Characterization and Modeling of Heat Affected Zone Microstructure in a blast resistant steel

Thesis

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By

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Abstract

BlastAlloy 160 (BA-160) is a steel that was developed to meet the requirements for blast-resistant naval hull applications. In order to study the weldability of BA-160, a Gleeble thermal mechanical simulator was used to simulate the heat affected zone (HAZ) microstructure in BA-160. The influence of simulated HAZ thermal cycles on microstructure evolution of BA-160 was investigated by optical microscopy, secondary electron microscopy, atom probe tomography (APT) and electron backscatter techniques. Microhardness testing revealed anomalous strengthening behavior in the inter-critical heat affected zone (ICHAZ). Strengthening and softening in different regions of HAZ was studied by evaluating strengthening due to precipitate and martensite high misorientation boundaries.

Coarsening and partial dissolution of Cu precipitates were observed in the sub-critical (SCHAZ) and ICHAZ. A low number density of Cu precipitates and high Cu concentration in the fine grained heat affected zone (FGHAZ) indicates the onset of Cu precipitate dissolution. Re-precipitation of Cu is found in the coarse grained heat affected zone (CGHAZ). Carbides were found to dissolve when the peak temperature of the HAZ is above 750ºC.
The segregation of Cu to grain boundaries was characterized by APT in ICHAZ and CGHAZ. The maximum concentration at the boundary was as high as 20 at. %. Finally, a model for Cu precipitate dissolution is proposed to explain dissolution phenomenon during welding.
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Chapter 1. Introduction

1.1 Problem

The material requirements for blast-resistant US Navy hull applications are rigorous, including high impact fracture toughness, [room temperature Charpy toughness: > 115 J (85 ft-lbs)], high strength [Yield strength: 150-180 ksi (1030-1240 MPa)] combined with good formability, weldability and resistance to hydrogen induced cracking. A new steel, referred to as BlastAlloy 160 (BA-160), has been developed at Northwestern University to meet these requirements [1,2] using a multi-scale materials modeling methodology. BA-160 is based on a low-carbon martensitic/bainitic matrix, which is strengthened through the precipitation of nanoscale (2-5 nm) Cu-rich precipitates and M$_2$C (Cr, Mo, V-rich carbides) carbides. In addition to strengthening by nanoscale precipitates, a maximum Charpy impact toughness of 176 J (130 ft-lb) was also achieved through the precipitation of Ni-stabilized austenite within the matrix. The austenite precipitates dispersed in the martensite matrix improves the toughness of BA-160. In order to employ these steels in shipbuilding applications, it is important to understand the fundamentals of their weldability.

The BA-160 steel has been assumed to be weldable and resistant to hydrogen induced cracking based on a low carbon concentration (0.05 wt. %). This
assumption is valid since the tendency for hydrogen embrittlement in the heat-affected-zone (HAZ) requires hard microstructure (carbon content of the martensite), hydrogen concentration and tri-axial state of stress [3]. It is noteworthy that the weldability of steel is not only related to the formation of hydrogen embrittlement at the HAZ. In addition to hydrogen induced cracking, weldability of steel must consider solidification cracking in the weld metal (WM) region, liquation cracking in the HAZ and WM, ductility dip cracking, reheat cracking, and the final weld metal and HAZ mechanical property gradients.

1.2 Approach

The focus of the current research is to develop a scientific basis for the heat affected zone evaluation of BA-160 using a Gleeble® thermomechanical simulation, optical microscopy (OM), hardness testing, analytical electron microscopy, and local electrode atom probe (LEAP) microscopy. The observed microstructure and strengthening behavior was rationalized using computational thermodynamic and kinetic models.
Chapter 2. Background

2.1 Cu in steels

As mentioned earlier, the BA-160 steels are partially strengthened by precipitation of nanoscale Cu precipitates within the martensitic matrix [1, 2]. Therefore, the weldability of this steel will be related to stability of these precipitates during continuous heating (coarsening and dissolution) and cooling (re-precipitation) conditions during welding. Therefore, a brief overview of Cu precipitate stability in Fe-Cu alloy systems is reviewed to provide a basis for the current work.

Cu has limited solid-solubility in ferrite, as shown in Fe-rich side of the Fe-Cu phase diagram (Figure 1). This diagram is calculated by Thermo-Calc software with TCBIN database. However, by austenitizing at temperatures above 900°C, a substantial amount (up to 3.6 wt. %) of Cu can be dissolved into austenite. Quenching this Cu-enriched austenite phase to room temperature results in a ferrite phase supersaturated with Cu. Extensive studies focused on the phenomenon of Cu precipitation in ferrite matrix [6-9]. Cu precipitate strengthening has also become an important factor in high strength, low carbon steel design. Cu precipitation-strengthened structural steels (e.g. HSLA-80, HSLA-100) are of considerable commercial importance due to their high strength,
good impact toughness, excellent weldability without preheat or postheat, and corrosion resistance [4,5].

![Fe-rich side of the Fe-Cu phase diagram](image)

**Figure 1**: Fe-rich side of the Fe-Cu phase diagram

### 2.1.1 Cu precipitates composition

During aging, Cu initially precipitates from supersaturated α-Fe as spherical, metastable, body-center-cubic (bcc) clusters [6,7]. Goodman et al., [8,9] found that bcc Cu precipitates were comprised of about 50 at. % Fe and 50 at. % Cu when their size is less than 2.5 nm. More recent atom probe investigations have shown general agreement with Goodman [2,10] and measured 70-80 at. % Cu in the Cu precipitates. The Cu concentration in the precipitate core could reach up to 97 at. % [11]. However, small angle neutron scattering (SANS) and small angle
X-ray scattering (SAXS) studies indicate that the bcc Cu precipitates contain a negligible amount of Fe [12,13]. Atom probe tomography result indicates that the Cu concentration in bcc precipitates is related to the size of precipitates. Large precipitates (4-5 nm) yield high Cu concentration (80-100 at. %) while Cu concentration in small precipitate (less than 2 nm) is around 50 at. %. Kozeschnik [14] evaluated the Cu precipitate concentration in Cu bearing steels using computational thermodynamic calculation. It was found that bcc Cu clusters become thermodynamically stable when their concentration is in the range of 30 to 50 at. %. Above this condition, larger precipitates are expected to be pure Cu, if the size is several nanometers or above. On the other hand, smaller precipitates may contain a certain amount of Fe (from about 30 at. % to 60 at. %) with medium to high supersaturation of Cu.

2.1.2 Cu precipitate evolution

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. [15]. The 9R Cu precipitate is roughly spherical and is recognized by a characteristic herringbone pattern in high resolution transmission electron microscopy (HRTEM), as
shown in Figure 2. The orientation relationship between the bcc iron matrix and the 9R Cu precipitate is [16]:

\[(111)_{\text{Fe}}//(-1-14)_{9R}; (1-11)/(-110)\]

The bcc and 9R form of Cu precipitates can be differentiated by the herring-bone angle. The continued growth of the spherical 9R precipitates leads to the formation of the 3R Cu precipitates with the radius larger than 18nm [15]. 3R structure is ellipsoidal untwined structure. The orientation relationship between 3R and Iron matrix is slightly away from Kurdjumov-Sachs (KS) orientation, which is shown in detail in section 2.2. When the precipitate grows to the size of about 26nm, ellipsoidal fcc \(\varepsilon\)-Cu precipitates with two variants are observed [15]. Many studies indicate that the orientation relationship between the fcc Cu precipitate and Fe matrix is of the KS type [15,17,18].

![Figure 2 9R Cu precipitate with herring-bone pattern shown in HRTEM image [15]](image-url)
The Cu evolution is also studied by differential scanning calorimetry (DSC) technique [19]. Three peaks are observed from DSC curve when the samples are heated to 720°C with heating rate of 10°C/min. It is believed that the three peaks correspond to the clustering, coarsening and bcc-9R transformation. The activation energy of nucleation and Cu diffusion in alpha-Fe are 54.4kJ/mol and 244kJ/mol, respectively. The measured activation energy could be applied further in the modeling of precipitate evolution. The enthalpy of bcc Cu to 9R calculated from DSC curve is 3J/g. From thermodynamics calculations, the author gets enthalpy value of 3.5J/g, which confirms the peak of DSC is because of bcc to 9R transformation.

Even though Cu precipitation during isothermal aging has been extensively studied, limited research has been devoted to Cu precipitates evolution under non-isothermal conditions. Kimura and Takaki [18] reported that ε-Cu precipitates out of the matrix for both air-cool and furnace cooling in a Fe-4 at. % Cu alloy. The dispersion of ε-Cu precipitates contribute to the strengthening of these steels. For welding condition, coarsening of Cu precipitates along martensite lath boundaries in the subcritical heat-affected zone is observed in HAZ of HSLA-100 by TEM[20]. It is also reported Cu is dissolved in reaustenitized regions in the intercritical heat-affected zone. Some Cu precipitates in the fine grain heat affected zone are assumed to be undissolved and no re-precipitation of Cu is observed in coarse grain heat affected zone [20].
2.1.3 Cu precipitates 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. However, 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 [21] 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 [22].

2.1.3.1 Misfit strengthening

Misfit effect is also named Coherency strain effect. Since bcc Cu have 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 [23]. For strengthening by precipitate which has an ordered structure, Brown and Ham [24]
reported the increment of shear stress ($\Delta \tau_{\text{mis}}$) by coherency strain effect as following:

$$\Delta \tau_{\text{mis}} = 4.1G(\epsilon_s)^{3/2} f^{1/2} (r/b)^{1/2}$$  \hspace{1cm} (2.1)$$

Where $G$ is the shear modulus of the matrix (Pa), $\epsilon_s$ 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 $\epsilon_s$ is expressed as:

$$\epsilon_s = \frac{2}{3} \frac{\Delta d}{d}$$  \hspace{1cm} (2.2)$$

$d$ 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 and $\epsilon_s$ =0.0057. The volume fraction of bcc Cu precipitates at aged condition is found to be 0.03 [11]. Shear modulus for iron is considered to be 80 GPa and $r/b$ is taken to be 2.5. The calculated misfit strengthen $\Delta \tau_{\text{mis}}$ is found to be 38.7 MPa, which is small compared to the overall strength of steels (1097 Mpa).

**2.1.3.2 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 [21]. 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 [22] 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. The evaluation of Fine’s error is elaborated in Appendix A. 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. The details of modulus difference strengthening are illustrated in section 6.2.

2.1.3.3 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 [22]:

\[
F_{cs} = (\Delta U / b)(2r / b) \tag{2.3}
\]
$\Delta U$ is the change in energy per atom for one 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-Bromm-Ham equation:

$$\Delta \tau_{cs} = \frac{2}{bL(1/2Gb^2)^{1/2}} \left( \frac{F_{cs}}{2} \right)^{3/2} \quad (2.4)$$

From calculation of Fine [22], $\Delta \tau_{cs}$ is less than 75 MPa. As a result, chemical strengthening should not be major contributor to the increase of yield stress.

2.1.3.4 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 [25, 26] and molecular dynamic calculation [27]. 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.
2.2 Martensite morphology and strengthening

In ferrous alloy, martensite can be divided into three groups based on morphologies: lath martensite, lenticular martensite and thin plate martensite [28]. Due to the superior industrial significance, lath martensite is widely studied [29, 30, 31, 32, 33]. The size of the martensite lath is about 300 nm in thickness, 2.8 μm in width and 100μm in length [34]. 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. Therefore, lath martensite exhibits a characteristic microstructure at the optical microscopic scale. Figure 3 shows optical and TEM micrographs of lath martensite in Fe-0.2C steel.

Figure 3: Morphology of lath martensite [29]
The current view of lath martensite holds 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 4 [35]. The morphology of lath martensite changes with respect to carbon content in steels, which is shown in Figure 5. As the carbon content increase, the packets and blocks become finer. 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 [28-35]. 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).
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 [36]. 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]:

\[ \{111\}_\gamma || \{011\}_\alpha \]

\[ <10-1>_\gamma || <11-1>_\alpha' \quad \text{Kurdjumov-Sachs (KS)} \]

\[ \{111\}_\gamma || \{011\}_\alpha' \]

\[ <10-1>_\gamma \text{ about } 5.3^\circ \text{ from } <11-1>_\alpha \text{ towards } <-11-1>_\alpha' \quad \text{Nishiyama-Wasserman} \]

\[ \{111\}_\gamma \text{ about } 0.2^\circ \text{ from } \{011\}_\alpha' \]

\[ <10-1>_\gamma \text{ about } 2.7^\circ \text{ from } <11-1>_\alpha \text{ towards } <-11-1>_\alpha' \quad \text{Greninger-Troiano} \]

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, which are summarized in Table 1. 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. Figure 6 shows orientations of all six KS variants within one single packet schematically [33]. For low carbon steels, a block consists of lath of two specific variant pair with small misorientations, such as V1 and V4, V3 and V6, V2 and V5 in Figure 6 [33].

