld heat treatment and creep test was speculated based on ex-situ observation. Since microstructure evolution during post-weld heat treatment and creep, especially carbide formation and coarsening, is very important to final creep properties, there is also a need for in-situ characterizing phase transformation. Hirata [45] showed high resolution LSCM can also be a good candidate to observe coarsening of carbides in real time.

Microstructure of FGHAZ of cross-weld sample is not fully understood. Future welding experiment can be performed with some thermal couples attached to
HAZ to measure the thermal history. Samples need to be cut out near the thermal couples and studied by characterization tool. As a result, microstructure in different scale can be understood as a function of thermal history.

Finite element analysis can also be used to study the stress and stain distribution during creep test. According to hardness maps, weld metal, FGHAZ, CGHAZ, base metal all have different mechanical properties. Stress and strain will not be distributed uniformly during creep test. How this affect the creep properties of the weld need to be further investigated.

Unexpected hardening was observed in the weld metal. Since the investigation of weld metal is out of the scope of current research, it is not further studied. Future research can characterize the microstructure in the weld metal and explain the unexpected hardening.

Current study has showed the importance of good microstructure in HAZ. However, both in-situ and ex-situ characterization techniques used are expensive and time-consuming. There is a need to build a microstructure model for microstructure evolution, especially carbide evolution. Dictra can predict carbide formation, coarsening and dissolution. However, Dictra can only simulate one carbide in one dimension. MatCalc can simulate simultaneous precipitation, however, it is lacking of ability to model precipitate-matrix interaction. Phase field, on the other hand, which can simulate 2D and 3D phase transformation, will be a good tool to modeling microstructure change in Grade 91 steels.
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Appendix A Diffraction and EDS data of HTT and LTT as tempered condition
Only $M_{23}C_6$ and MX are the only two found in the current study. Some selected area diffraction and EDS results are shown here.

Figure A1. Carbon extraction replica taken from LTT as-tempered condition, one $M_{23}C_6$ is annotated.
Figure A2 Select area diffraction of $M_{23}C_6$ in Figure A1
Figure A3 EDS spectrum of $\text{M}_2\text{C}_6$ in Figure A1
Figure A4. Carbon extraction replica taken from LTT as-tempered condition, one $\text{M}_{23}\text{C}_6$ is annotated.
Figure A5 EDS spectrum of M23C6 in Figure A4
Figure A6. Carbon extraction replica taken from LTT as-tempered condition, one $M_{23}C_6$ is annotated.
Figure A7 EDS spectrum of $\text{M}_2\text{C}_6$ in Figure A6
Figure A8. Carbon extraction replica taken from LTT as-tempered condition, one MX is annotated.
Figure A9 EDS spectrum of MX in Figure A8
Figure A10 Select area diffraction of MX in Figure A8
Figure A11. Carbon extraction replica taken from LTT as-tempered condition, one MX is annotated.
Figure A12 EDS spectrum of MX in Figure A10
Figure A13. Carbon extraction replica taken from HTT as-tempered condition, one $M_{23}C_6$ is annotated.
Figure A14 EDS spectrum of $\text{M}_{23}\text{C}_6$ in Figure A13
Figure A15. Carbon extraction replica taken from HTT as-tempered condition, one $M_{23}C_6$ is annotated.
Figure A16 EDS spectrum of $\text{M}_2\text{C}_6$ in Figure A15
Figure A17. Carbon extraction replica taken from HTT as-tempered condition, one $M_{23}C_6$ is annotated.
Figure A18 EDS spectrum of M$_{23}$C$_6$ in Figure A17
Figure A19. Carbon extraction replica taken from HTT as-tempered condition, one MX is annotated.
Figure A20 EDS spectrum of MX in Figure A19
Figure A21. Carbon extraction replica taken from HTT as-tempered condition, one MX is annotated.
Figure A22 EDS spectrum of MX in Figure A21