<table>
<thead>
<tr>
<th>Variant</th>
<th>Misorientation from Variant 1 (V1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V2</td>
<td>twin relation (Σ 3)</td>
</tr>
<tr>
<td>V3</td>
<td>10.53° from twin relation</td>
</tr>
<tr>
<td>V4</td>
<td>10.53°</td>
</tr>
<tr>
<td>V5</td>
<td>10.53° from twin relation</td>
</tr>
<tr>
<td>V6</td>
<td>21.06° from twin relation (Σ 11)</td>
</tr>
</tbody>
</table>

Figure 6 Six K-S variants in a packet [33]
Figure 7 Schematic representation of lath, blocks and packets in one prior austenite grain in low carbon alloy [33]

Figure 8 (a) A typical (001)$_\text{bcc}$ pole figure of martensite formed within a single austenite grain

(b) Theoretical K–S variant map according to one particular austenite orientation[37]
Table 1 Definition of 24 variants in KS orientation relationship [33]

<table>
<thead>
<tr>
<th>Variant No.</th>
<th>Plane parallel Austenite//Martensite</th>
<th>Direction parallel Austenite//Martensite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1 1 1)//(0 1 1)</td>
<td>[-1 0 1]//[-1 -1 1]</td>
</tr>
<tr>
<td>2</td>
<td>(1 1 1)//(0 1 1)</td>
<td>[-1 0 1]//[-1 1 -1]</td>
</tr>
<tr>
<td>3</td>
<td>(1 1 1)//(0 1 1)</td>
<td>[0 1 -1]//[-1 -1 1]</td>
</tr>
<tr>
<td>4</td>
<td>(1 1 1)//(0 1 1)</td>
<td>[0 1 -1]//[-1 1 -1]</td>
</tr>
<tr>
<td>5</td>
<td>(1 1 1)//(0 1 1)</td>
<td>[1 -1 0]//[-1 -1 1]</td>
</tr>
<tr>
<td>6</td>
<td>(1 1 1)//(0 1 1)</td>
<td>[1 -1 0]//[-1 1 -1]</td>
</tr>
<tr>
<td>7</td>
<td>(1 -1 1)//(0 1 1)</td>
<td>[1 0 -1]//[-1 -1 1]</td>
</tr>
<tr>
<td>8</td>
<td>(1 -1 1)//(0 1 1)</td>
<td>[1 0 -1]//[-1 1 -1]</td>
</tr>
<tr>
<td>9</td>
<td>(1 -1 1)//(0 1 1)</td>
<td>[-1 -1 0]//[-1 -1 1]</td>
</tr>
<tr>
<td>10</td>
<td>(1 -1 1)//(0 1 1)</td>
<td>[-1 -1 0]//[-1 1 -1]</td>
</tr>
<tr>
<td>11</td>
<td>(1 -1 1)//(0 1 1)</td>
<td>[0 1 1]//[-1 -1 1]</td>
</tr>
<tr>
<td>12</td>
<td>(1 -1 1)//(0 1 1)</td>
<td>[0 1 1]//[-1 1 -1]</td>
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<tr>
<td>13</td>
<td>(-1 1 1)//(0 1 1)</td>
<td>[0 -1 1]//[-1 -1 1]</td>
</tr>
<tr>
<td>14</td>
<td>(-1 1 1)//(0 1 1)</td>
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</tr>
<tr>
<td>15</td>
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<tr>
<td>16</td>
<td>(-1 1 1)//(0 1 1)</td>
<td>[-1 0 1]//[-1 1 -1]</td>
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<tr>
<td>17</td>
<td>(-1 1 1)//(0 1 1)</td>
<td>[1 1 0]//[-1 -1 1]</td>
</tr>
<tr>
<td>18</td>
<td>(-1 1 1)//(0 1 1)</td>
<td>[1 1 0]//[-1 1 -1]</td>
</tr>
<tr>
<td>19</td>
<td>(1 1 -1)//(0 1 1)</td>
<td>[-1 1 0]//[-1 -1 1]</td>
</tr>
<tr>
<td>20</td>
<td>(1 1 -1)//(0 1 1)</td>
<td>[-1 1 0]//[-1 1 -1]</td>
</tr>
<tr>
<td>21</td>
<td>(1 1 -1)//(0 1 1)</td>
<td>[0 -1 -1]//[-1 -1 1]</td>
</tr>
<tr>
<td>22</td>
<td>(1 1 -1)//(0 1 1)</td>
<td>[0 -1 -1]//[-1 1 -1]</td>
</tr>
<tr>
<td>23</td>
<td>(1 1 -1)//(0 1 1)</td>
<td>[1 0 1]//[-1 -1 1]</td>
</tr>
<tr>
<td>24</td>
<td>(1 1 -1)//(0 1 1)</td>
<td>[1 0 1]//[-1 1 -1]</td>
</tr>
</tbody>
</table>
If the $<$001$>$ austenite is plotted as cross in (001)$_{\alpha'}$ pole figure in Figure 8(b) [37], according to KS orientation relationship, $<$001$>$ of all 24 corresponding variants are plotted as dot in the pole figure. Experimental result of (001)$_{\alpha'}$ pole figure of martensite formed within a single austenite grain is shown in Figure 8 (a). Good matching between the theoretical pole figure and experimental pole figure could be seen. Since the true orientation relations between austenite and corresponding martensite are not rational, which the relationship could not be expressed by any rational number. The KS orientation relationship gives the approximate relationship. As a result, experimental plot for each variant is several degrees off the orientation of the theoretical calculated variant.

Most orientation measurement of martensite is done by EBSD on SEM due to its advantages of easy sample preparation and equipment operation [31, 32]. Typical Orientation maps obtained by EBSD are shown in Figure 9. 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 9 (c) and (d). The misorientation between sub-blocks inside a single block is around 7°. This result shows agreement with calculated misorientation between variants pairs listed in Table 2 [32].
<table>
<thead>
<tr>
<th>Variant pairs</th>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 3</th>
<th>Group 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1-V4, V3-V6, V5-V2</td>
<td>V1-V6, V3-V2, V5-V4</td>
<td>V1-V3, V3-V5, V5-V1, V2-V4, V4-V6, V5-V6</td>
<td>V1-V2, V3-V4, V5-V6</td>
<td></td>
</tr>
<tr>
<td>Misorientation Angle/axis</td>
<td>10.5°/[001]_α'</td>
<td>49.5°/[001]_α'</td>
<td>60°/[001]_α'</td>
<td>70.5°/[001]_α'</td>
</tr>
</tbody>
</table>

Figure 9 (a) and (b) Orientation image maps obtained from low carbon lath martensite and (c) and (d) {001} pole figure showing the crystallographic orientations corresponding the image (a) and (b) [32]

2.3 Field ion microscopy and atom probe microscopy

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 a 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\(^\circledR\) microscope is developed, as shown in Figure 10 [38] to have the capability of large volume analysis, typically 100 x 100 nm\(^2\). 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
Laser pulsing atom probe has the advantage of high mass resolution without the need for energy-compensating devices [39].

Figure 10 Schematic of Local electrode atom probe (LEAP) with laser pulse [38]

Figure 11 Typical mass spectrometry of BA-160 with main peaks marked
2.4 Segregation to boundaries

At elevated temperature, some solute atoms tend to segregate to surfaces or internal interfaces, like grain boundaries. There are two kinds of segregation, equilibrium segregation (ES), which is also called Gibbs type segregation, and non-equilibrium segregation (NES).

2.4.1 Equilibrium segregation (ES)

The mechanism of ES is initially proposed by Gibbs. Since the surface or grain boundaries have a disordered atom arrangement compared with crystalline grains, more room is available for solute to stay. Therefore, solute atoms have a tendency to move to grain boundaries or surface in order to lower their energies. As a result, if enough solute atoms are present and solute atoms have sufficient energy to move, a layer of solute atoms is expected to form at the grain boundaries. The concentration in bulk and in boundaries at equilibrium could be expressed [40]:

$$\frac{c_{gb}}{c_b} = \exp\left(\frac{E_b}{kT}\right)$$ (2.5)

Where $c_{gb}$ is concentration at grain boundaries, $c_b$ is concentration in bulk, $E_b$ is the binding energy of the solute atoms to the grain boundary, $k$ is the Boltzmann’s constant, and $T$ is absolute temperature.

In general, at low temperature (around room temperature or several hundred °C above), the diffusivity of solute atoms is low. It is impossible for them to segregate to grain boundaries. As a result, kinetics of solute element is an
important aspect of grain boundary segregation. McLean derived an equation to describe the ES with respect to time, which is cited by Faulkner [40]:

\[
\frac{c_x - c_b}{c_{gb} - c_b} = 1 - \exp\left(\frac{4Dt}{\alpha^2 d_i^2}\right)\text{erfc}\left(\frac{4Dt}{\alpha^2 d_i^2}\right)
\]  \hspace{1cm} (2.6)

where \( \alpha \) is the enrichment factor \( c_{ob}/c_{ab} \), \( c_x \) is the boundary solute atom concentration after time \( t \), \( d_i \) is the grain boundary width and \( D_i \) is the solute atom diffusion coefficient.

The mechanism of ES indicates if the equilibrium is achieved for the segregation, the solute concentration at the interface is a constant. Sharp concentration gradient exists at the grain boundary interfaces. An example of ES is shown in Figure 12 [41]. Material studied here is Ni-3.6 at. %P layer which is heated to 400 °C at 5°C/min and cooled down. The segregation of P to grain boundaries is observed by using atom probe tomography. The P concentration profile across the boundary in Figure 12 (b) shows large gradient at the distance of 15 nm and 24 nm. Between 15 nm and 24 nm, the concentration is almost constant.

**2.4.2 Non-equilibrium segregation (NES)**

The mechanism of NES can be explained by the formation of solute-vacancy complex and vacancy movement as shown is Figure 13. The heat treatment, where the equilibrium condition could not be achieved, can produce the inhomogeneity of vacancy distribution. For example, if the material is subjected to quench, vacancy concentration will decrease at grain boundaries. On the other hand, the grain center is supersaturated with vacancies. If vacancies have
Figure 12 (a) P atoms map of Ni-3.6 at.% P layer after heating up 400 °C at 5°C/min revealed by atom probe tomography (left) and P 2.5 at.% and 15 at.% isoconcentration surface (b) P concentration profile through P-rich interface [41]
sufficient energy, they will move down the gradient to grain boundaries. Some solute atoms will form complex with vacancies and move together with the vacancies towards grain boundaries.

![Schematic illustration of non-equilibrium segregation](image)

**Figure 13** Schematic illustration of non-equilibrium segregation [40]

The NES after quenching could be expressed by [40]:

\[
\frac{c_{vx} - c_{vgb}}{c_{vb} - c_{vgb}} = \text{erf} \left( \frac{x}{2(D_v \Delta t)^{1/2}} \right)
\]

where \( c_{vx} \) is the vacancy concentration at the distance \( x \) from the grain boundary, \( c_{vgb} \) is vacancy concentration at the boundary, \( c_{vb} \) is the vacancy concentration in the center of grain, \( D_v \) is the vacancy diffuse coefficient and \( \Delta t \) is the time after quenching.
According to the mechanism of NES, one feature of NES is that the solute concentration gradient at the grain boundary is smooth. Solute is enriched in grain boundaries and depleted near grain boundary inside the grain.
Chapter 3. Objectives

Project objectives

1. Understand Cu precipitates and carbides evolution in HAZ of BA-160 by atom probe tomography
   i) Determined the Cu precipitates size, composition and distribution in different regions of HAZ.
   ii) Examine the carbides in different regions of HAZ.

2. 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 by investigating martensite texture plot.

3. Apply existed model to explain hardening and softening in HAZ from the following two perspectives:
   i) Strengthening by martensite high misorientation boundaries.
   ii) Strengthening by Cu precipitates.

4. Study Cu segregation phenomenon in HAZ of BA-160 using atom probe tomography.

5. Rationalize observed microstructure using computational thermodynamic and kinetic model.
Chapter 4. Experimental procedure

4.1 Materials

The BA-160 experimental material was provided by QuesTek Innovations LLC, Evanston, IL in the form of 1.375-inch diameter barstock. The measured chemical composition of the BA-160 experimental material is provided in Table 3. The details of the heat treatment procedure for BA-160 are outlined in Table 4. 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 M$_2$C carbides [1].

<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>0.030</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 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>

4.2 HAZ simulation

To investigate the HAZ microstructure evolution of BA-160, thermal cycle simulations representative of the various HAZ regions were performed [42]. For steels, these four distinct regions are (1) the subcritical heat-affected zone (SCHAZ), where no detectable transformation to austenite occurs; (2) the intercritical heat-affected zone (ICHAZ), where partial transformation to austenite occurs; (3) the fine-grained heat-affected zone (FGHAZ), where full transformation to austenite occurs at a peak temperature slightly above the Ac3 temperature; and (4) the coarse-grained heat-affected zone (CGHAZ), where full transformation to austenite occurs at a peak temperature much above the Ac3 temperature. Plots of temperature vs. time for the HAZ simulations are provided in Figure 14.
The thermal cycle simulations were performed with a Gleeble$^\text{®}$3800 thermal-mechanical simulator using cylindrical samples of 6.35mm (0.25-inch) diameter and 101.6mm (4.0-inch) length. The sample temperature was controlled with a type-K thermocouple wire percussion welded at the midsection. The samples were heated to the peak temperature at a linear rate of 100°C/s and free-cooled at a rate simulating a high heat-input weld ($t_{8/5}$ is about 45 seconds). 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 $A_c_1$ and $A_c_3$ 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.

4.3 Material characterization

4.3.1 Optical microscopy and hardness test

Samples for metallographic analysis were sectioned with a Leco VC-50 precision diamond saw and mounted in Konductomet conductive mounting powder. The microhardness of the simulated HAZ regions was determined with a Leco M-400-H1 Hardness Testing Machine using a 981N (1kgf) load, in accordance with ASTM Designation E-384-08. All specimens used for the microhardness testing and microstructure characterization were taken from a single sample to ensure consistency of results.

4.3.2 Scanning Electron Microscopy

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. 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.

4.3.3 Local Electrode Atom Probe Characterization

Coupons (0.3×6×6 mm³) were cut from the center of Gleeble® specimens 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 [43]. 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. A typical specimen and the electrode in LEAP are shown in Figure 15.

Figure 15 Needle shape sample and local electrode in LEAP
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 from -198 to -188°C (75 to 85 K) under ultra-high vacuum (UHV) conditions of ca. 1.0×10^-8 Pa (7.5×10^-11 torr). Short-duration laser pulses (1 nJ) are used to induce field evaporation and the pulse repetition rate was up to 5×10^5 Hz. The voltage applied to the specimens is up to 12kv.

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 ion 3 dimensional distribution. 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 16 [44]. Typical graphical interface of IVAS is shown in Figure 16.
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. Based
on the pre-known composition knowledge of BA-160, iron should be main element in the analysis. The main peak mass spectrum should be $^{56}\text{Fe}^{2+}$ as shown in Figure 11. According to the position relationship with $^{56}\text{Fe}^{2+}$ and isotope abundance information, all other ions, such as Cu, Cr, Ni, Mo, could be identified in the mass spectrum. 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.

$$r = \frac{V}{kF}, \quad (3.1)$$

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 and mass to charge values. With atom position and mass information, all kinds of analysis could be done to evaluate nanostructure of sample.
Chapter 5. Experimental results and discussion

5.1. Phase transformation and microhardness

Plots of temperature vs. time for the HAZ simulations are provided in Figure 14. The thermal arrest that occurs on cooling is indicative of the martensite phase transformation for all thermal cycles except SCHAZ. The absence of a thermal arrest for the simulated SCHAZ sample is noted, confirming the 650°C peak temperature as being below the Ac$_1$ temperature, where no transformation to austenite occurs on-heating. As a result, no martensitic transformation occurs during cooling.

The dilatation curve for the simulated CGHAZ sample is provided in Figure 17. The Ac$_1$ and Ac$_3$ temperatures for BA-160 as determined from the on-heating dilatation data were 660 ±10°C and 810 ±10°C, respectively. From the on-heating austenite transformation curve, it can be seen that at 750°C, austenite volume fraction is 0.9, i.e. 10% untransformed martensite exists in the ICHAZ. The on-cooling phase transformation temperatures for the HAZ simulations are summarized in Figure 18. Martensite was found to be the only transformation product for each of the samples heated to a peak temperature above the Ac$_3$ temperature. Some variation was found for the determined martensite start (M$_s$) temperatures. The simulated CGHAZ exhibited the highest M$_s$ temperature,
which is also in best agreement with the 360 ± 8.4 °C reported by Saha and Olson [1]. The FGHAZ simulations exhibited the lowest measured $M_s$ temperature.

A plot of Vickers microhardness vs. peak temperature for the simulated HAZ samples is provided in Figure 19. Also shown in the figure for reference is the base metal hardness of 402 HV, as indicated by the dashed line. The hardness profile reveals a hardness peak in the ICHAZ sample with the lowest hardness occurring in the CGHAZ sample. A slight decrease in hardness was experienced in both the SCHAZ and FGHAZ samples.

![Figure 17 The dilatation curve (a) Transformed austenite volume percentage vs. temperature during heating in CGHAZ (b) Relative radius change vs. temperature during heating in CGHAZ (c) Transformed martensite volume percentage vs. temperature on cooling (d) Relative radius change vs. temperature during cooling [42]](image)
For common structural steel, as the peak temperature in HAZ increase, the hardness is expected to decrease because of dissolution of strengthening particles and coarsening of grains [45]. For naval steel HSLA-80 and HSLA-100, significant hardening has been seen in ICHAZ, FGHAZ and CGHAZ [20,46]. The hardness increase in HAZ is a result of fresh untempered martensite formation. The hardness increase for the ICHAZ is unexpected since strengthening particles are supposed to dissolve and produce a negative strength on material. Besides, high strength in ICHAZ is also anomalous with reference to published HAZ microstructural hardness for high strength steels.

![Graph showing cooling phase transformation temperatures for HAZ simulations](image)

**Figure 18** On-cooling phase transformation temperatures for HAZ simulations [42]
5.2. Martensite morphology in HAZ

Optical micrographs for specimens from different regions of the HAZ show martensitic microstructure (Figure 20). Some of the prior austenite grain boundaries can be observed. The martensite blocks and packets are observed clearly. In SCHAZ, martensite blocks and packets are visible, however, not clear. As a result, optical micrographs are not suitable for lath martensite morphology analysis.

The current investigation focused on martensite morphology and its crystallography using electron backscatter diffraction (EBSD) technique. EBSD maps for all simulated HAZ samples are shown in Figure 21. Large angle grain
boundaries with misorientation above 15 degrees are plotted by solid lines. The samples show a typical lath martensite microstructure for all heat treatment conditions. Since no detectable phase transformation occurred for the SCHAZ sample, no significant martensite and prior austenite grain morphology change is observed compared to the base metal. Fine martensite packets with diameters approximately 1 μm can be found in the ICHAZ. Dilatometry results (Figure 17) indicates that when the sample is heated to 750°C, around 90% of martensite is transformed to austenite. Due to the fast heating rate (100°C/second) and small dwell time above Ac₃, austenite grains did not grow. As a result, small austenite grains observed in Figure 21(c) correspond to the austenitized region. Two large martensite packets, which are indicated by the arrows, are considered to be untransformed martensite from the original microstructure. Fine and coarse prior austenite grains, martensite block and packets are clearly revealed in Figure 21(d) and (e).
In heat treated steel and simulated HAZ with peak temperature less than 1300 °C, the martensite block size is close to the prior austenite grain size, which means there is only one block or one packet inside each prior austenite grain. There are several packets, however, in one prior austenite grain in the CGHAZ. Three packets, designated P1 and P2, and P3, and two blocks, designated B1 and B2 are shown in Figure 21 (e).
Figure 21 EBSD map (a) base metal (b) SCHAZ (c) ICHAZ (d) FGHAZ (e) CGHAZ
5.3 Martensite Texture plot

The prior austenite outlined in Figure 21 (c) is cropped and shown Figure 22 (a). The corresponding (001)$_{bcc}$ pole figure is plotted in Figure 22 (b). All 24 martensite variants present inside this single prior austenite grain. The center of the three “rings” in the pole figure implies the orientation of the prior austenite according to theoretical KS relationship in Figure 8. As a result, if number of “ring” and “block” texture indicates the number of prior austenite in the region. In general, if all 24 lath martensite variants presents in one prior austenite grain, three “rings” and six “blocks” will exist in the pole figure of this prior austenite. However, when the prior austenite grain size is small (less than 10μm), there may be only one packet with 6 variants presented in a single prior austenite [47]. As a result, the pole figure in a specific area for lath martensite with different samples could use to evaluate prior austenite grain size and block size relatively.

For each sample, 40 by 40 μm area is selected in the orientation image and corresponding (001)$_{bcc}$ pole figure for all specimens are plotted in Figure 23. As expected, no significant texture difference is shown between base metal and SCHAZ. Pole figure of SCHAZ shows scatter point clouds and no “ring” and “block” texture could be seen clearly. This indicated large number of prior austenite grains in this region. Some “ring” texture in the pole figure of FGHAZ indicates large number of prior austenite grains in this region. The feature of “ring” and “block” could be clearly seen in pole figure of CGHAZ. The patterns in the pole figure of CGHAZ indicate two partial prior austenite grains exist in the region. Since blocks are consist of lath with small misorientations. The texture
plots also indicate for the same area, ICHAZ have the largest number of prior austenite grains and blocks.

Figure 22 (a) Inverse pole figure of one prior austenite grain in CGHAZ and (b) the corresponding (001) pole figure
Figure 23 (001)$_{bcc}$ pole figure for (a) base metal (b) SCHAZ (c) ICHAZ (d) FGHAZ (e) CGHAZ
5.4. Cu precipitates in HAZ of BA160

In the heat-treated condition, the number density of the Cu precipitates, average radius, and Cu concentration of the matrix was found to be $4.20 \times 10^{23} \text{ /m}^3$, 2.4 nm, 0.23 at.\%, respectively. We will hereafter refer to these previously published numbers in referring to the BA-160 “base metal” condition.

Cu atom maps in different simulated HAZ conditions are shown in Fig. 22. The regions of high Cu concentration are clearly noticeable in Figs. 22 (a) and (b). The presence of high Cu concentration regions in the SCHAZ and ICHAZ indicates Cu precipitates are not fully dissolved. In Figs. 22 (c) and (d), Cu enriched zones cannot be detected and it the Cu atoms appears to be distributed homogeneously in the FGHAZ and CGHAZ specimens. The absence of Cu precipitates reveals their dissolution in the FGHAZ and CGHAZ. However, atom maps can be misleading and may mask fine nanometer scale clusters and precipitates.
Therefore, the size, number densities, and composition of Cu precipitates were determined by the envelope method [43]. The value of maximum Cu-atom separation was set to 0.6 nm, minimum number of atoms in a cluster set to 30, and grid resolution for the envelope was 0.12 nm. Radius of gyration, Guinier radius, center of mass, and number of atoms for were derived for the Cu precipitates. The precipitate number density is calculated by the following equation [43]:

$$N_p = \frac{N_p \xi}{n \Omega}$$  \hspace{1cm} (4.1)
where \( N_p \) and \( n \) are the number of particles and total number of atoms detected in the volume, \( \Omega \) is the average atomic volume which is \( 1.2 \times 10^{-29} \text{ m}^3 \) for bcc Cu and \( \varsigma \) is the detection efficiency of a single ion detector, equal to 0.5 in the current calculation. The 3D reconstructions for Cu atoms in the precipitates detected by the envelope method are shown in Figure 25 for all conditions. The precipitates intersected by the reconstructed volume are eliminated in the number density calculation. For FGHAZ and CGHAZ, though no Cu concentrated area is seen in Cu atoms map, some small precipitates with average radius of about 1.6 nm are found by envelope precipitates analysis with the parameters given above. The summary of the Cu precipitates calculation is shown in Table 6. The composition profile in the matrix and in the precipitates is provided in Table 7 and Table 8.
Figure 25 3D LEAP reconstruction of Cu atoms in precipitates as detected by the envelope method (a) SCHAZ (b) ICHAZ (c) FGHAZ (d) CGHAZ
Table 5 Radius and number density of Cu precipitates for the different HAZ regions

<table>
<thead>
<tr>
<th></th>
<th>As-received</th>
<th>SCHAZ</th>
<th>ICHAZ</th>
<th>FGHAZ</th>
<th>CGHAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (nm)</td>
<td>2.4±1.2</td>
<td>3.3±1.4</td>
<td>2.3±1.1</td>
<td>1.6±0.4</td>
<td>1.7±0.5</td>
</tr>
<tr>
<td>Number density</td>
<td>4.2±2.2</td>
<td>1.83±0.5</td>
<td>2.26±0.7</td>
<td>0.32±0.2</td>
<td>2.02±1.1</td>
</tr>
</tbody>
</table>

Table 6 Composition profile in matrix (at. %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCHAZ</td>
<td>0.16%</td>
<td>2.03%</td>
<td>89.76%</td>
<td>6.50%</td>
<td>0.47%</td>
<td>0.84%</td>
<td>0.01%</td>
</tr>
<tr>
<td>ICHAZ</td>
<td>0.11%</td>
<td>1.79%</td>
<td>86.80%</td>
<td>7.90%</td>
<td>0.98%</td>
<td>2.00%</td>
<td>0.01%</td>
</tr>
<tr>
<td>FGHAZ</td>
<td>0.07%</td>
<td>2.10%</td>
<td>88.66%</td>
<td>6.05%</td>
<td>0.61%</td>
<td>2.43%</td>
<td>0.00%</td>
</tr>
<tr>
<td>CGHAZ</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>
<td>0.00%</td>
</tr>
</tbody>
</table>
Table 7 Composition profile in Cu precipitates (at. %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCHAZ</td>
<td>0.12%</td>
<td>1.34%</td>
<td>62.62%</td>
<td>6.38%</td>
<td>0.33%</td>
<td>29.04%</td>
<td>0.00%</td>
</tr>
<tr>
<td>ICHAZ</td>
<td>0.10%</td>
<td>1.10%</td>
<td>59.48%</td>
<td>6.74%</td>
<td>0.73%</td>
<td>31.48%</td>
<td>0.00%</td>
</tr>
<tr>
<td>FGHAZ</td>
<td>0.00%</td>
<td>0.00%</td>
<td>11.67%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>88.33%</td>
<td>0.00%</td>
</tr>
<tr>
<td>CGHAZ</td>
<td>0.04%</td>
<td>0.43%</td>
<td>17.22%</td>
<td>1.45%</td>
<td>0.12%</td>
<td>80.66%</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

In the SCHAZ, the average radius of Cu precipitates is larger and number density is smaller compared with the base metal, which indicates the precipitates are coarsening. When the material is heated to 650 °C, Cu coarsening accelerates with dissolution of the smaller cluster by the Ostwald-ripening effect (coarsening) [48]. As a result, the average radius of the Cu precipitates increases while the number density decreases.

In the ICHAZ, the number density of the Cu precipitates increases slightly compared to the SCHAZ. Because the area analyzed by atom probe is relatively small, (about 10³ to 10⁵ nm³), the small difference in number density of Cu precipitates between ICHAZ and SCHAZ could be considered to be not significant. However, based on the smaller average Cu precipitates radius (2.34 nm) and high Cu concentration in the matrix in the ICHAZ, we can reasonably conclude that partial dissolution of the Cu precipitates occurs upon heating to 750 °C. In the ICHAZ, only part of the microstructure is transformed to austenite upon
heating. Based on dilatometry analysis, the volume fraction of the austenitized region at 750°C is approximately 0.90. Also, since austenite has a much larger Cu solubility than ferrite, it is assumed that the atom probe data for the ICHAZ is from an austenitized region. The results are expected to be different in the untransformed regions due to the low solubility of Cu in ferrite. Further studies will be needed targeted using focused ion beam to prepare specimen in the untransformed regions for LEAP analysis.

A significant decrease in the number density of Cu precipitates (0.32×10²⁵ m⁻³) and the average precipitate radius (1.6 nm) is observed in the FGHAZ. Future analysis of data from FGHAZ indicates the Cu concentration (2.43 at. %) in the matrix is very close to the Cu concentration (2.48 at. %) in the bulk material. The low number density and small average precipitate radius indicate that Cu precipitates are almost fully dissolved when heated to 900°C. These small precipitates could be either non-dissolved or re-formed precipitates during cooling.

A high number density of Cu precipitates (2.02×10²³ m⁻³) with a small average precipitate size (1.7 nm) was found in the CGHAZ. Compared with the FGHAZ, the number density of Cu precipitates in the CGHAZ is much higher, which indicates Cu re-precipitation out of the matrix during cooling in CGHAZ. However, the optimum precipitate size for strengthening, which is 2-5 nm, is still not reached because of the short time in the Cu precipitation aging temperature range.
5.5 Cu precipitate core composition

Composition in Cu precipitates and matrix shown in Table 7 is determined by envelope method. The compositions of both Cu precipitates and matrix are from the result of envelope method. A sharp precipitate interface is assumed in envelope method. Since the Cu concentration across the precipitate interface gradually increase from the matrix to precipitate core, some of the transition zone is considered in the matrix and the other is considered in the precipitates. Cu concentration in precipitates by envelope method should be a little lower than core concentration. Due to large number of atoms in matrix, the effect of taking account of transition zone on Cu concentration in the matrix could be ignored.

Proxigram could use to determine the Cu composition in the precipitate core [49]. Proxigram describes the chemical inhomogeneity of the microstructure spatially. The proxigram is a composition profile across an isoconcentration surface. The generation of isoconcentration surface and proxigram is done by utilizing IVAS software. The bin size for the proxigram plotted in Chapter 5 and Chapter 7 in the present study is 0.2 nm. The error bars in the proxigram correspond to two-sigma standard errors of the calculated concentration values.

5.5.1 Precipitates composition in SCHAZ

Figure 26 (a) shows the 10 at. % Cu isoconcentration surface. The precipitate A with a radius of about 2.5nm is highlight and composition profile across the precipitate interface is plotted in Figure 26 (c). The composition profile shows the
Cu concentration gradually increase from the matrix to precipitate core. The transition region is about 2 nm. Ni and Cr are depleted in Cu precipitates. In the precipitate core, there is a plateau in Cu concentration (33 at. %). The core composition in SCHAZ is much less that in base metal, which is reported to be 92 at. % [11]. The precipitate B with a radius less than 1 nm is highlighted in Figure 26 (b). The corresponding composition profile across the interface is plotted in Figure 26 (d). The core composition is about 16 at. %. Therefore, small Cu precipitate radius yields low core concentration. Low Cu concentration in precipitate core proves the partial dissolution of Cu precipitates in SCHAZ.

Figure 26 (a) (b) 10 at.% Cu isoconcentration interface in SCHAZ; (c) (d) Composition profile for Ni, Fe, Cu and Cr of precipitate A and precipitate B across precipitate interface
Figure 26 continued
5.5.2 Precipitates composition in ICHAZ

Figure 27 shows the composition profile across the interface of one precipitates in ICHAZ. No plateau in Cu composition curve could be seen in precipitate. This indicates further dissolution above 650°C on heating. The transition zone in ICHAZ is the same as that in SCHAZ, which is about 2nm.

![Composition profile for Ni, Fe, Cu and Cr across interface of Cu precipitate in ICHAZ](image)

5.5.3 Precipitates composition in FGHAZ and CGHAZ

Small number of atoms in Cu precipitates in FGHAZ and CGHAZ is not sufficient to generate 10% Cu isoconcentration surface. As a result, isoconcentration surface and proxigram cannot be used for precipitates composition analysis in FGHAZ and CGHAZ. It is noticed that in SCHAZ and
ICHAZ, both envelope method and proxigram shows around 30 at. % Cu in large precipitates (radius more than 2 nm). However, envelope method gives high Cu concentration in small precipitates while proxigram shows low Cu concentration in small precipitate (radius around 1nm). The difference of result between two methods for small precipitates should be evaluated with in-house analysis programs.

5.6 Precipitates size distribution

The size distribution for Cu precipitates characterized from APT is plotted in Figure 28. For SCHAZ, ICHAZ and CGHAZ, the distribution could be nearly described by log-normal fits, which are shown as dash line in Figure 28. Due to the fact that only 5 Cu precipitates are captured in FGHAZ, data is not sufficient to describe the distribution of precipitates. Precipitates in CGHAZ are potentially formed by re-precipitation as discussed in section 5.5. Most of the precipitates in CGHAZ in the range of 1.5nm to 2nm indicates that most of precipitate nucleates from the matrix at the same time and do not have time to grow. Small number of larger precipitates (radius is larger than 2nm) are also observed.
Figure 28 Cu precipitate size distribution (a) SCHAZ (b) ICHAZ (c) FGHAZ (d) CGHAZ
5.7. Hypothesis of Cu precipitate evolution in HAZ

In a HAZ of a BA-160 weld, the solid state transformations involved are complex due to on-heating transformation of ferrite/martensite to austenite, precipitate
growth and coarsening, precipitate dissolution, reformation of precipitates during cooling, on-cooling transformation of austenite to martensite. Figure 29 shows a schematic where the thermal history of CGHAZ is divided into 5 stages. The equilibrium Cu solid solubility in austenite is also plotted as a function of temperature by JMatPro and Thermo-Calc using TCFE5 database.

Stage 1: At the temperature below Ac$_1$ on heating, no martensite is transformed to austenite. Cu precipitates may coarsen.

Stage 2: At temperatures between Ac$_1$ and Ac$_3$ on heating, some martensite is transformed to austenite. Bcc Cu precipitates in transformed region may transform to the fcc structure in order to lower their free energy. Due to the high solubility of Cu in austenite, fcc Cu precipitates will start dissolving with an increase in temperature. Bcc Cu in untransformed martensite may be continue coarsening or start dissolving since solubility of Cu in bcc Fe is increased to above 2 wt.% based on Fe-Cu phase diagram (Figure 1).

Stage 3: At the temperature above Ac$_3$, all martensite has been transformed to austenite. All bcc Cu precipitates could be transformed to fcc Cu precipitates and dissolving in austenite.

Stage 4: Both Thermo-Calc and JMatPro equilibrium calculations predict Cu precipitation out of austenite matrix below 800°C. As a result, on cooling before austenite is transformed to martensite, Cu precipitates will re-precipitate out of matrix below 800°C. Cu clusters which precipitate out of austenite are expected to adopt an fcc crystal structure.
Stage 5: At the temperature below $M_s$, Cu is not expected to re-precipitate out of martensite since the diffusivity of Cu at that temperature is so low ($<10^{-18}$ cm$^2$/s [50]).

![Figure 29 Different stages in thermal profile of CGHAZ Predicted Cu solubility in austenite by both JMatPro and Thermo-Calc (b) Thermal profile of CGHAZ](image)

5.8 Carbide analysis

Due to the complexity of $M_2C$ carbide, the envelope method cannot be used for carbide composition analysis. Current study applies 1 at. % carbon isoconcentration surface to study the morphology evolution of $M_2C$ carbide. It is reported that $M_2C$ carbide co-located with Cu precipitates in BA-160 base metal [51]. Figure 30 shows the 10 at. % Cu isoconcentration surface in gold and 1 at.
% carbon isoconcentration surface in grey. The co-location of Cu precipitates and carbides is also observed in SCHAZ. However, in ICHAZ, small number of carbon isoconcentration surface indicates the almost full dissolution of carbide when the specimen is heated to 750 °C. It is reported if the aging temperature is above 750 °C, no evidence of M2C precipitates can be found [52]. The full dissolution of M2C temperature is expected to occur between 650 °C and 750 °C, with the heating rate of 100 °C/second. In FGHAZ, as expected, no significant Cu precipitates are shown in the reconstruction. Several carbon isoconcentration surfaces may be a result of re-precipitation of carbide, which should be confirmed in the future work with targeted focus ion beam (FIB) and TEM analysis. Interestingly, a large carbon plate with the length larger than 100nm is observed. A cylinder is selected and composition profile across the carbon concentrated region is plotted in Figure 31. For materials with carbon, the formation of carbon molecular ions, such as C32+, C3+, C22+, C22+ and C42+. The mass spectrum of 3D reconstructed volume shown in Figure 31(a) is shown in Figure 32. All other peaks have already been indicated in Figure 11. C32+, and C22+ peaks are observed in mass spectrum. The concentration of C22+, C32+, and C42+ are plotted in Figure 31 (b) (c) and (d) respectively. The carbon concentration in the enriched region should be the sum of C22+, C32+, and C42+, which is about 3 at.%. The thickness of carbon concentrated region is about 5 nm. This carbon concentrated region could be carbide or retained austenite with high carbon content and need to be further evaluated.
Figure 30 10 at.% Cu and 1at.% isoconcentration carbon surface in (a) SCHAZ (b) ICHAZ
(c) FGHAZ (d) CGHAZ
Figure 31 Carbon atom map (a) and Composition profile of C (a) C₂ (b) C₃ (c) across the carbon enriched region the cylinder

Continued
Figure 31 continued

(c)

(d)
Figure 32 Mass spectrum of CGHAZ sample
Chapter 6. Modeling of strengthening

As shown in Figure 17, anomalous hardening and softening is observed in HAZ of BA-160. To interpret hardening and softening phenomena, the current study applies available models to evaluate the microstructural strengthening in the HAZ regions based on characterization data from chapter 3 and 4. Emphasis has been put on understanding of the morphology of lath martensite and the size of Cu precipitates on strengthening.

For martensitic strengthening, the yield stress of the lath martensite is calculated by the summation of the hardening mechanisms [53]:

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

(5.1)

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, \( \sigma_p \) is the strengthening term as a function of dislocations density, \( \sigma_g \) is the grain boundary strengthening and \( \sigma_p \) is the precipitate strengthening. Due to the insignificant contribution of solid solution strengthening and negligible change of dislocation densities in the martensite, only precipitation and grain boundaries strengthening are calculated to rationalize the hardening and softening.
6.1 Strengthening by martensite matrix

The packet size and block width in the different regions of the HAZ were measured by using the mean linear intercept method. Most researchers take the contributions from block width and packet size into account separately when considering grain boundary strengthening [54, 32]. As two important parameters which describe the morphology of lath martensite, packet size and block width should be considered together for grain boundary strengthening. Since the block boundaries inside a packet act as obstacles to dislocation motion, slip plane length can be described to a certain extent by block width \( (d_b) \) and packet size \( (d_p) \). Assuming that the block is rectangular and the length of the block is equivalent to the packet size, as shown in Figure 33, the slip plane length, \( M \), can be calculated [54]:

\[
M = \frac{d_b}{\cos \theta} \quad \text{for} \quad \theta \leq \frac{d_b}{d_p},
\]

(5.2)

Figure 33 Schematic of slip plane length as a function of lath width \( d_p \) and block size \( d_b \)
If the distribution of slip plane orientation with respect to block orientation is assumed to be isotropic, the average slip plane length can be calculated as a function of block width and packet size:

\[
\overline{M} = \frac{1}{\pi/2} \left[ \int_0^{\pi/2} \frac{d_b}{\cos \theta} \, d\theta + \int_{\cos \left( \frac{d_{p}}{d_{p}} \right)}^{\pi/2} d_b \, d\theta \right],
\]

(5.3)

From the calculated average slip plane length, the strengthening introduced by block boundaries can be calculated from the Hall-Petch equation:

\[
\sigma_g = K_y \overline{M}^{-1/2},
\]

(5.4)

where \( K_y \) is 0.363 Mpa m\(^{1/2}\).[54]

The calculated grain boundary strengthening contribution is summarized in Table 8.

<table>
<thead>
<tr>
<th></th>
<th>SCHAZ</th>
<th>ICHAZ</th>
<th>FGHA</th>
<th>CGHAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packet Size (μm)</td>
<td>9.4</td>
<td>1.58</td>
<td>3.36</td>
<td>56.0</td>
</tr>
<tr>
<td>Block width (μm)</td>
<td>6.26</td>
<td>1.48</td>
<td>2.19</td>
<td>12.4</td>
</tr>
<tr>
<td>Slip plane length (μm)</td>
<td>8.20</td>
<td>1.57</td>
<td>2.90</td>
<td>2.53</td>
</tr>
<tr>
<td>( \sigma_g ) (Mpa)</td>
<td>127</td>
<td>290</td>
<td>213</td>
<td>72.3</td>
</tr>
</tbody>
</table>
6.2 Strengthening by Cu precipitates

Due to the complicated evolution of the Cu precipitates in the HAZ, the strength contributions arising from Cu precipitation are more difficult to model [18]. Four contributors to Cu precipitate strengthening, misfit strengthening, chemical strengthening, modulus difference strengthening, and dislocation core-precipitate interaction strengthening have been introduced in section 2.1.3. The role of misfit strengthening and chemical strengthening could be ignored due to small strength increment produced [22]. Dislocation core-precipitate interaction has certain contribution to the strengthening. However, it requires modeling of precipitate and dislocation interaction at atomic scale and complex calculation. For simplicity, only modulus strengthening based upon the model of Russell and Brown [21] is discussed in the present investigation.

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:

$$\tau = 0.8 \frac{Gb}{L} [\cos \frac{\Phi_c}{2}] \quad \Phi_c \leq 100^0$$

$$\tau = \frac{Gb}{L} [\cos \frac{\Phi_c}{2}]^{3/4} \quad \Phi_c \geq 100^0$$

(5.5)

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 in Figure 34(b).

For the case that one dislocation is cutting through a precipitate, the equilibrium of the dislocation requires that

$$E_M \sin \alpha_M = E_P \sin \alpha_P$$

(5.6)

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 34(a).

---

**Figure 34** (a) a dislocation line is cutting a spherical precipitate (b) a dislocation is about to cut through with the critical angle
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 34 (b). The dislocation equilibrium and critical angle can be expressed as:

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

(5.7)

Substituting the critical angle into equation 5.5, the yield stress as a function of dislocation energy in precipitate and in matrix can be given by:

\[ \tau = 0.8 \frac{Gb}{L} \left[1 - \frac{E_P^2}{E_M^2}\right]^{1/2}, \quad \sin^{-1} \frac{E_P}{E_M} \leq 50^0 \]
\[ \tau = \frac{Gb}{L} \left[1 - \frac{E_P^2}{E_M^2}\right]^{3/4}, \quad \sin^{-1} \frac{E_P}{E_M} \geq 50^0 \]  

(5.8)
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:

\[
\frac{E_P}{E_M} = \frac{E_P^\infty \log \frac{r}{r_0}}{E_M^\infty \log \frac{R}{r_0}} + \frac{R}{R} \log \frac{r}{r_0}
\]

(5.9)

where \( E_P^\infty \) is dislocation energy per unit length in precipitate, \( E_M^\infty \) 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 \( E_P^\infty / E_M^\infty \) is around 0.6. Using the precipitate properties obtained from atom probe analysis into the modulus difference equation, an estimate of the strengthening by Cu precipitate is given.

The properties and strengthening of the Cu precipitates is listed in Table 9.

Figure 35 shows the predicted strength increase for the various HAZ simulated regions investigated, \( \Delta \sigma \), with respect to the measured hardness. A near linear relationship between the predicted strength and measured hardness imply that the current strengthening model can be used to evaluate the strengthening of lath martensite morphology and Cu precipitate in the HAZ regions of BA-160. The model could be improved if bcc Cu shear modulus value could be estimated.
### Table 9 Cu precipitates properties and strengthening

<table>
<thead>
<tr>
<th></th>
<th>BM</th>
<th>SCHAZ</th>
<th>ICHAZ</th>
<th>FGHAZ</th>
<th>CGHAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (nm)</td>
<td>2.4</td>
<td>3.28</td>
<td>2.34</td>
<td>1.6</td>
<td>1.71</td>
</tr>
<tr>
<td>Inter-precipitate spacing L (nm)</td>
<td>26.1</td>
<td>31.3</td>
<td>36.0</td>
<td>731</td>
<td>261</td>
</tr>
<tr>
<td>Volume Fraction</td>
<td>0.0292</td>
<td>0.0319</td>
<td>0.0152</td>
<td>0.0005</td>
<td>0.0045</td>
</tr>
<tr>
<td>(\tau_p) (Mpa)</td>
<td>116</td>
<td>113</td>
<td>76.5</td>
<td>1.96</td>
<td>6.27</td>
</tr>
<tr>
<td>(\sigma_p) (Mpa)</td>
<td>290</td>
<td>283</td>
<td>191</td>
<td>4.92</td>
<td>15.7</td>
</tr>
<tr>
<td>(\sigma_g) (Mpa)</td>
<td>127</td>
<td>127</td>
<td>290</td>
<td>213</td>
<td>72.3</td>
</tr>
<tr>
<td>(\sigma_{g+p}) (Mpa)</td>
<td>418</td>
<td>411</td>
<td>482</td>
<td>218</td>
<td>88.0</td>
</tr>
<tr>
<td>(\sigma_{g+p})HAZ-(\sigma_{g+p})BM (Mpa)</td>
<td>0</td>
<td>-7</td>
<td>64</td>
<td>-200</td>
<td>-330</td>
</tr>
</tbody>
</table>

![Figure 35 Predicted strength increment by martensite matrix and Cu precipitates with respect to measured hardness increment](image)

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Chapter 7. Cu segregation

Besides Cu precipitates evolution, evidence of Cu segregation was captured by atom probe tomography. Segregation phenomena from ICHAZ and CGHAZ specimens are observed in the current study. Figure 36 (a) shows Cu and Fe atom map near boundaries for simulated ICHAZ. Regions of increased Cu concentration are pointed to by arrows. Boundary A and boundary B are denoted as shown in the picture. Cu atoms maps for ICHAZ reveals elongated Cu precipitates near the boundaries due to the segregation. Since the distance between the two regions is about 50 nm, the Cu segregation is suspected to occur at martensite sublath boundaries.

In refining the atom probe analysis of boundary segregation, two cylinders of analysis were placed in the reconstructed volume to analyzed selected boundaries as shown in Figure 36(a). The radius of each cylinder is 6 nm and the length of that is 24 nm. Composition profiles along the cylinders are plotted in Figure 36 (c) and Figure 36 (d) for boundary A and boundary B, respectively. Composition profiles are obtained by generating proxigram along main axis of the selected cylinder in IVAS software [49]. The bin size selected is 0.2 nm. Cu segregation at boundary A and B is clearly revealed while Fe is depleted. As expected, the Cu concentration away from the boundary is approximately 2 at. %, which is the same as the matrix. It is also shown that the Cu concentration increases closer to
the boundary. The maximum Cu concentration found at the boundary A and boundary B are 16.83±4.41 at. % and 7.66±0.89 at. %, giving a coefficient of segregation of 8.41 and 3.83 respectively. Though Cu and Fe atoms maps in Figure 36 (a) reveals high Cu and Fe atom density at boundary B, Cu concentration at boundary B is less than that at boundary A. The possible reason would be trajectory aberrations effect at boundary B causing increased atomic density in the reconstruction [55,56].

Based on the shallow Cu peak in the composition profile in Figure 36 (c), the segregation type could be identified as non-equilibrium segregation [40]. During the quenching stage of initial heat treatment, vacancies concentration may decrease significantly near boundaries. When the specimen is heated to 750°C, some Cu atoms will be dragged towards boundaries with the movement of vacancies [40]. Due to the quenching of the initial heat treatment of BA160, the concentration gradient of vacancies near boundaries is higher than that away from boundaries. As a result, Cu atoms near boundaries have a high tendency to form complex with vacancies. Due to the short time of heating (around 7 seconds), thermodynamic equilibrium cannot be reached on a local scale. Upon cooling down to room temperature, the Cu precipitates are “frozen” in the microstructure due to low diffusivity of vacancy-atom complexes. As a result, Cu precipitates near the boundaries show elongated shape towards boundaries. This is also evident from the shape of Cu concentrated regions appearing to be stretched rod-like shapes. The 8 at.% Cu isoconcentration map, Figure 36 (b), shows spherical
Figure 36 (a) 3D LEAP reconstruction of regions containing a boundary for an ICHAZ sample displaying Cu and Fe atoms (b) 8 at. % Cu isoconcentration surface near boundary in ICHAZ sample. (c) Cu, Ni, Cr composition profiles across boundary A (d) Composition profiles across boundary B.
Cu precipitates away from the boundaries, rod-like Cu precipitates near boundaries and boundaries with high Cu segregation. Figure 37 shows the segregation of Cu atoms near a boundary in a CGHAZ sample. Boundary A, B and C are marked in the figure. Since only small volume is analyzed, the boundary type cannot be determined. Two cylindrical regions of interest are selected to generate concentration profiles across the boundary. Cylinders have a radius of 6 nm and a length of 24 nm. Concentration profile of the top cylinder clearly reveals two Cu peaks. The maximum concentration at the peak for boundary A and B are $18.05 \pm 5.44$ at. % and $20.31 \pm 6.18$ at. %. Compared with ICHAZ, the segregation of Cu in CGHAZ is much more severe. Longer dwell time at high temperature promotes the segregation of Cu to boundaries. Besides, slight segregation of Ni is also observed at boundary B. The maximum concentration of Ni at the peak for boundary B is $16.98 \pm 6.12$ at. %. There is a 0.8 nm offset between the Ni peak and Cu peak. A sharp Cu peak in the composition profile is observed at boundary C at the distance of 15 nm in Fig 37 (c). Sharp Cu peak indicates possible equilibrium segregation at boundary C.

At low temperature, segregation is kinetically limited. As the peak temperature increases, more time is provided for the material to stay at higher temperatures, which along with the higher diffusivity of Cu vacancies complexes at these temperatures and higher driving force, promote the segregation. The result implies that as the peak temperature of HAZ increases, the Cu concentration at the boundaries also increases.
As the peak temperature increases, dwell time at higher temperature increases, coupled with the higher diffusivity of Cu vacancy complexes at these temperatures, the segregation is promoted. The result implies that as the peak temperature of HAZ increases, the Cu concentration at the boundaries will also increases. The segregation of Cu will enhance the susceptibility of HAZ liquation cracking and reheat cracking.

Figure 37 (a) 3D LEAP reconstruction of regions containing martensite block boundaries in a CGHAZ sample (b) Composition profiles across boundary A (c) Composition profiles across boundary B
Figure 37 continued
Chapter 8. Cu precipitation dissolution modeling

Since Cu precipitates are one of contributor to the strengthening of BA-160, understanding of Cu precipitate dissolution in of importance in the HAZ. The dissolution of Cu precipitate can be described by Fick’s second law and invariable boundary (the position of the boundary do not move during dissolution), which is proposed by Whelan [57]. The dissolution rate of a spherical particle is expressed as a function of time at a certain temperature. However, the model is only for isothermal condition. For non-isothermal condition, particle/matrix interface concentration varies with respect temperature and the boundary conditions. As a result, the Whelan’s model cannot be used directly for non-isothermal precipitate dissolution. Grong [58] developed a precipitate dissolution model for welding condition by neglecting the transient item in Whelan’s model since precipitates dissolution takes place in a short period of time. Limited research has been carried out on the dissolution of bcc Cu precipitates in welding condition. Wang [59] evaluate the dissolution of fcc Cu precipitate during welding by using Grong’s approach. The predicted result shows the agreement with experimental data. Since the thermodynamic and kinetic data of bcc Cu is limited, Wang’s [59] approach on fcc Cu dissolution is adopted here to estimate the dissolution of bcc Cu in HAZ of BA-160.
For spherical particles embedded in an infinite matrix, Whelan [57] proposed that the dissolution of particles for isothermal conditions can be expressed as:

\[
\frac{dr}{dt} = k \left( \frac{D_m}{r} - \sqrt{\frac{D_m}{\pi t}} \right)
\]  

(7.1)

Where \( r \) is the average precipitate radius, \( t \) is time, \( k \) is the dimensionless supersaturation which is defined in Figure 38 and \( D_m \) is the diffusivity of the precipitate element in the matrix. Since the time involved in precipitate dissolution is limited during fast welding thermal cycles, the transient term in the equation can be neglected. [58]. As a result, it is possible to describe the precipitate radius as:

\[ r^2 = r_0^2 - 2kD_m t \]  

(7.2)

The volume fraction of precipitates can be further derived as:

\[
f = f_0 \left( \frac{r}{r_0} \right)^3 = f_0 \left[ 1 - \frac{2kD_m t}{r_0^2} \right]^{3/2}
\]  

(7.3)

For continuous heating and cooling, the volume fraction of precipitates can be obtained by integration of the time-temperature history, and can be described using the following equations:

\[
f / f_0 = \left[ 1 - \frac{2\int_{t_1}^{t_2} kD_m dt}{r_0^2} \right]^{3/2}
\]  

(7.4)
As a result, if all the kinetic parameters for Cu are known and the thermal history of a specific region in the HAZ is obtained, the volume fraction of Cu precipitates can be predicted from equation 7.4.

Since limited information is available for bcc Cu precipitate dissolution modeling, all the parameters used in the current research are from ε-Cu dissolution in steel [59], which are listed in Table 10. The dissolution of Cu precipitates is initiated at 650°C. Cu precipitates size and volume fraction at SCHAZ stage is considered as initial condition. Predicted Cu dissolution results are shown in Figure 39.
Table 10 Summary of the input parameters used in numerical solution to the kinetic equation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Dissolution start temperature T1</th>
<th>( r_0 ) (nm)</th>
<th>( C_i ) (%)</th>
<th>( D_m ) (cm(^2)s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>650°C</td>
<td>3.2</td>
<td>( \exp(9.982-10359/T) )</td>
<td>( 8.6\exp(-2.47\times105/RT) )</td>
</tr>
</tbody>
</table>

The volume fraction ratio comparison between experiment and modeling are summarized in Table 11. Figure 39 shows the change of Cu precipitate fraction ratio \( (f/f_0) \) with respect to temperature for different HAZ regions. The predicted volume fraction ratio for ICHAZ is 0.369, which is lower than the experimental value (0.476). For FGHAZ and CGHAZ, the model predicts full dissolution of Cu precipitates at 815°C on heating. The predicted full dissolution is in agreement of the experimental results. The re-precipitation on cooling is not modeled here and will be the subject of future research.
Table 11 The volume fraction ratio comparison between experiment and modeling

<table>
<thead>
<tr>
<th></th>
<th>ICHAZ</th>
<th>FGHAZ</th>
<th>CGHAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental f/f₀</td>
<td>0.476</td>
<td>0.015</td>
<td>0.141</td>
</tr>
<tr>
<td>Predicted f/f₀</td>
<td>0.369</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 39 Predicted Cu dissolution in difference HAZ region as a function of temperature
Chapter 9. Conclusion and Future work

9.1 Implications of the above research on weldability of BA-160

1. The current study indicates that welding thermal cycles modifies both Cu precipitates and martensite matrix in different HAZ regions of BA-160. Loss of strength or ductility may be a problem when welding BA-160.

2. Cu segregation to martensite lath boundaries is observed in HAZ with high peak temperature ($T_p > 750^\circ$C). For multipass welding condition, the segregation of Cu maybe enhanced. Extensive Cu segregation may cause liquation cracking during welding of high strength steels.

3. Strength decrease in FGHAZ and CGHAZ is primarily due to the dissolution of Cu and $M_2C$ precipitates. Post weld heat treatment (PWHT) is suggested for re-precipitation of Cu and $M_2C$. Since the martensite matrix in base metal is in tempered condition, effect of PWHT on martensite is insignificant.

9.2 Conclusions

1. Anomalous softening and hardening are observed in different region of simulated HAZs. This phenomenon is explained by the evolution of martensite matrix microstructure and Cu precipitates for different thermal cycles.
2. Cu precipitates were characterized by atom probe tomography. Coarsening and partial dissolution of Cu precipitates are observed in the SCHAZ. Cu precipitates are also partially dissolved in the ICHAZ. Cu concentration plateau could not be observed in precipitate core in ICHAZ. Low number density and small size of Cu precipitates in FGHAZ indicates rapid Cu precipitates dissolution above 750°C during heating. High number density of re-formed Cu precipitates is observed in CGHAZ.

3. Martensite packet size and block width play an important role in the strengthening of martensitic steels. Since prior austenite grain size plays an important role on block and packet size, emphasis must be placed on control of prior austenite grain size.

4. A kinetic model is proposed to predict the dissolution of Cu precipitates in HAZ. Comprehensive Cu precipitate nucleation, coarsening and dissolution model need to be developed to understand the Cu precipitates evolution during heating and cooling.

9.3 Future work

1. Although, atom probe have the capacity of analyzing Cu precipitate composition, position and distribution, the crystal structure information cannot be
obtained. Since Cu precipitates in CGHAZ is likely to be fcc structure, TEM characterization will be necessary to confirm this hypothesis.

2. It is realized that some limitation exists in the Cu precipitate strengthening model. First, fcc bulk Cu modulus is used instead of bcc Cu precipitate modulus. The first principle calculation suggests negative modulus of bcc Cu precipitate [60]. A negative modulus makes the strengthening model by Russell and Brown complicated. Dislocation core-precipitate interaction should also be taken into account in the future research.

3. It is important to note that if we consider the field-welding conditions, the range of microstructure that occurs in the HAZ regions can be too exhaustive to be described by laboratory experimental research programs. Therefore, there is a need to develop integrated process-microstructure models that are capable of predicting the microstructure a function of material and process parameters. The dissolution model presented in this thesis has some limitations and is not good enough to evaluate the microstructure evolution in HAZ. Some preliminary work has been done on austenite grain growth and precipitates simulation by MatCalc [61] software and Dictra [62] software. Future work will be focused on developing a plug-and-play microstructure model that can predict the microstructure in the HAZ for BA-160.
Chapter 10. Reference


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APPENDIX A
Correction to the paper “Origin of copper precipitation strengthening in steel revisited”

Xinghua Yu\textsuperscript{1}, S. S. Babu\textsuperscript{1}, M. Fine\textsuperscript{2} and D. Isheim\textsuperscript{2}

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Background

OSU researchers are working on quantitative evaluation of strengthening and softening due to copper precipitation in Blast alloy steels, by considering the dissolution, coarsening during complex thermal cycling imposed during welding [Ref. 1]. Recently, the role of shear modulus difference between the matrix and precipitate on strengthening ($\Delta \tau_{MF}$) was evaluated by Fine and Isheim [Ref. 2]. The equation (5) from their reference is given below.

$$\Delta \tau_{MF} = 0.8 \frac{G_M b}{L} \left[ 1 - \frac{G_P}{G_M} \right]^{\frac{1}{2}} \sin^{-1} \frac{G_P}{G_M}$$

(1)

In the above equation, $G_M$ is the shear modulus of the matrix, $G_P$ is the shear modulus of the precipitate, $b$ is the Burger’s vector, and $L$ is the spacing between precipitates. The above equation was adopted from the original equations proposed by Russell and Brown [3]. The Equations (2a and 2b) in their original reference is provided below.

$$\Delta \tau_{RB1} = 0.8 \frac{G_M b}{L} \left[ 1 - \frac{E_P}{E_M} \right]^{\frac{1}{2}} \sin^{-1} \frac{E_P}{E_M} \leq 50^\circ$$

(2a),

$$\Delta \tau_{RB2} = \frac{G_M b}{L} \left[ 1 - \frac{E_P}{E_M} \right]^{\frac{1}{2}} \sin^{-1} \frac{E_P}{E_M} \geq 50^\circ$$

(2b),

In the above equation, $E_M$ and $E_P$ are the energy of dislocation per unit length within matrix and precipitate, respectively. The ratio of dislocation energy is equal to the ratio of shear modulus.
Error and Impact on the Interpretation of Modulus Difference

Comparing the equations (1) to (2), we believe that the equation (1) is in error. Although the error was mentioned in a paper by Li et al [4], the details of the correction and impact of the same were not explicitly in that paper. Therefore, in this paper to avoid the propagation of our mistake we would like to present the correction.

The equations were used by misinterpreting the arc-sin parameter as an argument, rather than as conditional statement to identify the power (1/2) or (3/4). The impact of the above error is discussed below.

In the original paper by Russell and Brown [3], strengthening due to the difference in shear modulus was evaluated as a function of the ratio of \( G_P/G_M \), as well as, cutting angle between precipitate and matrix dislocation. This magnitude was compared with strengthening by Orowan looping mechanism given by the following equation.

\[
\Delta \tau_{\text{Orowan}} = 0.8 \frac{G_M b}{L}
\]  

(3)

The calculated ratio of \( \Delta \tau_{\text{MF}} \) and \( \Delta \tau_{\text{Orowan}} \), as well as, the ratios \( \Delta \tau_{\text{RB1}} \), \( \Delta \tau_{\text{RB2}} \) and \( \Delta \tau_{\text{Orowan}} \) are compared in Fig. 1. In addition to the strengthening, calculated cutting angle is also plotted on the same diagram similar to the plots of Russell and Brown [3]. Russell and Brown equations predict that the strengthening ratio decreased from a maximum value of 1 to zero with an increase in the \( G_P/G_M \). In contrast, the ratio of strengthening calculated by Fine and Isheim [2] increases from zero to a maximum and again reduces to zero with an increase in the \( G_P/G_M \). We believe there is no fundamental reason for such a behavior. This is purely due to the error in using the conditional statement as a parameter. More importantly, the above analyses shows that the strengthening due to elastic modulus difference will be very important when the ratio between the shear modulus of precipitate and matrix are in between 0 and 0.8. This is in contradiction to the conclusion made by Fine and Isheim [2].
Figure 1 Comparison of strengthening due to differences in elastic moduli between precipitate and matrix

References

1. Xinghua Yu and S. S. Babu, Unpublished Research, The Ohio State University, Columbus, Ohio 43221
APPENDIX B
Microstructure Characterization and Austenite Grain Growth Modeling of the Heat Affected Zone in X70/X100 Pipeline Steels

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Keywords: Pipeline steels, weld microstructure, HAZ softening, phase transformation model

Abstract: New generation of high-strength steels, with strength levels from 70 ksi (~480 MPa) to 120 ksi (~827 MPa), have been developed. In this paper, microstructure evolution in the heat-affected-zone is investigated by thermal simulation, optical microscopy and hardness measurements in X70 and X100 pipeline steels. The range of microstructures that can evolve in the HAZ is discussed in terms of initial microstructure and peak temperature. The HAZ microstructure in X100 steel showed softening with a peak temperature of 700°C. The measured prior-austenite grain was in agreement with a published austenite grain growth model.

Introduction.

To meet the high-pressure needs [1] of natural gas pipelines, high strength steels [from 70 ksi (480 MPa) to 120 ksi (827 MPa)] have been developed. The combination of high strength and good toughness of pipeline steels are achieved by controlled thermomechanical processing (TMCP). The goal of these thermomechanical processes is to produce fine (< 5 µm) ferrite grains either by refining austenite grain size or by promoting high-strength microstructural constituents. The microstructural constituent can range from polygonal ferrite (PF), ferrite-pearlite (FP), ferrite-bainite (FB), bainite-martensite (BM), and martensite-austenite (MA) [2, 3]. The above microstructural features are usually achieved by controlled rolling in austenite phase field and accelerated cooling. The challenge is to weld these steels without minimal degradation of the original microstructure and properties. The weldability of high strength pipeline steels is influenced by many factors including steel chemistry, original microstructure and production method. The balance of high strength and good toughness can be modified by the complex thermal cycles introduced during welding. These thermal cycles may induce microstructures with low strength and poor toughness in heat-affected-zone (HAZ). The origin and complexity of HAZ microstructure evolution can be understood by the sequence of phase transformations that occur during typical heating and cooling of steel during welding.

Low carbon steel often undergoes distinct events during one thermal cycle that determines its final microstructure in HAZ [4]. Ideally, the $\alpha \rightarrow \gamma$ transformation starts during heating above the Ac1 temperature and completes at the Ac3 temperature. However, due to rapid heating conditions, the complete austenitization may occur well above the equilibrium Ac3 temperature. This phenomenon occurs due to less time available for completion of nucleation and growth of austenite from the original microstructure. After the completion of $\alpha \rightarrow \gamma$ transformation, the austenite
grain growth occurs. In microalloyed pipeline steels, second-phase particles [e.g. Ti(C\textsubscript{x}N\textsubscript{1-x}) and Nb(C\textsubscript{x}N\textsubscript{1-x})] will inhibit austenite grain growth by exerting a pinning force on the mobile austenite grain boundaries. During cooling cycle, the austenite starts to decompose into various microstructural constituents (FP, FB, BM, and MA) below the Ar\textsubscript{3} temperature. Furthermore, the kinetics of phase transformations during heating and cooling, as well as, the austenite grain growth depends on the thermal cycle. In case of regions not heated above Ac\textsubscript{3} temperature, the microstructural change may include recovery, recrystallization and growth of ferrite grains in FP microstructure, as well as, tempering in MA phase. Therefore, any quantitative understanding of the final microstructure must include all these events as a function of spatial locations and initial microstructure. Although, there exists extensive amount of experimental data on the microstructure evolution in pipeline steel welds and its correlation to the properties, these data cannot be generic to all pipeline steels due to wide range of initial microstructures [5, 6]. An ideal tool to address this challenge is to use mathematical models [7, 8, 9]. Most previous studies on the mathematical modeling of microstructure in the HAZ focused on the heating and cooling cycle independently and ignored the effect of initial microstructure [10, 11]. The goal of this work is to develop a model that can predict the microstructure in the HAZ as a function of composition and initial microstructure.

Experimental Procedure.

The chemical compositions of the two steels are shown below in table 1. Selected samples from X70 and X100 pipelines were subjected to controlled thermal cycling experiments in a Gleeble\textsuperscript{®} thermomechanical simulator [12]. The samples were heated to different peak temperature (700°C, 800°C, 900°C, 1050°C, 1200°C and 1350°C) at 30°C/s. After reaching the peak temperature, the samples were cooled at 30 °C/s to room temperature. Slices were cut from the center of the sample at the point of thermocouple contact, polished and etched with 2% nital. Optical microscope was used for microstructure characterization. Grain sizes were measured by mean linear-intercept method according to ASTM standards given by ASTM E112-96. The hardness tests were performed with a LECO\textsuperscript{®} microhardness tester AMH43. The Vicker’s hardness was measured at 100 locations for all samples using a load of 10 gram and a dwell time of 10 seconds.

<table>
<thead>
<tr>
<th>Stee l</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
<th>N</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>X70</td>
<td>0.06</td>
<td>0.28</td>
<td>1.5</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.00</td>
<td>0.06</td>
<td>0.03</td>
<td>0.00</td>
<td>0.01</td>
<td>Bal .</td>
</tr>
<tr>
<td>X100</td>
<td>0.05</td>
<td>0.22</td>
<td>1.9</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.06</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>Bal .</td>
</tr>
</tbody>
</table>

Results and Discussions

Thermodynamic Calculations: In order to understand the phase transformation during heating and cooling, A\textsubscript{1} and A\textsubscript{3} temperatures and the volume fraction of stable phases are calculated using Thermocalc\textsuperscript{®} software with SSOL4 database [13]. For X70 steels, the predicted A\textsubscript{1} and A\textsubscript{3} temperatures are 674°C and 850°C, respectively. On the other hand, A\textsubscript{1} and A\textsubscript{3} temperatures predicted for X100 steels are 630°C and
815°C, respectively. To understand the role of microalloying additions, the tendency for the formation of precipitates were also calculated. The calculations show that the niobium-titanium ([Nb, Ti] C) carbides start dissolving at 900°C and disappears at 1100°C. The calculations also showed that carbo-nitrides [(Ti, V, Nb) (C, N)] are stable up to 1300°C in both X70 and X100 steels. This observation is in agreement with works of Ion et al [9] and Grong [12].

**Microstructural Observations from X70 steel**: Results of optical microscopy and hardness measurements from X70 (Fig. 1) are discussed below. The microstructure of as-received X70 steel contains PF and darkly etching secondary microstructure. The secondary microstructure is identified as martensite-austenite (MA) based on the maximum hardness (319 HV) measured from these samples. In the sample heated to peak temperature of 700°C, there was no significant change in microstructure compared to that of as-received sample. Although this temperature is above the equilibrium A_t temperature, there was no indication of austenite formation. The morphology of MA island changed on heating to 800°C. Since A_t temperature of X70 is predicted to 674°C, one could expect the austenite formation in these MA regions. In addition, the MA regions have a higher carbon concentration [2] and will aid the austenite nucleation. In X70 sample heated to 900°C, a uniform distribution of bainitic microstructure was observed. This suggests that the substantial amount of ferrite should have transformed to austenite on heating to 900°C. However, the prior austenite grain boundaries could not be delineated. This leads to a speculation that these samples could be still in the two-phase (α+γ) field region. In the sample heated to 1050°C, a PF microstructure was observed within an equiaxed prior austenite grains (~ 5 µm). Coarse austenite grains are observed in the samples heated to 1350°C due to longer time above A_s. An increase in hardness is attributed the formation of bainitic microstructure during cooling.

![Fig. 1 Optical micrographs and the average hardness of the X70 steel samples shows wide range of microstructure as a function of thermal cycles with different peak temperatures. For micrographs from samples heat treated ≥1050°C, some of the prior austenite grain boundaries are outlined.](image-url)
Fig. 2 Optical micrographs and the average hardness of the X100 steel samples shows wide range of microstructure as a function of thermal cycles with different peak temperatures. For micrographs from samples heat treated ≥1050°C, some of the prior austenite grain boundaries are outlined.

**Microstructural Observations from X100 steel:** The microscopy results from X100 steels are shown in Fig. 2. For X100 steel, as-received microstructures contain bainitic ferrite and small amounts of darkly etching MA in between bainitic ferrite laths. In the X100 samples heated to 700°C, a significant drop in the hardness was observed. This phenomenon may be caused by tempering of MA or recrystallization of bainitic ferrite. In addition, this softening could be related to recovery of cold worked microstructure. To understand the reasoning for such softening, further characterization is necessary with orientation imaging microscopy and transmission electron microscopy. Interestingly, in X70 steels, the softening phenomenon was not observed. This is attributed to the fact that the overall hardness of X70 samples is influenced by ferrite, rather than the MA microstructure. In X100 samples heated to 800°C, the hardness increased slightly. The A3 temperature of X100 steel is 630°C which is much lower than 900°C. As a result, there will be increased driving force for austenite formation in X100 steels, as the sample heats up to 900°C. This will lead to the formation of 100% austenite, which in turn will transform to PF microstructure on cooling. In the X100 samples heated to 900°C and 1050°C, the microstructure shows fine prior austenite grains (< 5 µm) and PF microstructure. In the samples heated to 1350°C, the underlying microstructure contained mostly lath type microstructure with a very high hardness.

**Modeling of Microstructure Evolution**

The above results clearly demonstrate a complex interaction between initial microstructure, peak temperature, austenite grain size on the final microstructure and hardness of HAZ in pipeline steels, for a given heating and cooling rate. In order to develop a comprehensive model to describe the above microstructure evolution, methodologies have to be developed to describe the following components: (1)
softening due to recovery and recrystallization of cold worked PF below A1 temperature (2) softening due to tempering of MA during heating; (3) microstructure evolution during heating and cooling with peak temperature in between A1 and A3 temperatures; (4) austenite grain growth during heating above A3; and (5) microstructure evolution during cooling from austenite phase field. In this paper, accuracy of a published austenite grain growth model was evaluated as a first step towards developing an overall microstructure model.

Model for Austenite grain growth: For microalloyed pipeline steels, high temperature stable precipitates play an important role in stifling austenite grain growth. In this work, the model by Moon [14] was coupled with other methodologies [15, 16] for predicting the austenite grain size. In the current steels, the [(Nb, Ti) C] carbide is expected to dissolve at 1100°C. As a result, they are not expected to play a role in pinning the austenite grain boundaries. In this paper, only [(Ti, V, Nb) (C, N)] carbo-nitrides are expected to limit the austenite grain growth. Ideally, the grain growth model must consider the growth, coarsening and dissolution of these precipitates during heating and cooling. In this work, only coarsening of [(Ti, V, Nb) (C, N)] carbo-nitrides is considered. A brief description of the steps in austenite grain growth model is given below. The first step is to predict the precipitate coarsening during heating and cooling. Ion et al [16] modified the classic precipitate coarsening theory and derived an equation to predict the precipitate radius \( r \) for continuous heating and cooling conditions:

\[
r^3 - r_0^3 = c_1 \int_T^{t_2} \frac{1}{T} \exp(\frac{-Q_s}{RT}) dt
\]

(1),

where \( r_0 \) is the initial precipitates radius (µm), \( T \) is temperature (in Kelvin) as a function of time \( t \) (sec), \( c_1 \) is a kinetic constant (µm\(^3\) K s\(^{-1}\)) and \( Q_s \) is the activation energy (J mol\(^{-1}\)). Once the precipitate radius, is known, we can predict the limiting austenite grain size using classical Zener’s theory [9, 17] with the following equation.

\[
D_{lim} = k r f_0
\]

(2),

where \( D_{lim} \) is the limiting grain size, \( k \) is the Zener coefficient (0.75), \( r \) (µm) is the average radius of precipitates, \( f_0 \) is the volume fraction of stable precipitates.

The \( f_0 \) for X70 and 100 were calculated to be \( 3.46 \times 10^{-4} \) and \( 3.03 \times 10^{-4} \), respectively. By integrating with equations (1) and (2), the limiting grain size as a function of temperature can be predicted with the following equation.

\[
\overline{D}_{lim} = \frac{k r}{f_0} \left( \frac{\overline{D}_{0, lim}}{r_0} \right)^3 \int_T^{t_2} \frac{1}{T} \exp\left(\frac{-Q_s}{RT}\right) dt
\]

(3),

where \( \overline{D}_{lim} \) is the limiting grain size for stable precipitates at room temperature and \( c_5 \) is kinetics constant. With the above equation (3) and using an estimated value of initial precipitate radius \( r_0 \) and volume fraction of stable precipitates \( f_0 \), the limiting grain size can be predicted as a function of thermal history.

The next step is to consider the kinetics of austenite grain growth as it increases from a small value (<5 µm) after the 100% austenite formation above Ac3 temperature. This subject has been investigated extensively. The grain growth can be described by the following classical relationship:

\[
\frac{dD}{dt} = nK \exp\left(\frac{A}{RT}\right) \left( 1 - \frac{1}{D_{lim}} \right)^{(1/n-1)}
\]

(4),
where \( D \) is the grain size (\( \mu m \)), \( D_{lim} \) is the limiting grain size (\( \mu m \)) which is determined by the equation (3). The parameter \( A \) is apparent activation energy for grain growth with the unit of (J mol\(^{-1}\)), \( K \) is a rate constant and \( n \) is time exponent. The values of \( A, K \), and \( n \) depend on the steel type and temperature. The activation energy \( A \) is governed by solute drag at the austenite grain boundaries. Moon et al. demonstrated that \( n \) is a constant (0.2324) and not related to the chemical composition of the steels. In addition, the same authors proposed that \( A \) is related to composition as given below [14]:

\[
A = 352185.31 + 21827.26X_C + 1995094X_{Mn} + 7185.49X_{Cr} + 7378.06X_{Ni} \quad (5),
\]

**Validation of the Model:** Prior average austenite grain sizes were measured (see Table 2) from micrographs (see Figs. 1 and 2). No significant difference in austenite grain size was observed between X70 and X100 samples with a peak temperature of 1050°C. On heating to 1200°C, the austenite grain size of both X70 and X100 steels increased. Interestingly, on heating to 1350°C, a slightly larger austenite grain size was observed in X100 steel samples compared to that of X70 samples. It will be of interest to rationalize this reversal in grain growth phenomenon as a function of temperature, using the grain growth model described above.

Using the equations (1) to (5), the austenite grain growth can be predicted as a function of thermal cycle. For titanium-alloyed steels, all the parameters in equations (1) to (5) are provided by references [7, 14, 16], for example, \( D_{lim} \) = 20 microns, \( Q_s \) = 240 kJ/mol and \( c_5 \) is \( 6.67 \times 10^4 \). The initial austenite grain size was assumed to be 5 \( \mu m \).

The calculated grain sizes for a thermal cycle with a peak temperature of 1350°C, as a function of time, is shown in Fig. 3. The calculations reveal that austenite grain starts to grow on heating above 1000°C. Interestingly, with temperatures below 1250°C, the grain growth rate for X100 is smaller than X70 steels. Above 1250°C,

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_p=1050°C )</th>
<th>( T_p=1200°C )</th>
<th>( T_p=1350°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X70</td>
<td>5.60</td>
<td>38.35</td>
<td>41.35</td>
</tr>
<tr>
<td>X100</td>
<td>5.15</td>
<td>29.25</td>
<td>49.05</td>
</tr>
</tbody>
</table>

Fig. 3 Simulated (a) thermal cycles and corresponding (b) predicted austenite grain size values for X70 and X100 steels
the calculations show a rapid growth in austenite grain size in X100 steels compared to that of X70 steel. The final calculated prior austenite grain size for X70 and X100 are 45.9 µm and 47.7µm, which is close to the measured 41.35 µm and 49.05 µm. The model predictions are in excellent agreement on the magnitude of final austenite grain size, as well as, the observed reversal in austenite grain size growth rate. However, it is important to validate these results through understanding of the physical mechanisms.

Careful analyses of equations (1) to (5) indicate that the grain growth is controlled by activation energy at low temperature. In contrast, at high temperature, the limiting grain size is decided by the volume fraction of grain boundary pinning precipitates. The activation energy (see equation 4) for X100 steels is higher than that of X70 steels due to higher alloying element concentrations. As a result, the grain boundary migration will be slower in X100 steels compared to X70 steels. As a result, the X100 steel will have a smaller austenite grain size at lower temperature. At high temperatures, with a lower precipitate volume fraction in X100 steels compared to that of X70 steels, the limiting grain size in X100 steels will be larger. As a result, on heating above 1350°C, the austenite grain size of X100 steels will tend to be larger than that of X70 steels. This hypothesis is supported by parametric analyses, which showed that the final austenite grain size is not sensitive to the initial austenite grain size.

Summary

Microstructure evolutions in X70 and X100 pipeline steels during simulated HAZ thermal cycles were characterized with optical microscopy and hardness measurements. Depending upon the peak temperatures, a wide range of microstructures was observed. A softening behavior was only observed in X100 steels on heating to 700 °C. Moreover, a reversal in austenite grain growth rates was observed on heating above 1200 °C. This reversal phenomenon is rationalized based on the differences in values of the activation energy for grain boundary migration and the limiting grain size in these steels.

Acknowledgements

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References

APPENDIX C
A GENERALIZED MICROSTRUCTURE MODEL FOR MICROALLOYED HIGH STRENGTH PIPELINE WELDMENTS

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ABSTRACT

Prediction of strength and toughness of weld metal (WM) and heat-affected zones (HAZ) are very important for the design of high strength pipeline steel welding. Although, there exists a wealth of semi-empirical, phenomenological and physics based models, these models are not generalized enough to predict both WM and HAZ microstructures. This paper pertains to a comprehensive project focusing on developing a generic microstructure model that can predict the microstructural constituents in the WM and HAZ regions with minimum experimental calibration. In this work, sensitivities of published austenite grain growth and simultaneous transformation kinetic models on final microstructure were calculated. The evaluations were performed for typical steel compositions corresponding to X70 and X100 line pipe steels and controlled thermal cycles with different peak temperatures. The austenite grain growth models indicated a complex interplay between the activation energy for grain growth and precipitate coarsening. The transformation kinetic models indicated a competition between allotriomorphic and Widmanstätten ferrite can be modified by promoting intragranular nucleation of idiomorphic ferrite. Possible use of these models for improving the HAZ properties of high-strength steel pipelines is proposed.

INTRODUCTION

In order to reduce the transportation cost in the commercialization of remote oil and gas resources, there is a need to design and fabricate steel line pipes with high strength and optimum toughness [i]. To satisfy this need, new generation of steels with strength levels from 70 ksi (~480 MPa) to 100 ksi (~ 827 MPa), which are classified as X70 and API X100 steels by American Petroleum Institute (API), have been developed. These steels are produced by (TMCP) thermomechanical controlled processing. The final microstructures of these steels contain mostly ferrite-pearlite or ferrite-bainite microstructure [ii, iii, iv, v]. In addition, experimental research program are being performed, to evaluate the properties of the same welds after welding [vi]. For example, some of these studies focus on minimizing both the softening and the formation of martensite in the HAZ regions. In other projects, the motivation is to develop weld metal microstructure that can match the base-metal strength of these pipelines in terms of strength- and strain-bearing capacity.

It is important to note that if we consider the field-welding conditions, the range of microstructure that occur in the WM and HAZ regions can be too exhaustive to be described by laboratory experimental research programs. In particular, for WM region, the inclusion formation [vii], solidification to delta-ferrite [viii], solid-state transformation of delta ferrite to austenite, and transformation of austenite to different ferrite
morphologies occurs [ix]. In HAZ, the solid-state transformation of ferrite to austenite, microalloying precipitate growth (e.g., NbC, TiN), precipitate dissolution, reformation of precipitates, on-cooling transformation of austenite to different ferrite morphologies [x]. The above microstructure changes will also interact with the evolving residual stress and distortion conditions. Based on the above, one can conclude that the design of welding processes and filler metals solely based on laboratory testing cannot meet the needs of changing needs of pipeline industries. Therefore, there is a need to develop integrated process-microstructure-performance models that are capable of predicting the microstructure and properties as a function of material and process parameters. These models must be capable of learning from the results obtained from limited laboratory testing, while being powerful enough to predict the integrity and performance for field welding conditions. Realizing this challenge, many organizations have embarked upon predicting the microstructure, residual stress, distortion and properties of the steel welds by integrated process modeling [xi, xii, xiii, xiv] tools with materials modeling tools. The overarching goal of this work is to develop a plug-and-play microstructure model that can predict the microstructure in the HAZ and WM region, for a given thermal cycle, as a function of steel and filler metal composition, respectively. The goal of the current paper is to evaluate the sensitivity of published austenite grain growth and simultaneous transformation kinetic models on the HAZ microstructure of typical X70 and X100 line-pipe steel for given thermal cycles.

OVERVIEW OF HAZ MICROSTRUCTURE MODELS

Chen et al. [xiii] related the HAZ softening in X100 steel to the reheating of the base metal microstructure to austenite and subsequent transformation of the same to non-optimal microstructure during cooling to room temperature. This is in agreement with numerous studies in the literature [xv]. A number of studies have been directed towards understanding the kinetics of phase transformation in the HAZ. Kirkaldy [xvi] showed that phase transformation in steels with relatively low alloy element could be modeled with a rate-based kinetics algorithm. Many other researchers have [xvii, xviii] developed Kirkaldy’s model further to allow the prediction for HAZ under continues cooling conditions. These models generally consider sequential formation of different ferrite microstructure during continuous cooling. For example, the austenite transforms first to grain boundary ferrite, which is then followed by Widmanstätten and bainitic ferrite. In rapid cooling conditions, some of the above microstructures can be bypassed with the formation of martensite. Jones and Bhadeshia [xix] developed a simultaneous austenite decomposition model that allows for the simultaneous formation of all the ferrite microstructures, which is close to the reality. Furthermore, Jones and Bhadeshia considered the inclusion effect in his phase-transformation model to allow for the formation of idiomorphic ferrite. However, both the above models do need experimental data to calibrate some of the kinetic parameters. In simultaneous phase transformation model, although the effect of prior austenite grain size on final microstructure was considered, the problem of predicting the prior austenite grain size still exists.

Ashby and Easterling [xx] developed an austenite grain growth model in welds. Many researchers have adopted this approach [xxi, xxii] due to its simplicity. However, the parameters for these models have to be determined by calibration of the models with experimental data form low-alloy steels. As a result, these parameters may not be generally extensible to the current generation of line-pipe steels. Research can be only used for a few chemical compositions. As a result, pipeline research has focused on developing a better austenite grain growth models that are depend on the base-metal microstructure and chemical composition. Recently, Moon et al. [xxiii] modified Ashby’s equation and related the activation energy to the chemical composition of steel. In this work, Moon related the activation energy for grain growth as a function of chemical composition. In this work, we have adopted the Moon’s work and coupled with precipitate coarsening [xxiv] and the simultaneous transformation kinetic model developed by Jones and Bhadeshia [xix]. Brief description of the above models and the steps taken to link all of them are described below.

Thermodynamics of Precipitation

It is well known that the austenite grain growth in the HAZ regions is stifled by pinning of grain boundaries by stable microalloying precipitates such as carbides and nitrides. Therefore, the tendency to form these carbides and nitrides were evaluated with computational thermodynamic models. The calculations were performed with ThermoCalc® software [xxv] with TCFE5 database. The equilibrium calculations considered the phases including liquid ferrite, austenite, and all forms of carbides and nitrides that can form with microalloying elements such as V, Nb, and Ti. The equilibrium calculations were performed as a function of temperature.

Precipitates coarsening

The next step is to evaluate the sensitivity of the above precipitates towards coarsening. Lifshitz and Slyozov [xxvi] and Wagner [xxvii] developed the classic theory of precipitates coarsening. The kinetics of precipitates coarsening is determined by volume diffusion through the matrix. At steady-state conditions, the time dependence of the mean particle radius \( r \) can be described as follow:
\[ r^3 - r_0^3 = \frac{8fD_mC_mC_p(V_m)^2}{9RT}t \]  \hspace{1cm} (1)

where \( r_0 \) is the initial precipitates radius (\( \mu m \)), \( \gamma \) is the precipitate-matrix interfacial energy (\( J mol^{-1} \)), \( D_m \) is the element diffusivity (\( \mu m^2 s^{-1} \)), \( C_m \) is the concentration of solute in the matrix, \( V_m \) is the molar volume of the precipitate per mole of the solute with the unit of \( \mu m^3 \), and \( t \) (s) is the retention time. Ion et al. [xxi] modified the classic precipitate-coarsening theory and derived an equation which can be applied to continuous heating and cooling as given below:

\[ r^3 - r_0^3 = c_1 \int_0^t \frac{1}{T} \exp(-Q_s/RT)dt \]  \hspace{1cm} (2)

where \( c_1 \) is a kinetic constant (\( \mu m^3 K s^{-1} \)) and \( Q_s \) is the activation energy (\( J mol^{-1} \)), for the coarsening process.

**Austenite grain growth**

The kinetics of austenite grain growth in metals has been intensively investigated and it has been empirically known that the behaviors of grain growth can be described by the following classic relationship:

\[ \frac{dD}{dt} = nK\left[1 - \frac{1}{D_{lim}}\right]^{(1/n-1)} \]  \hspace{1cm} (3)

where \( D \) is the grain size (\( \mu m \)), \( D_{lim} \) is the limiting grain size (\( \mu m \)) which is determined by the properties of precipitates in austenite. \( K \) and \( n \) is rate constant and time exponent of grain growth, which depend on the materials and temperature respectively. Moon et al. demonstrated that \( n \) is a constant and is not related to the chemical composition of the steels. From Moon’s work, \( n \) is equal to 0.2324 and \( K \) is related to composition and temperature as given by the following equation [xxiii]:

\[ K = (1.72 \times 10^{21}) \exp\left(-\frac{A}{RT}\right) \]
\[ A = 352185.31 + 21827.26X_C + 19950.94X_Mn + 7185.49X_{Cr} + 7378.06X_{Ni} \]  \hspace{1cm} (4)

where \( A \) is apparent activation energy for grain growth the unit of (\( J mol^{-1} \)). Therefore, if the composition and thermal cycle can be acquired from the steels and the welding parameters, the only thing needed for grain growth is the limiting grain size. Limiting grain size in the current work is determined by the retardation effect of precipitates. Theory of secondary phase effect on grain growth given by Zener [xxviii] is discussed extensively in the reference [xxiv]. The limiting grain size is a function of radius and volume fraction of precipitates, which is described in the following equation:

\[ \bar{D}_{lim} = k \frac{r}{f} \]  \hspace{1cm} (5)

Where \( \bar{D}_{lim} \) is the limiting grain size, \( k \) is the Zener coefficient which was first derived to be 0.75 by Zener, \( r \) is the average radius of precipitates with the unit of \( \mu m \), and \( f \) is the volume fraction of precipitates. From precipitate-coarsening theory, which is discussed above, the limiting grain size for growing precipitates is given by:

\[ \bar{D}_{lim}^{0} = (D_{lim}^{0})^3 + (k/f_0)^3c_5 \int_0^t \frac{1}{T} \exp(-Q_s/RT)dt \]  \hspace{1cm} (6)

where \( \bar{D}_{lim}^{0} \) is the limiting grain size for stable precipitates, \( f_0 \) is the volume fraction of stable precipitates, \( c_5 \) is kinetics constant with the unit of (\( \mu m^3 K s^{-1} \)).

**Simultaneous phase transformation**

The next step is to calculate the decomposition of austenite phase during cooling. Allotriomorphic ferrite is the first phase to form from austenite during cooling. It nucleates along the austenite grain boundary and grows by diffusion. As the temperature decreases, the growth rate of allotriomorphic ferrite decreases, and the growth of allotriomorphic ferrite finally gives way to the growth of Widmanstätten ferrite. Widmanstätten ferrite nucleates either directly from the austenite grain surfaces or indirectly from allotriomorphic ferrite and austenite interface. At even lower temperatures, the remaining austenite transforms into bainite and martensite, depending on the cooling rate. It is important to note that in real-life conditions, all the above microstructure may be evolving simultaneously during continuous cooling. To deal with the simultaneous formation, Jones and Bhadeshia developed overall transformation kinetics model [xix] for allotriomorphic ferrite, Widmanstätten ferrite, and pearlite. The final equation that describes this kinetics is described below.

If it is assumed that the total grain boundary area of the sample is \( O_B \) and the system has \( n \) precipitating phases, the total volume of each phase at the time \( t+\Delta t \) can be described as:

\[ V_{j,x+\Delta t} = V_{j,x} + \left(1 - \frac{j}{V}\right)\Delta y \sum_{y=0}^{m-1} \left(1 - \frac{j}{O_B}\right)\Delta O_{j,k} \]  \hspace{1cm} (7)

\[ \Delta O_{j,k} = O_{B} \sum_{k=0}^{m} \left(I_{j,k} \Delta A_{j,k} \Delta t\right) \]
where $O_{iy}$ is the total real area intersected by the ith phase in a plane parallel to the boundary but at a distance y normal to that boundary at time t; $\Delta O_{iy}$ is the change in the real area intersected with the plane at y by the phase j; $A_{j,k,y}$ is the rate of change of area of intersection on plane y of a particle of the phase j which nucleated at $\tau = k\Delta\tau$ at the current time $t = m\Delta t$; $I_{j,k}$ is the nucleation rate per unit area of the phase j during the time interval $t = k\Delta\tau$ to $t = (k+1)\Delta\tau$; $q_{j,max}$ is the maximum extended size of a particle of phase j in a direction normal to the grain boundary plane. Therefore, the volume of different austenite decomposition products can be derived if $A_{j,k,y}$ and $I_{j,k}$ are known. For different ferrite morphology, $A_{j,k,y}$ and $I_{j,k}$ have been derived by Jones and Bhadeshia [xix]. The software for this model is available over the Internet [xxix, xxx].

**APPLICATION OF THE HAZ MODELS**

Published X70 and X100 compositions (see Table 1) were considered in the current research [xiii]. Table 1 gives the compositions of X70 and X100. The thermal cycles used in current research are shown in Fig 1. The peak temperatures of thermal cycle 1, 2, and 3 are 900°C, 1,100°C and 1,300°C respectively.

**Table 1** Chemical composition (wt.%) of X70 (a) and x100 (b); the balance being iron concentration.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
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<th>Cu</th>
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<tr>
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<td></td>
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<tr>
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**RESULTS AND DISCUSSION**

**Precipitate Type and Stability**

To understand the role of microalloying additions, the tendency for the formation of precipitates were calculated [see Fig. 2]. The calculations show that carbonitrides [(Ti, V, Nb)(C,N)] are stable up to 1,300°C in both X70 and X100 steels. The calculations also showed that the niobium-titanium [(Nb,Ti)C] carbides are not stable above 1,100°C. The presence of stable [(Ti, V, Nb)(C,N)] suggests that the austenite grain boundary pinning will occur. Ion et al. [xxi] found out that nitrides will continuous coarsen as long as the peak temperature is below 1,500°C. This hypothesis is in agreement with thermodynamic calculations. Since the [(Nb,Ti)C] dissolved early, they are not expected to play a role in pinning the austenite grain boundaries. This observation is also supported by Grong [xxiv]. Therefore, in this paper [(Ti, V, Nb)(C,N)] is considered as the only contributor for limiting austenite grain size.
Austenite grain growth calculation

The prior austenite grain size can be calculated by equation (6) with respect to thermal cycles. For titanium-alloyed steels, all the parameters in equation (4), are provided by reference xxiv. The values are as following: \( D_{\text{lim}}^{0} = 20 \) microns, \( Q_s = 240 \) kJ/mol, and \( c_5 = 6.67 \times 10^4 \). The volume fraction \( f_0 \) was set to the volume fraction \([\text{Ti, V, Nb})(\text{C,N})]\) at room temperature. For X70 steels, \( f_0 \) is equal to \( 3.46 \times 10^{-4} \) and for X100 steels \( f_0 \) is equal to \( 3.03 \times 10^{-4} \). The calculated grain sizes for all thermal cycles (see Fig. 1) are shown as a function of time in Fig. 3. Figure 3 reveals that grain size will not change when the peak temperature is \( 900 \)°C or lower. With the peak temperatures above \( 1,200 \)°C, the austenite grain size increases quickly and the overall grain size reaches the limiting grain size. As a result, the final grain size above \( 1,200 \)°C is controlled by the precipitate volume fraction and X70 steels show slightly smaller austenite grain size. Interestingly, with peak temperatures below \( 1,200 \)°C, the maximum austenite grain growth is far below the limiting grain size and the growth rate is controlled by the activation energy values [see equation 4]. Since the activation energy for grain growth of X100 steels is higher than the X70 steels, the final austenite grain size of X100 steels are smaller than X70 steels. This apparent reversal phenomenon demonstrates interplay between the grain boundary mobility and pinning. Future research has to focus on controlling austenite grain boundary mobility by careful alloying additions and design of initial microstructure.

Simultaneous phase transformation kinetics

Using the calculated maximum austenite grain size and the imposed cooling rate (30°C/s or 1,800°C/min), the final microstructures were calculated using simultaneous transformation kinetic model. The values of the parameters needed for the model are listed below.

- Alpha/Gamma Interfacial Energy: 0.022 J/m²
- Activation Energy: 200 J/mole
- Austenite Grain Characteristics
- Shape Factor for Nucleation = 0.33

Two sets of calculations were performed with and without the effect of nucleation on intragranular precipitates.
The rate of formation of different ferrite morphologies for X70 steel is shown in Fig. 4a and the overall transformation rate of austenite is shown in Fig. 4b.

Fig 4 Calculated microstructure evolution for X70 steel composition; (a) individual microstructure constituent and (b) final ferrite fraction

The rate of formation of different ferrite morphologies for X100 steel is shown in Fig. 5a and the overall transformation rate of austenite are shown in Fig. 5b. The calculations showed that the transformation rate of austenite in X100 steels is sluggish. This is indeed expected due to the higher concentrations of manganese. As a result, the X100 steels are expected to form large fractions of martensite-austenite islands (MA islands). It is important to note that these islands may deteriorate or improve the properties depending upon their morphology and carbon concentration [ii, iii, iv].

Fig 5 Calculated microstructure evolution for X100 steel composition; (a) individual microstructure constituent and (b) final percentage of austenite transformed

Since the final microstructure of HAZ are sensitive to spatial variation of thermal cycles and peak temperature, there is a motivation to develop methodologies that will lead to a microstructure that is good irrespective of the prior austenite grain size. This is elucidated with an example. To improve the productivity of welding, there is a need to use large heat-input conditions. However, large heat-input conditions may lead to high peak temperatures (>1400 °C) and the austenite grain growth may be enhanced. These large austenite grain.
sizes may promote the formation of martensite due to limited grain boundary nucleation. To counteract this effect, Homma et al. [xxxi] developed inoculated steels that promote the intragranular ferrite formation on nonmetallic inclusions. In this work, the feasibility of such approach by assuming that the microalloying precipitates [(Ti, V, Nb)(C,N)] may act similar to the oxide inclusions used by Homma et al. [xxxi]. This assumption is consistent with some of the later works by Ichikawa et al. [xxxii] and Vanderiejk et al. [xxxiii]. The above hypothesis was evaluated with simultaneous transformation kinetic models. The following parameters were used to describe the inclusion characteristics and the results for X100 are shown in Fig. 6.

- Inclusion volume fraction \( f_0 = 3.03 \times 10^{-5} \)
- Shape factor for nucleation = 0.25
- Inclusion mean diameter = 8 nm
- Inclusion nucleation efficiency \(1 \times 10^{-5}\)

The results shown indicate that it is indeed possible to accelerate the transformation rate of austenite by promoting the intragranular ferrite (i.e., idiomorphic ferrite) at high temperature. This also reduces the volume fraction of Widmanstätten ferrite. It is also important to note the above calculations used very low nucleation potency. This will be determined by the spatial distribution of these precipitates within the sample volume and initial microstructure. The above mechanism of microstructure modification relies on the competition between grain boundary nucleation and intragranular nucleation. To analyze this relation, further sensitivity analyses were performed by varying the austenite grain size and nucleation potency and the results are shown in the matrix and contour format below.
function of austenite grain size and inclusion efficiency for nucleation

The calculations show that the steels with large nucleation efficiency will reduce the sensitivity of the austenite grain size on the final microstructure. For example, with a nucleation efficiency of $1 \times 10^{-3}$ for the same volume fraction and diameter, we can completely eliminate the formation of Widmanstätten ferrite. Although, these theoretical calculations show potential benefit, the following challenges exist.

- How can we maintain the nucleation efficiency of these inclusions for wide range of peak temperature?
- How is it possible to use the precipitates for grain boundary pinning, as well as, intragranular nucleation?
- Is the nucleation of ferrite possible on these small inclusions?
- Finally, how to introduce these precipitates and assure uniform distribution during subsequent processing?

ONGOING WORK

The current paper only describes the results from theoretical calculations. There is a need to evaluate these results with detailed experimental evaluations. The validation exercise is the subject of ongoing work. The steels have been subjected to thermally cycles shown in Fig. 1 in a Gleeble thermo-mechanical simulator. The microstructural characterizations are being performed with optical microscopy and hardness mapping.

SUMMARY AND CONCLUSIONS

Published precipitate coarsening, austenite grain growth and solid-state transformation models was integrated with computational thermodynamics model. The sensitivity of this model was evaluated for X70 and X100 steel compositions. The austenite grain growth rate is affected by activation energy for grain boundary motion at peak temperatures below 1200 °C and by the limiting grain size above 1200°C.

For a cooling rate of 30°C/s, in X100 steels, transformation kinetic model predicted a transformation of more than 80% of austenite to allotriomorphic and Widmanstätten ferrite. In contrast, the transformation rate of X100 steels was sluggish due to the high manganese concentrations indicating the possibility of martensite-austenite islands.

Theoretical calculations using simultaneous transformation kinetic model suggests that the nucleation of ferrite on intragranular precipitate as a feasible approach to modify the HAZ microstructure and properties. Many challenges to realize this approach are highlighted.

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